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Controlling Fouling with Rice Straw Blends in Biomass Boilers

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The illustration on the front page is a slag pellet made by melting 40% rice straw ash and 60% wood ash at 1268°C in air. The experimental product was quenched to a mixture of crystals and glass after 1080 minutes. Size of the pellet is about 2 mm in diameter. The dark rims are the Pt wire that held the pellet in position in the furnace. Large wollastonite crystals are seen in the center of the glass pellet. Experiment R40-7.

If the appendices are missing in this version, they can be obtained from the authors.
CONTROLLING FOULING WITH RICE STRAW BLENDS 
IN BIOMASS BOILERS

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Abstract

The purpose of this project is to design a simple procedure to test the feasibility of blending rice straw with wood fuel commonly used in biomass fueled power plants. The existing information on these fuel types has suggested that the main effects of blending with rice straw will be to increase slag and ash volume, to lower melting temperature, and surprisingly to restrict relative potassium loss during combustion and slag formation. To quantify changes in the compositional and physical properties of the inorganic slag formed from blending fuels, a simplified experiment was conducted in two steps. The first step was directly to determine the liquidus temperatures (complete melting points) and melting relations using rice straw and pure wood ash blends in an atmospheric, vertical quench furnace. The second step was to test the fuel blend with the lowest ash liquidus temperature using a laboratory scale, fluidized bed combustor.

The results of the melting experiments on the pure ashes and ash blends (to 50 % rice straw ash) confirm the high melting point of 1950-2050 °C of pure wood ash. The addition of rice straw ash causes a marked freezing point depression to a minimum of about 1260 °C for an ash blend with 30 % rice straw ash. After this minimum, the apparent liquidus temperature systematically increases to well over 1500 °C for pure rice straw ash. This surprisingly high liquidus for rice straw ash is attributed to a rise in the liquidus caused by partial loss of potassium from the slag.

The results show that potassium is completely lost from blends with a low content of rice straw ash (<30 % rice straw ash). The further addition of rice straw to the blends results in an enhanced relative retention of potassium in the solid slag. Melting temperature also affects the loss of potassium from the slag, such that dropping the temperature below the liquidus increasingly reduces potassium loss. Melting duration appears to have little effect on the overall relative potassium losses. The melting experiments further suggest that the melting intervals for the ash blends are typically 100-150 °C and that near the solidus (no or little melt present) potassium is bound in both the melt as well as in potassium silicate minerals (e.g., leucite) and, therefore, partially retained in the slag.

We selected fuel blends with 2.4 % and 9.6 % rice straw, respectively, for testing with the fluidized bed combustor. These blends are equivalent to 30 % and 70 % rice straw ash components, respectively. Two additional control experiments were conducted using either the pure wood fuel or a 10.7 % leached rice straw blend fuel. The 9.6 % rice straw blend caused bed agglomeration of an estimated 25 % of the original bed after 3-4 hours of operation and completely plugged the reactor. The 2.4 % rice straw and the 10.7 % leached rice straw blends resulted in only minor bed agglomeration without detectable restriction in bed circulation even after up to five hours of operation. No bed agglomeration was observed in the experiment based on the pure wood fuel.

The results reinforce previous observations that several factors including the amount of rice straw in the fuel blends and the potassium content of straw control agglomeration. The results also indicate that the amount of potassium loss to the flue gas can be significantly reduced for blends with high straw contents and if a relatively low temperature is maintained during combustion. The use of leached rice straw as a fuel addition further reduces the concentration of potassium in the fuel and increases the retention of potassium in the slag. An additional benefit of using leached rice straw is that the resultant slag will not show the strong freezing point depression seen for raw rice straw fuel blend.

The extent of bed agglomeration shows an exponential increase with unleached rice straw component. This result suggests that a maximum of 7-8 % unleached rice straw blends may be permissible for biomass boilers of designs relatively similar the experimental fluidized bed combustor. Boiler operation below the minimum solidus temperature (~1050 °C) will strongly restrict
melting, potassium losses, and therefore bed agglomeration. Good temperature control in fluidized beds may allow straw to be blended up to 7-8 % fuel mass; however, consistently maintaining low temperatures may lead to increasing CO emissions and reduced efficiency, so careful management would be required.

The correspondence between deposits formed on bed particles and the results of the simplified melting experiments confirms that it is the lowering of liquidus temperature of the ash blends that causes melting and defluidization in fluidized bed combustors.

Long term continuous feeding of a biomass boiler with a straw-blended wood fuel was not investigated by the present study. Bed agglomeration occurs as a result of liquid phases appearing on bed particles, leading to sticking and aggregation. The full mechanism when firing blends of wood and rice straw has not yet been developed, but likely includes reaction of bed particles both with vapor phase potassium and with molten ash particles. Future work will address this problem, but the latter is suspected of being the dominant effect, at least in short term operation. Over longer periods of time without bed let-down, bed reaction may contribute significantly. The main problem may be one of the accumulating ash volume fluxing through the bed. This accumulative effect on fluidized beds from straw blending can be minimized by controlling the reactor temperature to well below the liquidus temperature of the resultant ash and slag, although the compensating effects on emissions and efficiency must be considered.

In addition to advocating new combustion strategies, the bench and laboratory scale experimental testing of rice straw blends serve as bases for the formulation of future detailed experiments, including full scale testing in a commercial operating biomass fueled power plant. The results also provide a better understanding of ash and slag formation that may be important for future boiler design innovations.

**Key Words:** renewable energy, biomass power plants, rice straw fuel, wood fuel, leached rice straw fuel, fuel blends, ash, slag, potassium loss, combustion temperature, fluidized bed, bed agglomeration, fouling
Executive Summary

Introduction

The California biomass power industry is facing increasing economic and environmental pressures to utilize agricultural crop residues and other herbaceous biomass fuels. The intermediate as well as long term viability of the industry depends, in part, on devising new combustion strategies that utilize unconventional and lower cost herbaceous and annual growth fuels. Such fuels are known to increase the potential for deposition in fluidized bed reactors and on heat exchanges. This leads to a reduction in the efficiency of biomass power generation and to an increase in operating costs. The situation today is such that herbaceous fuels are virtually unused by most biomass power generators in California, even though operating permits to meet proposed emission reductions may originally have been granted based on the use of straw fuels.

The reason for the decremental effect of herbaceous fuels on biomass fueled boilers is attributed to the release of potassium and chlorine to the flue gas as well as to transported fly ash particles that may precipitate or agglomerate on boiler walls and heat exchangers. Recent experimental results by our group have shown that compared to conventional wood based fuels, rice straw fuel actually causes a reduction in the relative alkali volatilization to the flue gas. These findings, thus, imply that it is more the absolute ash and slag volumes and their physical properties than the relative alkali volatilization that is the main cause of the observed problems in biomass boilers.

The goal of this project is to provide a better background for understanding the causes and effects of slaging and fouling in biomass boilers. For this purpose, we developed a simplified test procedure that allows a quantification of the effects of blending rice straw with wood fuel. The procedure determines the effects on alkali volatilization, melting temperature, compositional and mineralogical melting relations and melting behavior, and absolute slag/ash amounts from adding rice straw to a wood fuel. The results aid optimal fuel selection at operating power plants by offering some of the required knowledge for efficient fuel selection. The results also provide some of the background knowledge for planing and formulating future research developments as well as provide guidance for improved boiler design development programs. This goal and the achieved results support the development of the PIER Renewable Energy Technologies program.

Objectives

The principal objectives of this study were to quantify the fouling and agglomeration potential of rice straw blended wood fuel and to determine the blending ratios leading to tolerable levels of fouling. This was done by (1) measuring slag formation and potassium volatilization under simplified and controlled conditions, (2) demonstrating the existence of a minimum melting temperature for a specific fuel blend, (3) measuring the relative loss of potassium for fuel blends to 10 % rice straw, and (4) testing the simplified results in a laboratory-scale fluidized bed combustor.

Approaches

The first task of this study was to select and prepare two principal fuels for use in experimental testing. We selected a rice straw fuel that is a common byproduct from California agricultural production and historically a disposal problem. As for the wood fuel, we selected a relatively clean, mixed fir and pine wood. Although this fuel may not always represent the typical ‘dirty’ wood fuel, as received at many operating power plants, we considered it important to conduct the experiments using the pure end-member fuel type and thus to eliminate wood material collected in an urban setting, with
its unknown content of herbaceous and annual growth material, surface soil, and other toxic, or nontoxic, waste products.

We selected to conduct the melting experiments on ash produced from the two fuels as well as on blends of known proportions from 10% rice straw and 90% wood to 50% rice straw and 50% wood (on a weight % ash basis). These experiments were done in a bench-top, vertical furnace that allowed rapid extraction and quenching of the experimental products and thus allowed us to examine the experimental products with the melt phase quenched as a glass. For each fuel ash and ash blend, the melting relations were investigated from the solidus (first melt appears) to the liquidus (last solid phase disappears) relations. The experimental temperatures were between 1000 °C and as high as permitted by the furnace design (~1550 °C). The very high melting temperatures found in this study were not anticipated at the outset of the project. The consequence was that the high temperature melting relations of some of the fuel ashes had to be extrapolated from lower temperature experiments. The melting products were examined with optical and scanning electron microscopes. Each product was further analyzed with the electron microprobe to obtain precise compositional information on coexisting mineral and melt (glass) phases for all major and minor elements (Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, P, Cl).

