SLAG FORMATION AND POTASSIUM VOLATILIZATION FROM RICE STRAW BLENDED WOOD FUEL

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Introduction

There is experimental evidence that the addition of straw to conventional biomass boiler fuels in some instances may reduce potassium fouling. The results of an evaluation of urban wood fuel ash[1] show that potassium is strongly partitioned into the vapor phase. It is also known[2] 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. The potential of these preliminary findings is that the addition of rice straw to conventional wood based fuels may be beneficial and may reduce potassium losses and thereby fouling.

We present the results of a systematic experimental study of the high temperature melting relations of ashes produced by mixing rice straw and wood. 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 predictions of the subscale ash experiments are tested using an atmospheric fluidized bed combustor (AFBC). The laboratory scale combustor allows us to better simulate the complexities of full-scale application than is possible with the atmospheric rapid quench furnace.[3,4]

Ash Melting Experiments

Experimental and Analytical Procedures

Starting materials for the melting experiments consist of two biomass fuels. The first is mixed whole tree chips of white fir and ponderosa pine, typical of clean fuel types received at commercial plants (ash content 1.1%, dry basis). The other is a M202 rice straw variety from California (ash content 20%). The two fuels were ashed at 525 ^{o}C using standard procedures. A total of six ash blends with from 10 to 50 % rice straw ash were prepared from the wood and rice straw ashes (Figure 1; Table 1). The compositions of the ashes and the ash blends are summarized in the Table 1, normalized to 100 % volatile free.

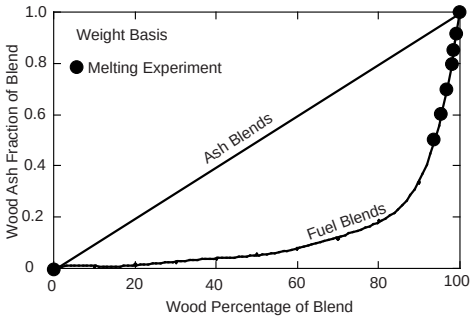

Figure 1. Wood ash fraction as a function of wood percentage in blend (ash or fuel) on a weight basis. Dots are the investigated fuel ash blends.

About 50-mg powder for each experiment were pressed in a pellet and mounted onto a 0.004" diameter Pt-wire. These mounted pellets were suspended into the furnace at the desired temperature. Temperature was monitored by a Pt/^{90}Pt^{10}Rh thermocouple that was positioned near the ash pellet. Duration of the experiments varied to about 24 hours and temperature from the near solidus to the liquidus conditions. The experiments were terminated in air by pulling the sample out of the furnace.

Table 1. Summary of Ash Blends Used in the Experiments

	Rice Straw	R 50% W 50%	R 40% W 60%	R 30% W 70%	R 20% W 80%	R 15% W 85%	R 10% W 90%	Wood
SiO2	82.28	53.91	47.07	39.74	31.87	27.72	23.40	14.26
TiO2	0.01	0.09	0.11	0.13	0.15	0.16	0.17	0.20
Al2O3	0.10	2.04	2.51	3.01	3.55	3.84	4.13	4.76
Fe2O3	0.11	0.79	0.95	1.13	1.32	1.42	1.52	1.74
MnO	0.10	0.43	0.51	0.60	0.69	0.74	0.79	0.90
MgO	1.79	4.18	4.76	5.37	6.04	6.39	6.75	7.52
CaO	1.75	21.42	26.16	31.24	36.69	39.57	42.56	48.90
Na2O	0.15	0.34	0.38	0.43	0.48	0.51	0.54	0.59
K2O	13.04	14.42	14.76	15.11	15.50	15.70	15.91	16.35
P2O5	0.67	2.38	2.79	3.24	3.71	3.96	4.22	4.77
Total	100.00	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 %.

