

0961-9534(95)00058-5

# ON THE PROPERTIES OF WASHED STRAW

B. M. JENKINS, R. R. BAKKER and J. B. WEI

Department of Biological and Agricultural Engineering, University of California, Davis, CA 95616, U.S.A.

(Received 26 June 1995; accepted 14 August 1995)

Abstract—The removal of troublesome elements in biomass to reduce slagging and fouling in furnaces and other thermal conversion systems was tested by washing (leaching) the fuel with water. Rice straw and wheat straw were washed by various techniques and analyzed for composition and ash fusibility. Potassium, sodium, and chlorine were easily removed in both tap and distilled water. Total ash was reduced by about 10% in rice straw and up to 68% in wheat straw, although washing was more effective in increasing ash fusion temperatures for rice straw than for wheat straw due to the higher initial silica concentrations in rice straw. Untreated straw ash which fused below 1000°C was observed to become more refractory at higher temperatures when washed. Scanning electron microscopy of untreated and treated rice straw ashed at 1000°C revealed all untreated ash particles to be fused and glassy, while treated particles remained unfused, were heavily depleted in most elements other than Si, and displayed structures characteristic of original cellular morphology. The fusion temperatures of the straw ash were consistent with predicted temperatures from alkali oxide-silica phase systems based on the observed concentrations of elements in the ash. A simple attempt at simulating a possible full scale washing process was carried out by spraying the surface of a bed of straw with water for an arbitrary time of 1 min. This proved less effective in removing alkali metals and chlorine than soaking the samples in water, flushing water through them in a more controlled manner, or leaving the straw exposed in the field to natural precipitation. Electrical conductivity measurements of leachate revealed that extraction was mostly complete after application of 0.04 l g<sup>-1</sup>, equivalent to 24 mm of precipitation over uniformly spread rice straw. Full scale furnace experiments have not yet been conducted, and issues involving the practical application of the technique require further investigation, but these results suggest that fouling rates should decline for treated fuels compared to untreated fuels in conventional and advanced biomass power systems. Copyright © 1996 Elsevier Science Ltd.

Keywords-Biomass; straw; combustion; inorganic elements; ash fusibility; slagging; fouling; washing; leaching; leachate.

## **1. INTRODUCTION**

Straw fuels have proved to be extremely difficult to burn in most combustion furnaces, especially those designed for power generation. None of the biomass power plants built to date in California can economically fire straw, even though some of the plants were constructed with air permits requiring them to do so. Experience in Denmark with straw has been somewhat more successful, although straw does create significant maintenance problems there as well. The problems of straw are also those of many herbaceous fuels currently proposed as energy crops and annual growth biomass from short rotation, intensive culture systems, if intended for use in similar combustion furnaces.

The combustion of straw in power boilers employing stoker-fired grate furnaces, fluidized beds, and suspension units leads to the rapid formation of unmanageable deposits on the fireside surfaces, in particular cross-flow screen tubes and superheaters. Such deposits, comprised commonly of alkali and alkaline earth chlorides, sulfates, carbonates, and complex silicates, retard the rate of heat transfer as a result of their low thermal conductivity and high reflectivity. Deposits can bridge across tube bundles, increasing the combustion side pressure drop, and reducing the flow through the convection pass, or increasing the fan work needed to sustain proper flow. Deposits are associated with accelerated corrosion of tube metal. Slag formation in the furnace and on grates hinders fuel feeding, combustion, and ash removal and handling. All of these problems increase the cost of generating power from low quality biomass fuels, because they reduce the facility efficiency, capacity, and availability. In many areas where power generation from straw and other wastes would serve a vital public service in reducing atmospheric emissions from open burning, they remain unutilized for reasons including fouling. Given the current interest in the production of herbaceous species (e.g. switchgrass) and the use of annual growth biomass tissues (e.g. limbs from pulp trees) as fuels not only for biochemical conversion, but for thermochemical power generation as well, methods to reduce the fouling characteristics of these fuels are needed.