Finally, we tested some of the rice straw fuel blends for which the ash melting behavior was known. These experiments were conducted in a laboratory scale, atmospheric fluidized bed combustor using the same fuels as for the ash studies. Two fuels with 2.4% and 9.6% rice straw (equivalent to 30% and 70% of ash coming from rice straw) were selected for the combustion experiments. Two additional fuels were selected as controls (pure wood fuel and leached rice straw). It was anticipated, based on the slag studies, that the 2.4% rice straw blend would only cause limited bed agglomeration, while the 9.6% rice straw blend would result in agglomeration as a result of melting of the ash particle blends.

The experimental design and procedures of the fluidized bed combustor were selected to resemble commercial boiler operations. Preheating of reactor wall, fuel feed rate, and air volume intakes were used to control the combustion at manageable reactor temperatures and CO and NO\textsubscript{x} emission levels. The temperature variation during the experiments was continuously monitored both in the reactor and in the down-stream ash disengagement zones. Ash and other particles were collected on air-cooled stainless steel probes as well as from the ash disengagement sections, down-stream from the main reactor. The bed material was inspected and sampled after each experiment. The composition of the flue gas was continuously monitored for the concentrations of NO\textsubscript{x}, SO\textsubscript{2}, CO, CO\textsubscript{2}, and O\textsubscript{2}.

The fundamental approach taken in this study is to use cost-effective quench furnaces that allow the experimental conditions to be controlled (temperature, gas mixture) and the experimental products to be retrieved directly from the high-temperature equilibrium conditions. A necessary requirement in order to control the furnace gas was to conduct the experiments on ash fractions of fuels. Since all melting experiments reported here were conducted in air at atmospheric pressure, the results do not DIRECTLY apply to the complex atmospheres present in boilers. However, the conditions we presently simulate in the laboratory provide the opportunity to isolate and characterize critical variables of slaging processes. In this respect our laboratory experiments represent a necessary first step to the design, execution, and interpretation of more realistic fluidized bed combustion experiments as discussed in this report.

**Outcomes**

The results of the melting experiments demonstrate that the addition of rice straw to a dominantly wood fuel causes a marked freezing point depression in the liquidus temperature of the
inorganic slag from perhaps above 2000 °C to a minimum of about 1260 °C for an ash blend with about 30 % rice straw ash. Potassium is completely lost from slag for blends with below 30 % rice straw ash content. Addition of rice straw to the fuel ash blend results in an enhanced retention of potassium in the solid slag. Ash melting temperature for fuel blends with above 30 % rice straw ash is positively correlated with potassium loss with the result that subliquidus temperatures promote retention of potassium. The melting interval (liquidus to solidus) for the ash blends is typically 100-150 °C. As the temperature approaches the solidus (little melt present), potassium is increasingly bound in the melt phase as well as in potassium silicate minerals and, therefore, partially retained in the slag. Melting experiments on blends with above 30 % rice straw ash show that the majority of potassium is retained in the slag. There are indications that ‘excessive’ temperature above the ‘true’ liquidus will cause partial potassium loss and consequently an apparent rise in liquidus for blends with high rice straw content.

Fluidized bed experiments were conducted on two fuel blends with unleached rice straw representing (1) minimum melting point, strong potassium loss, and low ash content (2.4 % rice straw) and (2) higher melting temperature, restricted potassium loss, and high ash content (9.6 % rice straw). The result for these experiments indicates that the amount of rice straw in the fuel blend is the principal control of the extent of bed agglomeration. The fuel with a high rice straw content completely plugged the bed with an agglomerated mass comprising an estimated 25 % of the original bed after 3-4 hours of operation. The fuel with low rice straw content as well as the leached rice straw blend resulted in only minor bed agglomeration without detectable restriction in bed circulation after up to five hours of operation. No bed agglomeration was observed in the experiment based on the pure wood fuel.

The similarities between the compositions of the melt deposit in agglomerated beds and the liquidus and subliquidus experimental melts obtained using the rapid quench furnace confirm that the approach taken in this study is a viable and a cost effective approach to understand agglomeration of fluidized beds.

Conclusions

Blending of rice straw with wood based biomass fuels can be predicted to result in marked change in the behavior of potassium and its partitioning between the solid inorganic slag and the flue gas. Potassium is increasingly retained in the slag with increasing rice straw component in the slag. Strong retention is in addition controlled by low melting temperature approaching the solidus temperature for the slag and the saturation of potassium-silicate minerals. The liquidus temperature shows a marked freezing point depression from above 2000 °C for pure wood ash to about 1260 °C for blends with a content of about 30 % rice straw ash. This content is equivalent to about 3 % rice straw content in the fuel. The complete melting intervals of ash blends are about 100-150 °C. It is this lowering of melting temperature that causes bed agglomeration for blends with high straw components.

Small additions of straw to a predominantly wood fuel should have the effect of lowering melting temperature and reducing potassium loss to the flue gas. If combustion temperature can be controlled to within, or below, the melting interval of the ash (<1100 °C), the loss of potassium can be minimized. An obvious drawback of adding straw materials is that the total volume of ash and slag will dramatically increase by a factor of 10-20.

Fuel blend composition, reactor temperature, and duration are the principal controls on bed agglomeration in fluidized bed combustors. The extent of bed agglomeration in the laboratory scale experimental combustor shows a hyperbolic increase with rice straw component that suggests that a maximum of 7-8 % rice straw blends may be permissible for this type of biomass boiler. Another important factor that affects bed agglomeration is the combustion temperature. It is also shown that
boiler operation below the minimum solidus temperature (~ 1050 °C) will strongly restrict potassium losses and, therefore, bed agglomeration. There is no indication in this study that volatilization of potassium is the main factor causing bed agglomeration. The main reason appears to be the accumulative volume of ash fluxing through the bed and the interaction between molten potassium-silicate particles and the bed material. The latter effect of the molten ash flux through the bed can be reduced, but not eliminated, by restricting reactor temperatures. Restricting the total ash flux requires reductions in the straw blending ratio.

**Recommendations**

Continued research in the fundamental aspects of ash and slag formation of commercially common biomass fuels is required to build a better basis for future development and testing of the use of biomass fuels for power generation. This involves building on the present melting experiments to include more complex gas mixtures that better represent actual flue gas compositions in biomass combustion. Further experiments on bed agglomeration in laboratory scale combustors will also be needed. Full-scale studies of the use of straw fuels in biomass boilers will be useful to test the conclusion that 7-8 % unleached straw can be used in fluidized beds with temperatures held below about 1050°C. The results of laboratory scale investigations like those reported here indicate that the use of straw fuels at proper concentrations may contribute to reduce the extent of potassium volatilization and fouling in superheater and other heat exchange systems. Well-controlled longer-term tests, even at the laboratory scale, would reveal whether these conclusions are supported in practice.

**Benefits to California**

This study shows that it may be feasible to burn small amounts of straw in existing biomass boilers under proper conditions. This result can have both near and long term impact on the viability of the biomass power industry and can result in practical improvements in fuel flexibility. Increasing use of straw has immediate environmental and energy benefits. The results also suggest ways to incorporate straw additions into new facility design, possibly leading to higher straw consumption as the industry repowers with more advanced boiler systems.
Introduction

Development of biomass and other renewable power generation has distinct economic and environmental advantages to California. Despite this, the situation today is such that herbaceous fuels are virtually unusable by many biomass power generators, even though these may originally have been granted operating permits based on the use of straw fuels to meet proposed emission reductions. The reason is that build-up of residual deposits on firesides and heat transfer surfaces are so severe that plants experience rapid declines in efficiency and increasing metal corrosion leading to increasing maintenance costs and reductions in energy revenues.

Annual growth plant materials contain substantial concentrations of alkali and alkali earth metals (Marschner, 1986; Jenkins et al., 1994) that, in combination with chlorine, sulfur, silicon, and other fuel elements, are known to be linked to formation of tenacious surface deposits in combustion furnaces (Baxter, 1993). Of greatest concern is the excessive build-up of deposits on firesides and heat transfer surfaces that result in reduced efficiency and metal corrosion. More advanced technologies that offer substantial increase in thermal efficiency, such as integrated biomass gasifier combined cycles, are in many cases even more sensitive to fouling due to alkali metal concentrations in fuels. Although some technologies may provide partial solutions to the fouling problem, they may not be economically viable for the existing U.S. biomass power plants because of high cost of retrofitting existing boilers. Separate or add-on facilities, such as whole-bale combustion units for straw, can result in higher maintenance costs despite lower fuel preparation costs, but the issue of ash fouling remains critically important. Design modifications to improve performance of such units might be possible if we have a better understanding of how to mitigate the high alkali flux from herbaceous fuels. Fuel blending can thus play a role in all design categories as well as future developments.

The formation and behavior of inorganic byproducts from biomass combustion is a complex process that involves volatilization of organic and inorganic compounds, residual ash and slag formation, organic and inorganic vapor phase reaction and condensation, and transport and deposition of solid and semisolid particles (Baxter, 1993; French and Milne, 1994; Jenkins et al., 1994; Miles et al., 1996). The release of volatile inorganic species from biomass fuels is partly dictated by the volatilization of organic compounds. During combustion, the organic structure of plant material is decomposed and the inorganic material is released and transported either in the form of solid particles or as vapor species in the combustion gas. In addition, soil particles incorporated in the fuel may undergo phase transformations and reaction with other inorganic components. Ash particles,
principally composed of refractory silicate minerals and melt, land on fireside surfaces and agglomerate. Entrained particulate matter is carried to the lower temperature parts of the boiler and may be emitted to the atmosphere as fly ash. Reactions between silicate particles, oxides, hydroxides, and chloride vapor species and the combustion gas result in precipitation of potassium carbonates, sulfates, and chlorides on fireside surfaces and heat exchangers.