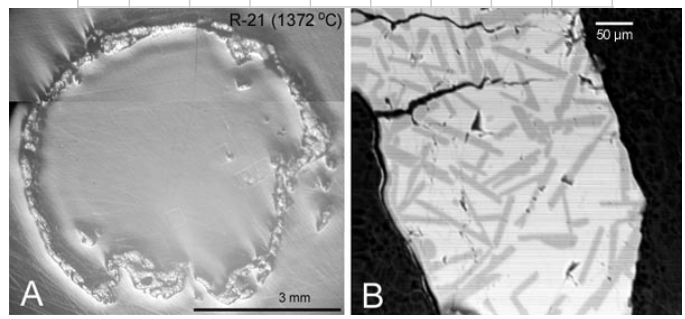

Figure 2. Rice straw ash products. (A) Reflected microscope image of experimental product at 1372°C. The product is composed of a large bubble with a thin outer wall. Scale bar is 3 mm. (B) Back-scattered electron image of the silicate wall in Figure 2A. The dark tabular grains are a quartz polymorph. Light gray is glass. Scale bar is 50 µm.

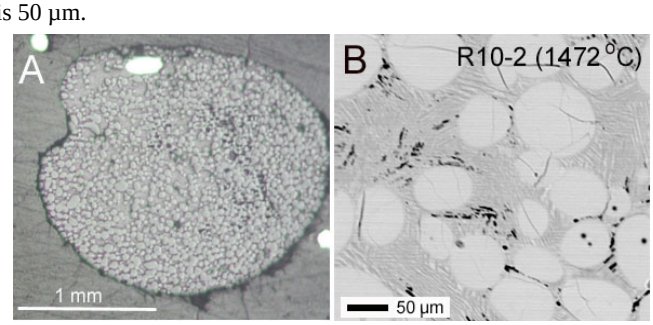

Figure 3. 10% rice straw ash blend products. (A) Reflected microscope image of the product heated at 1472°C. The experimental product is a compacted droplet of rounded larnitic grains and an interstitial quenched melt. Scale bar is 1 mm. (B) Back-scattered electron image of the center of the same experimental product as in Figure 3A. The lighter rounded grains are larnite. The quenched interstitial melt is composed of two unidentified phases. Scale bar is 50 µm.

Melting Results

The initial tests involve the 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 basis for testing the effects on melting blends of the two ashes. Here we only show two examples of the experimental products. Figure 2A shows a reflected light microscope image of pure rice ash heated to 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. The back-scattered electron image of the silicate wall indicates dark, needle-shaped quartz polymorphs and light gray glass.

The experimental products on an ash blend with 10 % rice straw ash are illustrated in Figure 3. Figure 3A shows a reflected microscope image of the product from 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 3B shows the textural relationships between rounded larnite grains and quenched interstitial melt composed of two unidentified phases.

Elemental Losses and Phase Appearances

The proportions of the solid phases and the coexisting liquid in the experimental products are estimated by least-squares, linear approximations of the compositions of the phases in the experimental products to the composition of the starting ash mixtures. 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 by including the element in question as an oxide in the calculations. This was done for K_2O and Na_2O for which the largest losses were detected.

The calculated losses of K_2O are illustrated in Figure 4. K_2O is strongly volatilized 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_2O 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.

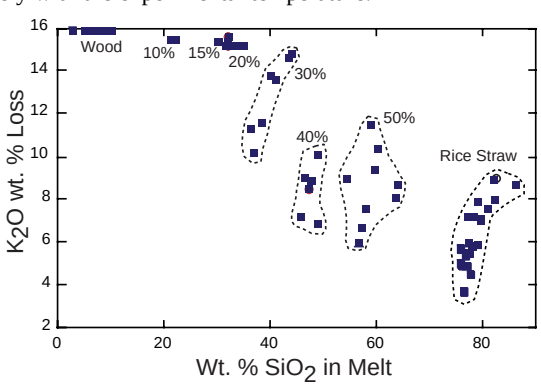

Figure 4. Losses of K_2O (wt. %, ash basis) from the experimental products as a function of SiO_2 content of melt.

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 a rather uncertain liquidus temperature of 1950-2050°C.