The principal causes of fouling in boilers have recently been investigated for biomass fuels.1-6 Although the principal mechanisms have been described, the actual phenomena are far from being completely understood. Clearly, however, the fouling can be related to the presence of certain key elements in the fuel and other materials in the boiler (e.g. sand media used in fluidized beds). Primary among these for the herbaceous fuels are potassium, chlorine, silicon, and sulfur. Calcium, and to some extent magnesium, are also important for wood fuels, and if limestone or dolomite are added to the system. Phosphorous appears to be a significant element in manure combustion. Another alkali metal, sodium, is not normally present at high concentration in plant tissues, unless added by some process (e.g. soaking in seawater, or processed in salt solutions as are olive pits). If present, sodium also contributes to fouling. For herbaceous materials, including grasses and straws, the reactions between potassium and silicon (in the form of silica), with chlorine as a facilitator, lead to the rapid formation of heavily sintered and fused glassy deposits and slags at normal furnace operating temperatures (average temperatures run 800-900°C, peak flame temperatures are likely much higher). The liquid component of these deposits leads to the further capture of flyash on surfaces through inertial impaction and sticking. Even when blended at relatively low concentration with a

more benign fuel such as wood, straws can lead to a facility outage within a matter of days or hours.<sup>3</sup> Additives used to combat fouling have not proved particularly successful.

A comparison of the ash compositions for selected fuels appears in Table 1. These are representative only, individual compositions among the same fuel type can vary appreciably. All fuels listed in the table are either considered as fuels, or currently used as fuel (bagasse and wood). Several features can be readily observed in the table. The grasses (gramineae) have high silica concentrations and generally high potassium concentrations, with the exception of sugar cane bagasse. The total ash concentrations are also high for the gramineae, again with the exception of sugar cane bagasse. The high alumina concentration for bagasse implies substantial contamination from soil, which may account for some portion of the silica and other elements. The clean wood fuel, in this case Douglas fir, has a low silica concentration, and low total ash concentration. The potassium concentration in the ash is the highest shown, but the low ash concentration yields a low total potassium in the fuel. The wood fuel also has a low chlorine concentration in comparison to the herbaceous materials, again with the exception of sugar cane bagasse, which is leached of potassium and chlorine during extraction of sugar from the cane. This leaching action results in a reduction of total ash concentration. Bagasse and clean wood are commonly burned without excess fouling.

The possibility of removing substantial amounts of key fouling elements is suggested by the composition of sugar cane bagasse, and by the results of chemical fractionations carried out as part of biomass fuel analyses. Several fuels

Oxide(% ash)	Rice straw	Wheat straw	Switch-grass	Sugar cane trash†	Sugar cane bagasse	Douglas Fir wood
SiO <sub>2</sub>	74.31	35.84	65.18	57.38	46.61	12.26
Al <sub>2</sub> O <sub>3</sub>	1.40	2.46	4.51		17.69	2.83
TiO <sub>2</sub>	0.02	0.15	0.24		2.63	0.08
Fe <sub>2</sub> O <sub>3</sub>	0.73	0.97	2.03	1.74	14.14	4.24
CaO	1.61	4.66	5.60	13.05	4.47	37.08
MgO	1.89	2.51	3.00	4.30	3.33	5.86
Na <sub>2</sub> O	1.85	10.50	0.58	0.27	0.79	3.16
K <sub>2</sub> O	11.30	18.40	11.60	13.39	4.15	17.00
SO <sub>3</sub>	0.84	5.46	0.44	7.31	2.08	11.20
P <sub>2</sub> O <sub>5</sub>	2.65	1.47	4.50	2.27	2.72	1.86
Und.*	3.40	17.58	2.32	0.29	1.39	4.43
Total Ash (% dry fuel)	19.60	13.00	8.97	5.04	2.44	0.45
Cl (% dry fuel)	0.74	2.02	0.10	0.22	0.03	0.01

Table 1. Ash compositions of selected herbaceous fuels and wood

\*Undetermined, may consist primarily of chlorine and carbonates.

†Tops and leaves. Blank indicates not analyzed.

have been analyzed in this way.<sup>3</sup> The chemical fractionation test is used to characterize the nature of the inorganic components of the fuel by sequentially leaching the fuel in water, ammonium acetate, and hydrochloric acid. The amount of each element removed at each step is quantified. In general, such tests show that large fractions of potassium, chlorine, and phosphorous in biomass are removed by water, and that most of the inherent alkali and alkaline earth components are water soluble or ion exchangeable. Another test, used to characterize the water soluble alkali by leaching in water at 90°C, shows large removal fractions for alkali elements. Encouragement is also found in the work<sup>7</sup> conducted for NASA on the leaching of crop residues for nutrient recycling in controlled ecological life support systems (CELSS). Based on our current understanding of the way biomass fuels foul thermal conversion systems, the removal of these elements prior to conversion should greatly diminish the fouling tendencies of biomass fuels.