For the practical concern of achieving economically viable biomass power generation, an understanding of the high temperature behavior of inorganic components in biomass fuels requires detailed information on the condensed and volatile phases over wide ranges of temperatures and fuel compositions. Few systematic studies under controlled combustion temperatures (500-1400 °C) exist for ash of wood and rice straw fuels (Misra et al., 1993; Olanders and Steenari, 1995; Thy et al., 1999, 2000). More information is available for coal ash and slag (Huffman and Huggins, 1981; Huffman et al., 1981; Kalmanovitch and Williamson, 1986) that, however, contain higher alumina and sodium contents than typically found for biomass ashes. There are quite a few studies that focus on the effects of fuel type on the characteristics of agglomeration in fluidized bed combustors (Dawson and Brown, 1992; Manzoori and Agarwal, 1993; Öhman, 1997; Öhman and Nordin, 2000; Öhman et al., 2000, 2003; Zevenhoven-Onderwater et al., 2001a,b; Bhattacharyo and Harttig, 2003; Yan et al., 2003; Arvelakis et al., 2003; Ishom et al., 2004).

Formation of deposits not only depends on the refractory inorganic components of the fuel, but also on the boiler design and operating conditions. The latter determines the spatial and temporal temperature and atmosphere variation, and material fluxes in the furnace. Slag forms in the high temperature boiler parts and accumulates on grates, walls, and fuel feed ports. Agglomeration of bed and molten ash particles can occur in fluidized bed combustors. Fouling of fireside surfaces and superheaters in Rankine cycle steam power generators occurs when chemical species and ash particles from the fuel land on and react with furnace and boiler materials (Raask, 1985; Baxter, 1993). Such condensation and deposition on superheaters depends to a large extent on the furnace exit gas temperature, typically above 900°C. Ash particles for some fuels may still be partially molten at such high exit temperatures.

The principal factors that control fouling is the furnace temperature and the fuel type. It has been demonstrated by Jenkins et al. (1996) that leaching of inorganic constituents from straw prior to combustion will reduce boiler fouling. The practical application and economical feasibility of leaching straw fuels are still unresolved. Straw washing and drying together with leachate treatment and
disposal are important considerations before commercial application of the technique can be tested. Nevertheless, the direct and more cost effective utilization of untreated straw will be preferable, provided fouling can be controlled. Another traditional method has been to blend, on a purely empirical basis, the fuel with various inorganic mineral materials in order to raise the melting temperature of the slag.

There are experimental suggestions that the addition of straw to conventional biomass boiler fuels in some instances may reduce fouling. The results of an evaluation for urban wood fuel ash (Thy et al., 1999) show that potassium is strongly partitioned into the vapor phase, while sodium is preferentially retained by solid and liquid phases. This confirms observations from operating power plants. Recent work (Thy et al., 2000) illustrates that fundamental differences exist at superliquidus conditions between wood and rice straw ash melts. Contrary to expectations, potassium is retained in rice straw slag, but strongly volatilized from wood slag. This may relate to differences in the extent of polymerization of the melts. If the alkali metals occur in highly depolymerized melts, such as wood ash melts, they will be easily evaporated during prolonged heating and subsequently deposited on heat exchangers. If the melt is highly polymerized, such as rice and wheat straw ash melts, they are strongly retained in the polymerized network. The potential of our preliminary findings (Thy et al., 1999, 2000) is that the addition of rice straw to conventional wood based fuels may be beneficial and may reduce potassium losses and thereby fouling (cf., Salour et al., 1993).

The addition of rice straw to wood fuels is expected to decrease both solidus and liquidus temperatures (i.e., the classic freezing point depression), but the magnitude of the depression cannot be predicted based on the available experimental data. In addition to the strong compositional effects on melting temperatures, the severity of slag formation and its ease of removal will depend on the amount of melt present as well as its composition and polymerization. It is plausible that typical boiler conditions during combustion are within the melting temperature for the slag from blended wood and straw fuel and, therefore, that melt is present in the slag. A melting point depression resulting from added rice straw may strongly increase melt fraction for the same combustion temperature. An increase in the melt fraction and changes in its composition will affect the physical properties (bulk viscosity and surface tension) of the slag and thereby its ease of removal after cooling. Likewise, potassium volatilization may be dependent on melt fraction, as well as, on melt composition. Our previous results indicate that the addition of highly polymerized rice straw melt will increase the retention of potassium
in the slag, thereby preventing its transport to heat exchanger surfaces, but still yielding a slag with a lower melting point.

The principal objective of this study is to quantify the fouling potential of rice straw blended wood fuel and to determine the optimal fuel blend that could result in minimized fouling. We present the results of a systematic study of the high temperature melting relations of ashes produced by mixing rice straw and wood and then apply these results in pilot fluidized bed combustion tests with eventual application at full-scale. We use a high temperature vertical quench furnace that let us determine the phase relations at various temperatures by allowing run products to be rapidly quenched and recovered from the high-temperature environment. The rapid vertical quench furnace is a very inexpensive testing tool compared to laboratory scale fluidized bed combustors (or full-scale testing). An additional advantage of using the vertical quench furnace is that the furnace gas is controlled and that the experimental products easily equilibrate with the furnace atmosphere. The results are thus likely to represent equilibrium conditions for the solid-melt-gas system under investigation. This approach allows us to constrain the experimental conditions and provides a first approximation for understanding slag and ash formation in more complex combustion systems.

The predictions of the subscale ash experiments are tested using an atmospheric fluidized bed combustor (AFBC). This laboratory scale combustor allows us to better simulate the complexities of full-scale application than it is possible with the inexpensive atmospheric rapid quench furnace proposed for the majority of the testing (Salour et al., 1993; Jenkins et al., 1996). The similarities or dissimilarities between the results of simplified melting experiments and agglomerated beds provide insight into processes in fluidized beds as well as for formulation of future research strategies.

Report Organization: The project results and this report are organized in two sections. The first section contains the results and evaluations of vertical quench furnace testing of fuel ash blends. The second section contains the results and evaluation of testing the optimal fuel blends using a pilot fluidized bed combustor. Two appendices contain the detailed experimental and analytical results.
Part 1: Vertical Quench Furnace Testing of Fuel Ash Blends

Fuels and Fuel Ashes

Starting materials for the melting experiments consist of two biomass samples. The first sample is mixed white fir and ponderosa pine, whole tree chips obtained from Wheelabrator-Shasta Energy Company, Inc., Anderson, California. The wood was collected on the northeastern slopes of Mt. Shasta. This relatively clean and high quality fuel is one of many types received at the plant. However, reclaiming, conveying, and stoking operations at the plant often produce a lower purity fuel stoked to the boilers. The other sample is a M202 rice straw variety from Colusa Country, California. The two samples were ashed in air in a large-volume, electric muffle furnace at 525 °C using standard procedures. The ultimate compositions and ash fusing temperatures for the biomass fuels were determined following the analytical recommendations of Miles et al. (1996) (see Appendix 1). The compositions of the ashes were determined by X-ray fluorescence directly using the ashes produced at 525 °C (Table 1).

Experimental and Analytical Procedures

A total of six ash blends with from 10 to 50 % rice straw ash were prepared by mixing during dry grinding a total of 2 g in the desired weight proportions of wood and rice straw ashes. About 50 mg powder for each experiment were pressed in a pellet and mounted onto a 0.004” diameter Pt wire (Figure 1). These mounted pellets were suspended into the furnace (Figure 2) at the desired temperature. Temperature was monitored by a Pt/90Pt10Rh thermocouple that was positioned near the ash pellet (Figure 1). Duration of the experiments varied to about 24 hours and temperature between the solidus and the liquidus conditions. The experiments were terminated in air by pulling the sample out of the furnace. The compositions of the ashes and the ash blends are summarized in the Table 1, normalized to 100 % volatile free. A summary of the experimental conditions and the principal results for the pure ashes and ash blends are given in Appendix 1.

The experimental procedures used in this study are in many respects similar to those commonly used for studying silicate systems using vertical quench furnaces (e.g., Williams and Mullins, 1981) and wire-loop techniques (Donaldson et al., 1975). The principal difference is that biomass material contains elements that under certain conditions are volatile, such as K and Cl. To avoid loosing
particularly K, the powder is prepared dry and the pellets mounted without sintering it to the Pt wire with an H₂-O₂ gas torch, as is commonly done in silicate studies. This restricts unintended loss from heating or leaching of the sample and is a further development of our previous techniques (Thy et al., 1999, 2000).