The addition of rice straw ash to the wood ash causes a strong drop in liquidus temperature. With 10 % added rice straw ash, the liquidus temperature is still too high to be directly 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. With 30 % added rice straw ash, wollastonite and åkermanite appear nearly simultaneously on the liquidus at 1264±11°C and are followed by leucite at 1217±11°C. With 40 % added rice straw ash, the liquidus phase is wollastonite at 1282±14°C and with leucite and diopside appearing nearly simultaneously at a temperature of 1212±11°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.

Because temperature dependent losses of K_2O 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 liquidus temperature cannot be based on bulk ash compositions, as often done, but must take into consideration temperature dependent changes in bulk composition.

An important observation is that the retention in the slag of K_2O can be correlated with the appearance of leucite. Leucite is a K_2O and Al_2O_3 rich phase that is stabilized at relatively low temperature and low melt fraction in coexisting melts relatively enriched in Al_2O_3 and K_2O. The appearance of leucite, thus, strongly controls retention of K in the slag. This is seen for the 30 to 50 % rice straw blends. 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.

The liquidus temperature (or complete melting point) was bracketed in four series of experiments (50, 40, 30, and 20 %). The liquidus temperature for pure rice was extrapolated to approximately 1575°C. The true liquidus for a starting composition with 12 wt. % K_2O may very well be below 1100°C; however, for practical purposes the 'elevated' liquidus temperature shown on Figure 5 may be more relevant.

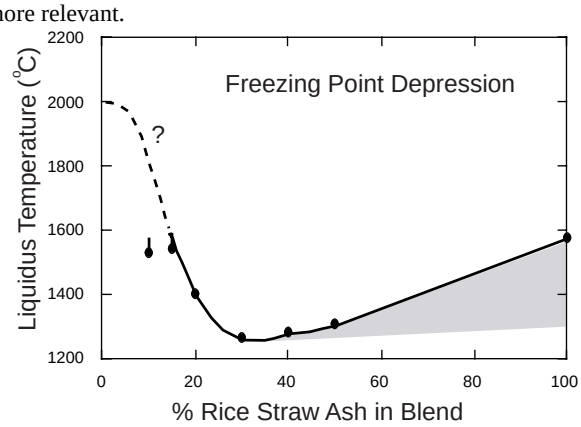

Figure 5. Experimentally determined liquidus temperatures as a function of weight % rice straw ash in the ash blend.

The resulting freezing point depression as a function of the percentage of rice straw ash in the blends is shown in Figure 5. 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 rises steadily to 50 % straw ash, and probably also beyond, to an apparent 1536°C for pure rice straw ash (4°C/wt.% rice ash).

Fluidized Bed Combustion

Combustion tests were conducted in an atmospheric laboratory scale fluidized bed combustor.[5,6] 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.

The fuel blends for the fluidized bed testing were selected based on the results of the bench top melting experiments on fuel ash blends. In these experiments, a minimum liquidus temperature was observed for a 30 % rice straw ash blend. We selected two fuel blends bracketing this ash 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. Pure rice straw fuel and higher straw blends were not tested since these fuels are well know readily to cause bed agglomeration.[6,7]

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. The agglomeration was estimated to have affected 25 % of the total bed material, but was concentrated in the central part of the reactor (Figure 6). This agglomeration estimate is based on the extracted bed after the experiment and is calculated on a weight basis relative to the original bed material. Figure 6 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 that indicate about 1 % agglomeration of the bed and an experiment using the leached rice straw blend likewise showed minor bed agglomeration (~0.1 %).

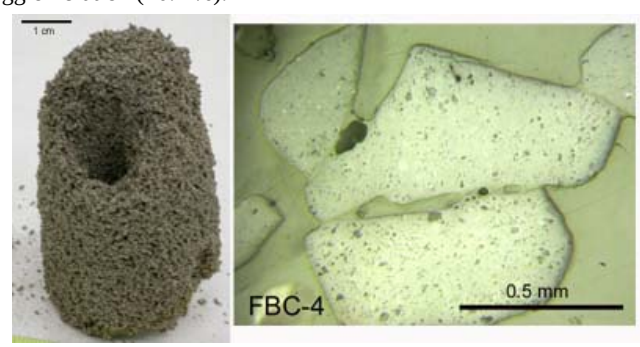

Figure 6. Agglomerated bed extracted from the fluidized bed reactor after termination of an experiment using a 9.6 % rice straw blend and a reactor temperature of 1030°C. The vertical channel is after a thermocouple rod. Right is shown bed agglomeration of bed particles (mullite) by silicate cement (Ca-K-Mg-P-Si).