The purpose of the preliminary study reported here was to determine the extent to which various fuel elements could be removed by leaching the fuel with water, and to characterize the effect of such removal on ash fusibility. Samples of two types of fuels, rice straw and wheat straw, were washed in various ways and analyzed for elemental composition. In addition to controlled washing experiments in the laboratory, samples of rice straw were collected from the same field at several times during the winter season to determine the extent of leaching by natural precipitation. Ion concentrations in leachate from laboratory washed samples were determined. Furnace studies were conducted on untreated and washed samples to investigate differences in ash fusibility resulting from the treatments. Structure and point compositions of ash samples were analyzed using scanning electron microscopy and electron beam microprobe. The results of these analyses show distinct differences in the fusion behavior of washed fuel samples compared to untreated samples, and suggest possible process options for mitigating slagging and fouling when burning straw and other biomass fuels.

## 2. METHODS

## 2.1. Rice and wheat straw samples

Samples of rice straw were collected from the same field in Sutter county, in northern California, on three separate occasions. The first sample was collected immediately after grain harvest, and prior to any precipitation on the cut straw. The grain had been harvested in the conventional manner using a combine harvester, with straw spread behind the harvester in a layer on top of the standing stubble. The second sample was collected after the first rain of the season. The third sample was collected late in the season, following a period of nearly continuous precipitation that flooded the field. At this last sampling event, samples were collected of straw lying both on top of the stubble and on the ground. The sampling times are indicated in the precipitation history displayed in Fig. 1.

Wheat straw was obtained from a power plant in the Imperial Valley, in southern California. The straw was purchased locally in bales and was originally to be used as fuel. Because of difficulties caused by boiler fouling, most of the straw was not burned. A sample was collected from the bale storage. The sample had not been exposed to precipitation. Some contamination from wood chips and soil particles was observed with this fuel; these were removed by screening prior to any of the tests described here. This wheat straw is characterized by a very high chlorine content typical of crops grown under saline irrigation.

After observing the ash fusion characteristics of the wheat straw from the Imperial Valley source, another sample of wheat straw grown in Yolo County, northern California, was evaluated. This wheat straw was produced under low salinity conditions, and had lower chlorine and alkali metal concentrations. The results for this straw are included in the discussion by way of comparison to the straw from the Imperial Valley source.

## 2.2. Leaching techniques

Five laboratory treatments were applied to most samples of rice and wheat straw. These treatments included leaching with room temperature  $(20-25^{\circ}C)$  water by three different methods:

• Spraying water over the top of a 30 mm thick straw bed supported on an expanded steel mesh. The total weight of straw in each batch was 100 g (at original moisture contents of approximately 8% wet basis). Each batch was uniformly hand sprayed using UCDavis tap water (EC = 485  $\mu$ S cm<sup>-1</sup>) for a period of 1 min.



Fig. 1. Precipitation for Sutter County, California, fall/winter 1994-95. Sampling dates by treatment number indicated by vertical dashed lines.

Whole straw as collected from the field was used for all tests. Some fine particles were lost in this process.

- Pouring either tap or distilled water (EC <2 $\mu$ S cm<sup>-1</sup>) through the sample spread over a fine mesh stainless steel screen, with all leachate and fine particles collected beneath the sample. A total of 20 l of water was poured through each 100 g sample in 1 l increments. The electrical conductivity (EC) of the leachate collected from each 1 1 increment was measured. The cumulative leachate EC was also measured at each increment. For most tests, straw was hammermilled through a 19 mm round hole screen prior to leaching. Some fine particles were lost as dust in the milling process. A separate test was conducted on a 50 g pulverized straw sample obtained by milling through a 20 mesh screen. This test was conducted by leaching under vacuum through a paper element filter. A total of 71 of water in 0.5 1 increments was used.
- Submerging and soaking the samples in distilled water. 100 g samples were completely submerged and soaked in 7 l of water over 24 h. EC was measured at various times during soaking.

In addition to the laboratory washed samples, natural rain washed samples of rice straw were collected, as noted above. The first of these was

collected during the fall of 1994 (8 November 1994, day 312 in Fig. 1), after receiving approximately 65 mm of rainfall. The second and third samples were collected in mid- to late February 1995 after a cumulative 480 mm of precipitation. The second sample was picked up off the soil surface, where it had been left by heavy precipitation and flooding. The third sample included straw from the soil surface as well as a separate sample remaining on top of the standing stubble. The latter sample appeared cleaner and relatively free from soil contamination. Field samples were air dried in the laboratory immediately following collection. Moisture content of rice straw after air drying was about 8% wet basis. Wheat straw was obtained in an air dry condition at 9% moisture. Treatments are summarized by number in Table 2.