**Figure 1.** General sample holder configuration. An alumina rod with a Pt wire sample holder and a central thermocouple position. (A) Rice ash pellet before experiment. (B) Same rice straw pellet after experiment.  
**Figure 2.** The PIER Deltech furnace seen at left in its bay in the Experimental Petrology Laboratory at UC Davis. Below the bench is the power supply and temperature controller. On the wall to the left is part of the gas plumbing system to which the furnace is attached. To the right is a similar, but smaller bore, Deltech furnace used for basaltic silicate melts.

| Table 1. Summary of Ash Blends Used in the Experiments |
|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
|                | Rice R 50%    | R 40%          | R 30%          | R 20%          | R 15%          | R 10%          | Wood W 50%     |
| Rice Straw     |               |                |                |                |                |                |                |
| SiO₂           | 82.12         | 53.45          | 46.59          | 39.27          | 31.44          | 27.32          | 23.04          |
| TiO₂           | 0.01          | 0.09           | 0.11           | 0.13           | 0.15           | 0.16           | 0.17           |
| Al₂O₃          | 0.10          | 2.02           | 2.49           | 2.98           | 3.50           | 3.78           | 4.07           |
| Fe₂O₃          | 0.11          | 0.78           | 1.2            | 1.12           | 1.30           | 1.40           | 1.50           |
| MnO            | 0.29          | 1.28           | 1.52           | 1.77           | 2.04           | 2.18           | 2.33           |
| MgO            | 1.79          | 4.14           | 4.71           | 5.31           | 5.95           | 6.29           | 6.65           |
| CaO            | 1.74          | 21.23          | 25.90          | 30.87          | 36.20          | 39.00          | 41.91          |
| Na₂O           | 0.15          | 0.33           | 0.38           | 0.42           | 0.47           | 0.50           | 0.53           |
| K₂O            | 13.02         | 14.30          | 14.61          | 14.94          | 15.29          | 15.47          | 15.66          |
| P₂O₅           | 0.66          | 2.36           | 2.76           | 3.20           | 3.66           | 3.90           | 4.16           |
| Total          | 100.00        | 100.00         | 100.00         | 100.00         | 100.00         | 100.00         | 100.00         |

R, rice straw ash; W, wood ash. Each blended composition is calculated to 100%.

All experimental products were examined using optical and scanning electron microscopes. The crystalline products were analyzed using the CAMECA SX50 electron beam...
microprobe at the UC Davis Geology Department. The precision of the electron microprobe analyses is generally within 1-3 % for major elements and 5 % or above for minor elements (see Thy et al., 1999, for details). The oxides reported were SiO$_2$, TiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$, MnO, MgO, CaO, Na$_2$O, K$_2$O, and P$_2$O$_5$. It is assumed that all iron occurs as Fe$^{3+}$. Other elements, including Cl, were not present in sufficient amounts to be detected. The analytical results are summarized in Appendix 1.

**Experimental Results**

The initial tests involve the determination and characterization of the melting relations of the two pure ashes (rice straw and wood) as a function of temperature between their respective liquidus and solidus conditions. These initial experiments form the foundation for testing the effects on melting from blending the two ashes. Details of the experimental results can be found in Appendix 1. Only typical products are illustrated here.

Figure 3 illustrates experimental products of pure wood ash showing the ash pellet before inserted into the furnace as well as after heated to temperatures to above 1500 °C. Figure 4 shows a back-scattered electron image of the experimental products of wood ash heated at 1517 °C. Larnite (Ca$_2$SiO$_4$) is gray with slight compositional zoning toward the rims. Black grains are periclase (MgO). The interstitial melt has quenched as an unidentified, two-phase composite (white and gray).

Figure 5 shows a reflected microscope image of pure rice ash heated at 1372 °C. This experimental product is composed of a large bubble with a thin outer wall, likely caused by the release of CO$_2$ during heating (Figure 5A). Back-scattered electron image of the silicate wall indicates a dark, tabular quartz polymorph and light gray glass (Figure 5B).

The experimental products obtained on an ash blend with 10 % rice straw ash are illustrated in Figure 6. Figure 6A shows a reflected microscope image of the product obtained at 1472 °C. This product is highly compacted and composed of droplets of rounded larnitic grains and an interstitial quenched melt. The back-scattered electron image of Figure 6B shows light colored, rounded larnite grains and a quenched interstitial melt composed of two unidentified phases.
Photographs of the experimental product of a 40% rice straw and 60% wood ash blend heated at 1268 °C are shown in Figure 7. A complete pellet with a large wollastonite crystal barely visible in the upper right corner is shown in Figure 7A. When mounted in plastic, cut, and surface polished a large wollastonite crystal is clearly visible in a diagonal position (Figure 7B).

Figure 3. Representative photographs of experimental wood ash product. Upper left is the ash pellet before inserted into the furnace. W-2 is the unconsolidated material after 24 hours at 1263 °C. Pellet fragmented after being extracted from the furnace. W-4 is the pellet after 25 hours at 1347 °C. The pellet retains its original shape. W-14 is the pellet after 6 hours at 1510 °C. Significant shrinking in size due to sintering, volatile loss, and breakdown of calcite. The scars on the surface are after the Pt wire that has been removed. The scale bar is 2 mm.

Figure 4. Back-scattered electron image of experimental wood ash product at 1517 °C. Larnite (Ca$_2$SiO$_4$) is gray with slight compositional zoning toward the rims. Black grains are periclase (MgO). The interstitial melt has quenched as an undetermined, two-phase composite (white and gray). Scale bar is 20 µm.
Figure 5. Rice straw ash products. (A) Reflected microscope image of experimental product at 1372 °C. The product is composed of a large bubble with a thin outer wall. Scale bar is 3 mm. (B) Back-scattered electron image of the silicate wall in Figure 5A. The dark tabular grains are a quartz polymorph. Light gray is glass. Scale bar is 50 µm.

Figure 6. 10 % rice straw ash blend products. (A) Reflected microscope image of the product heated at 1472 °C. The experimental product is a compacted droplet of rounded larnitic grains and an interstitial quenched melt. Scale bar is 1 mm. (B) Back-scattered electron image of the center of the same experimental product as in Figure 6A. The lighter rounded grains are larnite. The quenched interstitial melt is composed of two unidentified phases. Scale bar is 50 µm.


**Elemental Losses and Phase Appearances**

*Mass Balance Calculations*

The proportions of the solid phases and the coexisting liquid in the experimental products can be estimated by least-squares, linear approximations of the compositions of the phases in the experimental products (Appendix 1) to the composition of the starting ash mixtures (Table 1). In addition to the phase proportions in weight percentages, this type of calculation also allows estimates of the elemental losses, either directly from the deviations from the actual composition of ash mixtures or alternatively as done here by including the element in question as an oxide in the calculations. This was done for K$_2$O and Na$_2$O for which the largest losses were detected. All analyses used in the calculations are recalculated to 100 % on a volatile free basis. See Appendix 1 for the details of the calculations.

*Elemental Losses*

The calculated losses of K$_2$O and Na$_2$O are illustrated in Figure 8 and should be compared to the ash blend contents given in Table 1. K$_2$O is strongly lost from the pure wood ash as well as from the wood ash blended with small amounts of rice straw ash (10 and 15 %). On the other hand, K$_2$O is partly retained in the blends with higher rice straw ash as well as in the pure rice straw ash. The loss correlates positively with the experimental temperature. Thy et
al. (2000) melted a slightly different rice straw ash just above its liquidus temperature at about 1070°C over a range in experimental duration to 11,000 minutes without observing detectable loss of K$_2$O. The present finding stresses that high temperature, well exceeding the liquidus temperature, for some ash compositions can result in significant losses of K$_2$O (see the section on phase appearances below for further discussion). There is in the present experimental data no indications for a time dependent loss as also found by Thy et al. (2000). Despite that Na$_2$O is low in both starting compositions (0.15-0.60 wt. % Na$_2$O), Na$_2$O is still observed to be strongly lost from the wood ash dominated blends and is completely retained in the rice ash dominated blends with above 40 % rice ash. No detectable losses were observed for other elements, except for Cl that was undetected for all ash compositions.

![Figure 8. Losses of K$_2$O and Na$_2$O (wt. % of original ash) from the experimental products as a function of SiO$_2$ content of melt. See text and Appendix 1 for detailed explanation of the calculations. For 30-50 % rice straw blends, there is a weak positive correlation between melt composition and loss of K$_2$O and SiO$_2$ (temperature effect). The points for Na$_2$O between ‘wood’ and ‘30 %’ is for 10-20 % rice straw blends.](image)

There is independent support for these calculated losses. The weight losses during the experiments were measured for most of the melting products and can be compared to the calculated losses (Appendix 1). The experiments on the pure rice straw ash show measured 13-17 wt. % losses that can be completely accounted for by the calculated losses from the mixing experiments together with the determined loss of ignition of the ash (~8 %). Similarly, the measured weight losses during the experiments on the wood ash vary from 39 to 46 % and can
be reasonably accounted for by the calculated mass balance losses together with the determined loss of ignition of the ash (~27%). The loss on ignition is largely associated with carbon that was not driven off during ashing. This suggests that other elements were not to a significant extent lost during the experiments.

Figure 9. Phase proportions (wt. %) as a function of melting temperature (°C) for pure wood and rice straw ashes calculated by least-squares approximations to the starting material. See text and Appendix 1 for details of the calculations. For pure rice straw ash, the liquidus temperature can be extrapolated to ~1575°C. The nearly constant melt content for rice straw ash is suggested to be a result of progressive K₂O loss during the experiment (see text for discussion).