The bed agglomeration percentages are summarized in Figure 7 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 (1090°C) without agglomeration. Minor agglomeration was found for the experiment using the leached straw fuel blend (1040-70°C). The highest agglomeration was found for the experiment using the 9.6 % rice straw blend (1030°C). Of the experiments based on the 2.6 % rice straw blend, only the experiment with the highest reactor temperature (1050°C) showed modest bed agglomeration. Two experiments using the same 2.6 % rice straw blend revealed no bed agglomeration (825 and 920°C, respectively). These results indicated that the fuel composition and combustion temperature control the extent of bed agglomeration. Figure 7 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 (2-6 hours) to allow the effect of continuous combustion and duration on agglomeration to be evaluated.

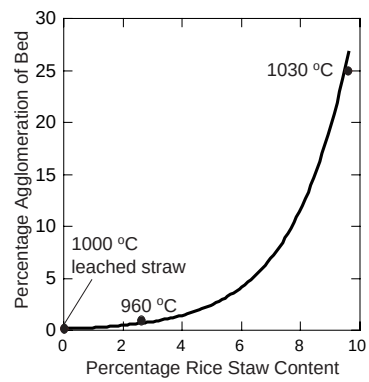

Figure 7. Estimated bed agglomeration as a function of rice straw in the fuel.

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 duration tests conducted reveal no clear correlation between duration and extent of bed agglomeration.

Analyses of 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.

Conclusions

The blending of rice straw with wood based biomass fuels is shown 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 ash component. 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 in the slag. 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.

These results suggest the addition of a small amount of straw to a predominantly wood fuel will have the effect of lowering melting temperature and the relative potassium loss to the flue gas. If combustion temperature can be controlled to within, or below, the

melting interval of the resultant ash/slag (<1260°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 compared to clean wood. A pure wood fuel will loses most of its K_2O content, around 2 g K_2O/kg fuel. On the other hand, rice straw fuel will lose a lower fraction (0.3) of its original K_2O content, around 8 g K_2O/kg fuel. The determined (and interpolated) K_2O losses on a fuel intake basis are illustrated in Figure 8 showing a rapid increase in K_2O loss until a rice straw fraction of 20% after which the loss levels and remains fairly constant at 7-8 g/kg fuel.

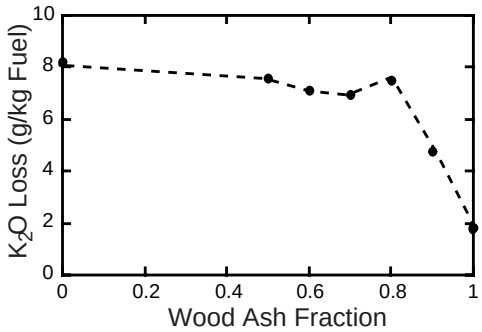

Figure 8. Experimental determined, near-solidus K_2O losses (g) on basis of fuel intake (kg) plotted as a function of wood ash fraction of blend. (wt. basis).

Fuel blend and bed medium 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 suggesting that a maximum of 7-8 % rice straw blends may be permissible for this type of biomass boiler. It is also shown that boiler operation below the minimum solidus temperature (~ 1050°C) dramatically reduces potassium losses and therefore bed agglomeration.

Addition of rice straw to wood fuel decreases the fractional volatilization of potassium. However, because of the large difference in the ash fractions of the two fuel components, will not decrease the total fuel potassium volatilized that will rapidly increase until a straw fuel component of 20%. The principal problem in fluidized bed combustion thus appears not to be the fractional potassium loss to the flue gas, but rather the large increase in inorganic material that can severely affect the bed operation, may be deposited on firesides, and will be transported as ash particles to the heat exchange surfaces.

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