Phase Proportions and Phase Appearances

The results of the calculation of the phase proportions are summarized in Figure 9 for the two pure end-member fuels and in Figure 10 for the ash blends, all as functions of melting temperature. Here we briefly discuss the phase proportions and phase appearances as well as their bearing on the calculated elemental losses.

The liquid-mineral relations for wood ash were only determined in a narrow interval between 1400 and 1550°C. Within this temperature interval, the melt proportion increases and the larnite proportion decreases with increasing temperature. The proportion of periclase is relatively constant except for a slight drop at the highest melting temperatures. We can extrapolate to rather uncertain liquidus and solidus temperatures of 1950-2050°C and 1200-1100°C, respectively. The liquidus phase was also not determined, but can only be larnite and/or
periclase. The solidus phase assemblage is unknown, but must involve an Al$_2$O$_3$ bearing phase as this oxide is strongly enriched in the melt. It is thus possible that near the solidus a SiO$_2$-Al$_2$O$_3$-K$_2$O phase may appear (such as leucite) and as a consequence stabilize potassium in the slag.

Figure 10. Melting relations for the intermediate fuel ash blends with 50 %, 40 %, 30 %, and 20 % rice straw ash, respectively. The phase proportions are determined by least-squares approximations to the starting material. See text and Appendix 1 for details of the calculations. Woll - wollastonite; leu - leucite; ake - åkermanite; lar - larnite; dio – diopside.

The addition of rice straw ash to the wood ash causes a strong drop in liquidus temperature. The phase proportions of the rice straw blends are illustrated in Figure 10 for the 20 to 50 % rice straw ash blends. With 10 % added rice straw ash, the liquidus temperature is still too high to be directly or indirectly determined. The mineral phases detected well below the liquidus are, as for the pure wood ash, larnite and periclase. With 15 % added rice straw ash, the liquidus has dropped sufficiently to allow an indication of the liquidus phase as larnite. Periclase is no longer detected at any melting temperature. With 20 % added rice straw ash, the liquidus mineral is larnite at 1403±11°C. Åkermanite appears at 1299±10°C. An uncertain solidus temperature of about 1225°C can be estimated. With 30 % added rice straw ash, wollastonite and åkermanite appear relatively simultaneously on the liquidus at 1264±11°C and are followed by leucite at 1217±11°C. The solidus can be estimated by extrapolation to 1100-1150°C. With 40 %
added rice straw ash, the liquidus phase is wollastonite at 1282±14°C and with leucite and diopside appearing relatively simultaneously at a temperature of 1212±11°C. The solidus temperature can be estimated by extrapolation to 1050-1100°C. With 50 % added rice straw ash, the liquidus phase is wollastonite at 1307±11°C and diopside appears at a temperature of 1263±11°C. The solidus temperature can be estimated by extrapolation to a very low temperature of 900-1000°C.

All the ash blends show systematic increases in the proportions of minerals with decreasing temperature and melt proportion. This allows an estimate of the solidus temperature to be estimated, despite uncertainty often due to large extrapolated temperature intervals. Because temperature dependent losses of K₂O are seen for some blends, it is possible that the estimated liquidus temperatures in part reflect the changing bulk composition of the slag. This mean that estimates of melting relations and the liquidus temperature cannot be based on bulk ash compositions, as often done, but must take into consideration temperature dependent changes in bulk composition. This latter effect of changing bulk composition of the slag has strongly influenced the shape of the ‘phase diagram’ for pure rice straw as, as discussed below.

An important observation is that the retention in the slag of K₂O can be correlated with the appearance of leucite. Leucite is a K₂O and Al₂O₃ rich phase that is stabilized at relatively low temperature and low melt fraction in melts relatively enriched in Al₂O₃ and K₂O. The appearance of leucite, thus, strongly signifies retention of K in the slag. This is seen for the 30 and 40 % rice straw blends. A similar appearance of leucite in the 50 % rice straw blend would be predicted from the significant drop in the calculated loss of K₂O for the melting experiments below 1200°C. Because of the heterogeneous nature of the low temperature experiments, leucite (or other potassium silicates) may have been undetected in these latter experiments. For all experiments for which a potassium-containing mineral phase was detected, this phase is leucite (KAlSi₂O₆). However, it is possible that other potassium silicates (e.g., kalsilite or potassium tetrasilicate) with much higher potassium contents may appear near the solidus for ash blends with low aluminum content.

An examination of the compositions for the rice straw blended slag shows that potassium, in addition to in leucite, also occurs in high concentration in the melt. This is a reflecting of changes in the melt structure with increasing silica content (or rice straw ash) that better accommodate the large potassium cations (Thy et al., 2000).
The melting relations and phase proportions as a function of melting temperature for the pure rice straw ash poses some difficulties that cannot easily be explained in terms of equilibrium melting relations. The ‘phase diagram’ in Figure 9 shows nearly constant proportions of the melt and mineral proportions independent of temperature, except perhaps at temperatures above 1500°C. Thus, these phase proportions cannot be extrapolated to an estimated solidus temperature and only allows the liquidus temperature to be extrapolated based on a single melting experiment at 1536°C. All the melting experiments contain a quartz polymorph as the only mineral phase. The lack of another K₂O rich phase is conspicuous and is difficult to understand based on expectations from the simple SiO₂-K₂O systems (Osborn and Muan, 1960).

We base a tentative interpretation in part on the previous determination of an ~1050°C liquidus temperature for a relatively similar rice straw ash (Thy et al., 1999) and the observation that the K₂O content of the melt in the present experiments decreases with increasing melting temperature. We suggest that a ‘progressive depletion’ in K with increasing melting temperature results in a ‘progressive increase’ in liquidus temperature. The result would be seen as an ‘extended’ subliquidus range that reflects the variation in ash compositions from the ‘equilibrium’ K₂O content of 12 wt. % to an uncertain amount of perhaps 2-3 wt. % remaining in the melt.

The observed variation in the behavior of potassium for the range of slag compositions investigated in this study can be explained by a marked decrease in potassium loss with increasing rice straw in the slag.

*Liquidus Temperatures and Freezing Point Depression*

The liquidus temperature (or complete melting point) was bracketed in four series of experiments (50, 40, 30, and 20 %). For the 10 and 15 % rice straw ash blends, the experiments only gave minimum values of 1530°C and 1543°C, respectively. For the 15 % blend this value is relatively close to the liquidus temperature, judging from the high amount of melt in the experimental products. The liquidus temperature for pure rice was extrapolated to approximately 1575°C. This value is substantiated by a significant increase in melt proportion for the 1536°C experiment, but may only apply to a bulk composition with relatively low K₂O. The true liquidus for a starting composition with 12 wt. % K₂O may very well be below 1100°C; however, for
practical purposes the ‘elevated’ liquidus temperature shown on Figure 11 may be more relevant. For pure wood ash a liquidus temperature was estimated by extrapolation to an uncertain value of 1950-2050°C.

The resulting freezing point depression as a function of the percentage of rice straw ash in the blends is shown in Figure 11. It is seen that the addition of small amounts of rice straw ash to the blend will strongly affect the melting points until an amount of about 20 % rice straw ash (~25°C/wt.% rice ash). From about 20 % rice straw, the liquidus levels out and reaches a minimum at about 30 % rice (1264°C). With increasing rice straw ash, the liquidus temperature raises steadily to 50 % straw ash, and probably also beyond, to an apparent 1536°C for pure rice straw ash (4°C/wt.% rice ash). Because of the temperature dependent loss of K\textsubscript{2}O, the true variation in liquidus for rice straw ash blends with above 50 % rice straw ash is uncertain.

![Figure 11](image.png)

**Figure 11.** Experimentally determined liquidus temperatures as a function of weight % rice straw ash in the ash blend.

**Summary**

Blending of rice straw with a dominating wood fuel markedly affects the composition and properties of the resultant inorganic slag (and ash). Ashes were produced at 525 °C from the raw fuels. A series of ash blends were produced from these two ‘pure’ ashes with 10, 15, 20, 30, 40, and 50 % by weight of rice straw ash. The compositions of these 8 ashes and ash blends varies in SiO\textsubscript{2} from 14 wt. % to 82 wt. % and in CaO from 50 wt. % to 2 wt. %. The potassium content shows less marked variation from 16 to 13 wt. % K\textsubscript{2}O.
The ashes were pressed into pellets and inserted into a vertical quench furnace at temperatures above ~950 °C and with duration to 24 hours. The maximum temperature attainable with the chosen experimental setup was ~1550 °C. Pulling the products out of the furnace into air terminated the experiments. For each ash composition, experiments were made between their respective solidus and liquidus temperatures. The experimental products were examined with the scanning electron microscope and their mineral and melt phases analyzed with the electron microprobe.

The experiments show that potassium is completely lost from the ash blends with below 30 % rice straw ash. The experimental products of these ashes contain periclase (MgO), larnite (Ca$_2$SiO$_4$ with appreciable amounts of P substituting for Si), and quenched melt without detectable concentrations of K$_2$O. A nearly pure åkermanite appears in the 20 % rice straw blend (Ca$_3$Mg(SiAl)$_2$O$_7$). Wollastonite (CaSiO$_3$) first appears in the 30 % rice straw blends and diopside (CaMgSi$_2$O$_6$) first appears in the 40 % rice straw blend. None of these phases contains detectable potassium. It is first with the appearance of leucite as a subliquidus phase (KAlSi$_2$O$_6$) at temperatures in general below 1200 °C that potassium partly is retained in the slag (melt and minerals). There is thus a strong correlation between the retention of potassium in the slag and the appearance of leucite. The melt phase in the experiments with 30 % rice straw ash, and above, readily quenched to a glass, while for the other experiments the melt quenched to a two phase intergrowth.

The experiments on the pure rice straw ash showed that a quartz polymorph was the only detectable mineral present. The slag readily quenched to a glass that retained large proportions of the potassium of the starting ash. The retention of potassium in the quenched melt is negatively correlated with temperature. This partial retention of potassium in the slag and its dependency on temperature result in a progressive raise of liquidus temperature with increasing melting temperature and loss of potassium.

Mass balance calculations of the experimental products quantify the extent of potassium loss during melting and slag formation. The loss strongly decreases for rice straw slag from 60 % to 25 % of the original K$_2$O content with decreasing melting temperature. Likewise, there is a significant lowering of the loss of potassium in the ash blends with increasing rice straw ash content.

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The results of the vertical quench furnace experiments show that two factors control the retention of potassium in the fuel slag and ash. Increasing rice straw ash stabilizes potassium in the slag and consequently reduces the relative loss of potassium to the furnace gas. The effect of lowering the temperature is likewise to stabilize potassium in the slag. For the wood ash blends, the retention in the slag at low temperature can be related to changes in the melt structure (cf., Thy et al., 1999) and the stabilization of leucite (or other potassium silicates). For the pure rice straw ash the retention appears only to be dependent on changes in the melt structure with lowered temperature; however, none of the conducted experiments may have reached sufficient low temperatures to stabilize potassium silicates.

The wide variation in slag composition (SiO$_2$, CaO) results in a marked freezing point depression. The extrapolated melting point for pure wood ash is estimated at above 2000 °C. The addition of rice straw ash lowers the melting markedly (~25 °C/wt. % rice straw ash) until a minimum of 1264 °C at about 30 % rice straw ash. There is an apparent increase in the melting point with increasing rice straw ash above 50 % due to the effect of progressive depletion of K$_2$O from the slag with increasing temperature.

Petrographic examinations of glassy deposits from commercially operating biomass-fueled power plants (Oden, 1993, 1994) show that these contains the same silicate minerals (monticellite, garnet, augite, wollastonite, melilite, leucite). It is also conspicuities that the glass compositions are large similar to those experimentally produced in this study.

**Conclusions**

The blending of rice straw with wood based biomass fuels results in marked changes in composition and physical properties of the inorganic slag. Important observations include:

- The silica content of the slag increases from 14 to 82 wt. % SiO$_2$, while calcium decreases from 49 to 2 wt. % CaO.
- The melting point drops markedly from an estimate above 2000 °C to a minimum of 1264 °C for 30 % added rice straw.
- Potassium is completely lost from blends with less than 30 % rice straw and partly lost from intermediate rice straw blends due to structural changes in the melt that also results in the stabilization of leucite (and perhaps other potassium silicates) at temperatures below 1200 °C.
• Potassium is partially retained in the slag of pure rice straw as a function of decreasing temperature.
• The melting temperature for pure rice straw slag increases as a function of the progressive loss of potassium. This is in contrast for the wood based fuels for which potassium is completely lost even near the solidus conditions.
• The addition of rice straw fuel to a dominantly wood based fuel reduces the relative loss of potassium, lowers the melting point, and increases the total volume of ash and slag.
• The result of the melting experiments shows mineralogical and compositional similarities with slag formed in commercially operating biomass-fueled power plants.

Methods

Starting materials for the fluidized bed combustion experiments were selected to approximate those for which the melting behavior of the ash was examined (Part 1). From these starting materials, two different fuel blends were prepared for the combustion experiments. The first blend was prepared by mixing 2.4 % rice straw with 97.6 % mixed conifer (on a weight basis). The second blend was prepared by mixing 9.6 % rice straw with 90.4 % mixed conifer. Pure wood and leached rice straw fuels were used as controls. The leached rice straw was prepared from the rice straw fuel following the procedures of Jenkins et al. (1996). Similarities (or dissimilarities) between the simplified melting experiments in air (Part 1) and the results in fluidized bed combustors with complex flue gases including sulfur and potassium are crucial for formulating models for bed agglomeration and elemental mobility during combustion.

The combustion tests were conducted in an atmospheric laboratory scale fluidized bed combustor (FBC), as schematically illustrated in Figure 12. The main combustor consists of a 915 mm long stainless steel cylinder reactor tube with a 73 mm internal diameter and surrounded by an insulated electric heater utilized for preheating. A distributor nozzle at the base of the reactor supplies electrically preheated air and fluidizes the bed. The bed material is refractory alumino-silicate refractory sand composed predominantly of mullite and subordinate cristobalite. Fuel is fed to the bed near the bottom of the reactor through a high-speed auger and a variable speed belt. Feeder purge air (5 l/min) was admitted with the fuel. The reactor tube is connected to a disengagement zone for internal recirculation of bed material. Secondary air was admitted at the center of the reactor 14” above the base. Connected to the disengagement zone is a horizontal pass that is equipped with an ash dropout. Removable, stainless steel, air-cooled heat exchangers before and after the disengagement zone act as deposit probes. Another ash dropout trap is placed down-stream after passing through a cyclone for separation of larger fly ash particles. The flue gas was sampled after passing the cyclone for continuous on-line analyses of $\text{NO}_x$, $\text{CO}$, $\text{CO}_2$, and $\text{O}_2$ using a Horiba PG-250 portable gas analyzer.

The combustion tests were carried out with the fuels and fuel blends listed in Table 2. The first three experiments used the 2.4 % rice straw blend with either an 800-900 °C or a 1000
°C reactor wall temperature. The fourth experiment used the 9.6 % rice straw blend and a reactor wall temperature of 1000 °C. Two control experiments were conducted using either a pure wood fuel or a leached rice straw fuel, both with a reactor wall temperature of 1000 °C.

Figure 12. Experimental design of the atmospheric fluidized bed combustor. A. The experimental equipment in the laboratory. Air inlet rotameters are seen on the front panel with the upper part of the reactor and the cyclone behind. The operator is facing the on-line computer and gas analyzer. B. Schematic drawing of the combustor. The disengagement zone thermocouples were located away from the reactor in the order D1 to D3. Secondary air was admitted to the reactor at 14" above the reactor base. Feeder purge air was admitted together with the fuel.

<table>
<thead>
<tr>
<th>ID</th>
<th>Date</th>
<th>Target Wall Temp.</th>
<th>Duration</th>
<th>Fuel Type</th>
<th>Comments</th>
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<tbody>
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<td>Feb. 15, 2003</td>
<td>800</td>
<td>2 hours 30 min</td>
<td>2.4 % rice straw - 97.6 % mixed conifer</td>
<td>1</td>
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<tr>
<td>FBC-2</td>
<td>Feb. 23, 2003</td>
<td>900</td>
<td>2 hours</td>
<td>2.4 % rice straw - 97.6 % mixed conifer</td>
<td>1</td>
</tr>
<tr>
<td>FBC-3</td>
<td>Mar. 2, 2003</td>
<td>1000</td>
<td>5 hours</td>
<td>2.4 % rice straw - 97.6 % mixed conifer</td>
<td>2</td>
</tr>
<tr>
<td>FBC-4</td>
<td>Mar. 8, 2003</td>
<td>1000</td>
<td>3 hours 30 min</td>
<td>9.6 % rice straw - 90.5 % mixed conifer</td>
<td>3</td>
</tr>
<tr>
<td>FBC-5</td>
<td>Mar. 15, 2003</td>
<td>1000</td>
<td>5 hours 30 min</td>
<td>100 % mixed conifer</td>
<td>2</td>
</tr>
<tr>
<td>FBC-6</td>
<td>Mar. 26, 2003</td>
<td>1000</td>
<td>4 hours 30 min</td>
<td>10.7 % leached rice straw and 89.3 % mixed conifer</td>
<td>2</td>
</tr>
</tbody>
</table>

1. Terminated because of fuel transfer problems
2. Terminated by fuel consumption
3. Terminated because of bed agglomeration

The principal objective of the tests was to achieve stable combustion with good bed fluidization, and manageable SO₂, NOₓ and CO gas emissions. The stabilization was monitored by a series of thermocouples inserted along the length of the reactor. Additional thermocouples
were positioned both up and down-stream from the reactor. Air-fuel ratios were maintained with 30-50 % excess air to simulate commercial boiler operations. Feeder purge air was maintained at 5 l/min for all experiments to prevent combustion gases from backing up into the feeder. The reactor was electrically preheated to the target temperature. The furnace controller shut off power to the furnace whenever reactor temperature exceeded setpoint temperature, usually a short time after starting fuel feeding. Primary air admitted to the reactor during the experiments was electrically preheated to temperatures up to 400 °C. Secondary air was admitted at 14” (354 mm) above the base of the reactor through a 1/8 “ diameter stainless steel lance descending from the top of the reactor. Secondary air was not preheated except by passing through the hot combustion gas flowing upward around the lance. Deposit probes inserted in the disengagement section were forced air-cooled to maintain a constant wall temperature of 500 °C during steady operation. The deposit probes inserted into the horizontal pass were cooled by natural draft to temperatures in the range of 400 – 500°.

After each experiment, the interior of the reactor was visually inspected and the bed material collected and examined for agglomeration. The deposit probes were removed and inspected. Samples of the accumulated deposit were taken by brushing before the remaining

---

Table 3. Summary of Results

<table>
<thead>
<tr>
<th>ID</th>
<th>Date</th>
<th>Fuel Consumed (g)</th>
<th>Cyclone Pass</th>
<th>Horizontal Pass</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Total Mass (g)</td>
<td>Heating (% loss at 105 °C)</td>
</tr>
<tr>
<td>FBC-1</td>
<td>15-Feb-03</td>
<td>1497</td>
<td>0.2</td>
<td>-</td>
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<tr>
<td>FBC-2</td>
<td>23-Feb-03</td>
<td>1722</td>
<td>7.1</td>
<td>4</td>
</tr>
<tr>
<td>FBC-3</td>
<td>2-Mar-03</td>
<td>6039</td>
<td>8.1</td>
<td>5</td>
</tr>
<tr>
<td>FBC-4</td>
<td>8-Mar-03</td>
<td>4214</td>
<td>4.2</td>
<td>5</td>
</tr>
<tr>
<td>FBC-5</td>
<td>15-Mar-03</td>
<td>5049</td>
<td>16.5</td>
<td>4</td>
</tr>
<tr>
<td>FBC-6</td>
<td>26-Mar-03</td>
<td>5349</td>
<td>28.4</td>
<td>2</td>
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</table>

<table>
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<tr>
<th>ID</th>
<th>Date</th>
<th>% Agglom.</th>
<th>IMP1 Gain (g)</th>
<th>IMP2 Gain (g)</th>
<th>IMP3 Gain (g)</th>
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</thead>
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<tr>
<td>FBC-1</td>
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<td>-</td>
<td>31.4</td>
<td>0.0</td>
<td>-</td>
</tr>
<tr>
<td>FBC-2</td>
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<td>-</td>
<td>28.3</td>
<td>2.6</td>
<td>3.6</td>
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<td>FBC-3</td>
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<td>89.6</td>
<td>6.7</td>
<td>10.3</td>
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<td>FBC-4</td>
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<td>68.0</td>
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<td>7.9</td>
</tr>
<tr>
<td>FBC-5</td>
<td>15-Mar-03</td>
<td>-</td>
<td>58.7</td>
<td>4.3</td>
<td>-</td>
</tr>
<tr>
<td>FBC-6</td>
<td>26-Mar-03</td>
<td>0.16</td>
<td>97.0</td>
<td>9.0</td>
<td>12.3</td>
</tr>
</tbody>
</table>
material was removed by rinsing with distilled water. The fly ash material accumulated in the ash dropouts was also collected.

**Experimental Results**

The experimental results are summarized in Table 3. Detailed results are presented in Appendix 2. Here we illustrated the results of firing with the 9.6 % unleached rice straw blend (FBC-4). This experiment used a furnace wall preheated initially to about 900 °C and stabilized at 1030 °C during the main part of the experiment. The inlet air temperature was decreased from 400 °C to 260 °C early during the experiment (Figure 13). The air inlet flow rate was 120 l/min. Secondary air was admitted to the reactor at 30 l/min. Fuel feeding rate was decreased 20 % during the experiment. The run duration was 3.5 hours and the average fuel consumption was 23 g/min. The experiment was terminated by bed agglomeration signified by a sudden and marked late raise in reactor temperature to 1195 °C (Figure 13) and decrease in differential bed pressure, both common indicators of bed agglomeration and defluidization. An estimated 25 % of the total bed material was agglomerated. The temperature variation in the reactor as a function of time is illustrated in Figure 15. Conditions remained relatively steady with reactor temperature at 1030 °C through the most of the experiment (Figure 13).

![Figure 13. Temperature variation as monitored with time for the FBC-4 experiment using a 9.6 % rice straw blend. The red lines are the reactor temperatures as monitored by thermocouples at 25, 178, 356, 572, and 756 mm positions above the base of the reactor. ‘Furnace wall’ is the temperature of the preheated wall (furnace off when wall temperature exceeded control setpoint temperature). ‘Inlet air’ is the temperature of the preheated inlet air. D1, D2, and D3 are the down-stream disengagement zone temperatures.](image-url)
The measured gas concentrations fluctuated with fuel input variations resulting from the typical non-uniform discharge from the high speed rotating auger used for fuel injection into the lower bed. CO₂ varied from above 15 to 12 % and O₂ to about 8-9 % (Figure 14). The CO concentration varies widely again because of inherent non-uniformity in fuel feed by the auger, but is mostly below 2000 ppm (maximum detectable CO from the analyzer is 5000 ppm). The average concentrations are 8 % for O₂, 12 % for CO₂, 1120 ppm for CO, 180 ppm for NOₓ (most from fuel nitrogen), and 18 ppm for SO₂ during stable combustion, although the latter may be too high because of interference from CO.

Figure 14. The flue gas composition (by volume) as a function of time of day during for the FBC-4 experiment using a 2.4 % rice straw blend. O₂, CO₂, CO, NOₓ, and SO₂ are shown. CO₂ and O₂ are in percent, while the other components are in ppm.

**Bed Agglomeration**

*Selection of Fuel Blends*

The fuel blends for the fluidized bed testing were selected based on the results of the bench top melting experiments on fuel ash blends (Part 1). These results show a marked freezing point depression on the liquidus relations with increasing rice straw ash in the blend. A minimum liquidus temperature was observed for a 30 % rice straw ash and 70 % wood ash blend. The results also suggest that increasing rice straw ash in the blend would serve to retain potassium in the slag and thus restrict potassium loss to the flue gas and eventually as deposits on the down-stream, heat exchange elements. The results finally show that the ash or slag volume would markedly increase with increasing rice straw in the fuel blend.
The selection of an optimal fuel blends thus includes consideration of melting temperature, potassium loss, and slag/ash volume. The ash blend showing the largest liquidus temperature depression was selected as our target fuel blend (30 % rice straw ash and 70 % wood ash). A hyperbolic relationship between fuel and ash wood content (Figure 15), translates a 30 % rice straw ash content into a 3 % rice straw component in the equivalent fuel blend due to the large difference between pure wood and pure rice straw ash concentrations. Therefore, we selected two fuel blends bracketing this composition: (1) 2.6 % rice straw and 97.4 % wood fuel and (2) 9.6 % rice straw and 90.4 % wood fuel. As control fuels, we selected two additional fuels; (3) 100 % wood fuel and (4) a 10.7 % leached rice straw and 89.3 % wood fuel blend. The leached rice straw fuel was selected in order to evaluate the effects of the removal of potassium and chlorine form the straw. Pure rice straw fuel and higher straw blends were not tested since these fuels are well known readily to cause bed agglomeration (Bakker et al., 1999; Salour et al., 1993).

![Figure 15. Wood ash fraction as a function of wood percentage (ash or fuel) on a weight basis. Dots are the investigated fuel blends.](image)
Figure 16. Agglomerated bed extracted from the fluidized bed reactor after termination of experiment FBC-4 using a 9.6 % rice straw blend and a reactor temperature of 1030 °C. The vertical channel is after a thermocouple rod.

Bed Agglomeration

Fuel blends were tested in a pilot scale fluidized bed combustor. The main findings discussed here relate to observation of bed agglomeration. The experiment using the 9.6 % rice straw fuel blend was terminated by strong bed agglomeration that plugged the reactor and defluidized the bed. This was seen as a marked drop in differential bed pressure and rise in bed temperature to 1195 °C. The agglomeration was estimated to have affected 25 % of the total bed material, but was concentrated in the central part of the reactor (Figure 16). This agglomeration estimate is based on the extracted bed after the experiment and is calculated on a weight basis relatively to the original bed material. Figure 17 shows how silicate material forms as a film along the grain boundary and cements the bed particles together. The result is a highly porous bed cemented along a few grain boundaries. Minor agglomeration was observed in two other experiments, in both cases insufficient to have affected combustion. These were an experiment using the 2.4 % rice straw blend indicated an about 1 % agglomeration of the bed and the experiment using the leached rice straw blend likewise showed minor bed agglomeration (~0.1 %). Bed agglomeration in the latter cases may increase over the much longer term without bed replacement, but this effect was not evaluated in the present study.
The bed agglomeration percentages are summarized in Figure 18 as a function of percent rice straw content in the fuel blend. Bed agglomeration is expected to depend on fuel composition, combustion temperature, and duration. All experiments showing bed agglomeration were done with a 1000 °C furnace wall temperature and maximum reactor temperature between 1030 and 1090 °C. The highest reactor temperature was achieved for the experiment using the pure wood fuel (FBC-5, 1090 °C) without agglomeration. Minor agglomeration was found for the experiment using the leached straw fuel blend (FBC-6, 1070-40 °C). The highest agglomeration was found for the experiment using the 9.6 % rice straw blend (FBC-5, 1030 °C). Of the experiments based on the 2.6 % rice straw blend, only the experiment with the highest reactor temperature (FBC-3, 1050 °C) showed modest bed agglomeration. Two experiments using the same 2.6 % rice straw blend revealed no bed agglomeration (FBC-1 and FBC-2, 825 and 920 °C, respectively). These results indicated that the fuel composition and combustion temperature control the extent of bed agglomeration. Figure 18 illustrates the effects on adding rice straw to a wood based fuel. The bed agglomeration measured as fraction of total bed on a weight basis increases exponentially with increasing rice straw in the fuel blend. The duration of the individual combustion experiments was not significantly different to allow the effect of continuous combustion and duration on agglomeration to be evaluated.
The combustion temperature also has a significant effect. For the 2.6 % rice straw blend, only the experiment with the highest combustion temperature showed minor agglomeration, while the lowest temperature experiments on the same fuel blend did not reveal agglomeration. The effect of duration was not investigated in the present study. The results for the short tests conducted reveal no clear correlation between duration and extent of bed agglomeration, despite the fact that the experiments with the lowest combustion temperatures and the lowest rice straw ash ratio also had the lowest run duration.

Bed and Ash Composition Analyses on the agglomerates revealed no significant mineralogical changes in the bed material with extent of agglomeration. Bed agglomeration is, therefore, attributed to either sintering of bed particles aided by potassium released during combustion or to the deposition of partially molten ash fragments or particles. Studies of the cause of agglomeration are currently in progress using the scanning electron microscope.

Table 4 shows the composition of glass layer (binder) developed on bed particles and compares it to the predicted slag composition for the respective ash blends (Part 1). The composition of the binder show similarities with the slag formed from the melting experiments for a 50 % rice straw ash blend. Best correspondence is seen for the low temperature experiments (1180 °C) although the binder is deficient in both potassium and silica by comparison. It is clear that complex particle segregation and fractionation may occur during bed agglomeration and that these processes require further study.
Table 4. Bed Binder and Corresponding Slag and Ash Compositions

<table>
<thead>
<tr>
<th></th>
<th>Binder FBC#3</th>
<th>R50-6 1180 oC</th>
<th>R50-9 1318 oC</th>
<th>Ash Blend</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>58.42</td>
<td>63.77</td>
<td>58.62</td>
<td>53.45</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.81</td>
<td>0.22</td>
<td>0.09</td>
<td>0.09</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>9.83</td>
<td>4.31</td>
<td>2.45</td>
<td>2.02</td>
</tr>
<tr>
<td>FeO</td>
<td>2.94</td>
<td>1.11</td>
<td>0.82</td>
<td>0.78</td>
</tr>
<tr>
<td>MnO</td>
<td>0.48</td>
<td>1.58</td>
<td>1.39</td>
<td>1.28</td>
</tr>
<tr>
<td>MgO</td>
<td>3.62</td>
<td>3.92</td>
<td>4.94</td>
<td>4.14</td>
</tr>
<tr>
<td>CaO</td>
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<td>12.66</td>
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</tr>
<tr>
<td>Na₂O</td>
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<td>0.33</td>
</tr>
<tr>
<td>K₂O</td>
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<td>9.50</td>
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</tr>
<tr>
<td>P₂O₅</td>
<td>2.82</td>
<td>2.28</td>
<td>0.78</td>
<td>2.36</td>
</tr>
<tr>
<td>Total</td>
<td>99.44</td>
<td>99.94</td>
<td>98.27</td>
<td>100.00</td>
</tr>
</tbody>
</table>

The bed material is transported down-stream in the reactor and disengagement zones and is deposited on the heat exchangers and found in the ash dropouts after the horizontal pass and cyclone. Most of the bed particles are disengaged above the reactor and fall back along the wall in the lower speed boundary layer (Figure 19). Finer particles become entrained on the gas flow, elutriated from the bed, and some separate from the flow by settling in horizontal pass. These ashes are often predominantly composed of bed material as revealed by mullite and cristobalite XRD reflection peaks in all ashes collected from the horizontal pass. The ashes collected from cyclone fallout do not show the presence of bed material. These results are not unexpected, as attrition and elutriation of bed material would result in an increasing fraction in the horizontal pass.

Figure 19. Trajectories of bed material in window into the disengagement zone with deposit probes.
The only crystalline material present in the fly ash is calcite that is observed in most cyclone dropout ashes (except FBC-1). Calcite is not consistently present in ashes collected from the horizontal pass and is not observed in any of the bed materials. Because the combustion temperatures were mostly above the thermal decomposition temperature of calcium carbonate, it is possible that the calcite found in the cyclone ash precipitated from the flue gas.

**Conclusions**

Fluidized bed combustion of rice straw and wood fuel blends results in bed agglomeration under certain conditions. Important findings include:

- Fuel blend composition, reactor temperature, and duration are the principal controls on bed agglomeration for the atmospheric laboratory scale fluidized bed combustor used in the present tests.
- Strong bed agglomeration occurs with fuel blends containing ~10% rice straw fuel sufficient to arrest bed circulation after 3-4 hours of operation.
- Minor bed agglomeration occurs with fuel blends containing ~3% rice straw fuel without causing detectable disturbances of bed circulation up to 5 hours of operation.
- An apparent exponential increase in agglomeration with rice straw in the fuel blend suggests a practical rice straw content of 7-8% without restricting bed circulation and causing major agglomeration.
- A test using ~10% leached rice straw fuel blend revealed only minor bed agglomeration and suggests that leaching can efficiently restrict bed agglomeration.
- The composition of the melt deposit on the bed particles support the conclusions from the melting experiments that rice and wood ash particle blends causes melting point depression. This results in fusion of bed material and eventually defluidization.
- The compositional correspondence between the observed melt deposit and the result of melting experiments support that simplified melting experiments can approximate complex combustion processes.
Project Conclusions

The blending of rice straw with wood based biomass fuels can be predicted to results in marked changes in the behavior of potassium and its partitioning between the solid inorganic slag and the flue gas. Potassium is increasingly retained in the slag with increasing rice straw ash component. This is caused by systematic increases in polymerization of the melt phase and ease of accommodation of potassium with increasing rice straw ash in the blends. Strong retention is in addition controlled by low melting temperature approaching the solidus temperature for the slag and the saturation of potassium-aluminum-silicate minerals. The liquidus temperature shows a marked freezing point depression from above 2000 °C to about 1260 °C for blends with a content of about 30 % rice straw ash. This content is equivalent to about 3 % rice straw content in the fuel. The complete melting intervals from liquidus to solidus conditions of ash blends are about 100-150 °C.

This suggest that the addition of a small amount of straw to a predominantly wood fuel will have the effect of lowering melting temperature and potassium loss to the flue gas. If combustion temperature can be controlled to within, or below, the melting interval of the resultant ash/slag (<1100 °C), the loss of potassium can be further minimized. An obvious drawback of adding straw materials is that the total volume of ash and slag will dramatically increase by a factor of 10-20 compared to clean wood.

Fuel blend composition, reactor temperature, and duration are the principal controls on bed agglomeration in fluidized bed combustors. The extent of bed agglomeration in our laboratory scale experimental combustor shows an exponential increase with rice straw component that suggests that a maximum of 7-8 % rice straw blends may be permissive for this type of biomass boiler. It is also shown that boiler operation below the minimum solidus temperature (~ 1050 °C) strongly will restrict potassium losses and therefore bed agglomeration.

The similarities between the compositions of the bed deposits and the liquidus and subliquidus experimental melts obtained using the rapid quench furnace confirm that the approach taken in this study is a viable and cost effective approach to understand agglomeration of fluidized beds. The quench experiments also duplicate the phase compositions and mineralogy observed in commercial operating power plants. Future experimental work should be undertaken to include gas components and gas mixtures that better approximate actual commercial boiler conditions. It is also of interest that slag deposits observed in commercial biomass boilers
contains the same minerals and glass/melt compositions as found in the simplified laboratory melting experiments on ash blends of commonly used biomass fuels.

The principal problem in fluidized bed combustion thus appears not to be the relative potassium loss to the flue gas and its deposition on heat exchangers, but rather the large increase in inorganic material that will affect the bed operation, be deposited on firesides, and transported as ash particles to the heat exchange surfaces. The effect of potassium is to lower ash melting temperature and to increase slag formation on firesides and in the fluidized bed.

**Project Recommendations**

Continued research in the fundamental aspects of ash and slag formation of commercially common biomass fuels is required to build a better basis for future development and testing of the use of biomass fuels for power generation. This involves building on the melting experiments reported in this study to include more complex gas mixtures that better represent actual flue gas compositions in biomass combustion. Further experiments on bed agglomeration in laboratory scale combustors will also be needed. Full-scale studies of the use of straw fuels in biomass boilers will be useful to test the conclusion that 7-8% unleached straw can be used in fluidized beds with temperatures held below about 1050 °C. The results of laboratory scale investigations like those reported here indicate that the use of straw fuels at proper concentrations may contribute to reduce the extent of potassium volatilization and fouling in superheater and other heat exchanger systems. Well-controlled longer-term tests, even at the laboratory scale, would reveal whether these conclusions could be supported in practice.

**Public Benefits to California**

This study shows that it may be feasible to burn small amounts of straw in operating biomass boilers under the proper conditions. This result can have both near and long termed impact on the viability of the biomass power industry and can result in immediate practical improvements in fuel flexibility. Increasing use of straw has immediate environmental and energy benefits. The results also suggest ways to incorporate straw additions into new facility design, possibly leading to higher straw consumption as the industry repowers with more advanced systems.
References


Williams, R.J. and Mullins, O., 1981. JSC systems using solid ceramic oxygen electrolyte cells to measure oxygen fugacities in gas-mixing systems. NASA Technical Memorandum 58234.