Rain washed rice straw from treatments 7 and 8 was first oven dried at  $105^{\circ}$ C and then rinsed to remove soil. Rinsing was performed on 50 g batches of whole straw for 2 min in 2 l distilled water with manual agitation. The straw was removed, and the rinsate filtered through 14 mesh to recover fine straw particles, which were then recombined with the coarse fraction. The rinsate was allowed to settle for 4 days under refrigeration, and then decanted to remove the settled fraction. The settled solids were oven dried, weighed, and ashed at 575°C. The EC of the decanted rinsate was measured. For

comparison, samples of fresh rice straw (treatment 0) and fall harvested rice straw (treatment 6), as well as a sample of fresh wheat straw (treatment 0) were processed in the same way.

### 2.3. Analytical

Solid samples were analyzed for moisture and ash content, heating value, and elemental composition. Liquid leachate samples were analyzed for ion concentration in addition to electrical conductivity. Fusibility of samples was evaluated by temperature controlled furnace. One sample of rice straw from treatment 5 was inspected by light microscope and scanning electron microscope (SEM). An electron beam microprobe was used for point compositions on SEM specimens.

Moisture analysis was by air oven at 105 C to constant weight. Ash content was determined by igniting the fuel in air for 2 h in a muffle furnace at 575°C. Ash content was also determined for selected samples at 750, 900, and 1000 C to check for weight changes.

Higher heating value at constant volume was determined by adiabatic bomb calorimeter. All samples were pelletized to prevent expulsion of the sample from the crucible during ignition and burning.

Elemental analyses for rice straw treatments 0, 1, 5 and 6 and wheat straw treatments 0 and 5 (see Table 2) were performed by Hazen Laboratory, Golden, Colorado. Samples were ignited at 600°C in air prior to analysis of ash elements.

Electrical conductivity of leachate was measured at room temperature using a YSI model 33 conductivity detector. As indicated above, both incremental and cumulative EC were determined on leachate from treatments 2–4. EC on treatment 5 was monitored intermittently.

Concentrations of ions in the leachate were determined on a Waters HPLC using a model

1

3

430 conductivity detector and WISP sample processor. Cations were analyzed on a 4.6 mm  $\times$  50 mm Waters IC-PAK Cation M/D column. Anions were analyzed on a Waters IC-PAK Anion column of the same size. The analysis was capable of detecting F<sup>-</sup>, Cl<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, Br<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, HPO<sub>4</sub><sup>=</sup>, SO<sub>4</sub><sup>=</sup>, Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Mg<sup>++</sup>, Ca<sup>++</sup>, Sr<sup>++</sup>, and Ba<sup>++</sup>, although not all of these were detected. Carbonate could be detected, although it was difficult to quantify and the ionic state was unknown (i.e. did not differentiate carbonate from bicarbonate).

Ash fusibility was investigated using a temperature controlled Kanthal high temperature furnace ( $800-1650^{\circ}C$ ). Samples of prepared ash ( $575^{\circ}C$ ) were placed in the furnace at various temperatures and examined after 1 h. State of fusion, color and bulk volume change were observed manually. All samples were heated in an air atmosphere flowing at 2.5 1 min<sup>-1</sup>. Standard pyrometric cone tests for ash fusibility were not conducted. Ash fusibility along with weight change at different ashing temperatures ( $575-1000^{\circ}C$ ) were used as a qualitative indicators of potential changes to fouling behavior.

Furnace experiments were also carried out on pelleted fuel samples (without prior ashing) of approximately 0.7 g each. The pellets were 12 mm in diameter and typically about 10 mm in height prior to testing (approximately 0.6 specific gravity). Each pellet was placed on the stage of the furnace and introduced at a temperature of 1500°C for rice straw and up to 1500°C for wheat straw. Treated wheat straw proved more likely to fuse at temperatures below 1500°C, and the temperature was varied in an attempt to determine the point of initial fusing or sintering. For rice straw, pellets were held for 1 h, removed and inspected. A replicate was held for a total of 10 min, with the furnace stage lowered for visual inspection at intervals of 2 min. During the inspection period for rice straw, the furnace temperature dropped from

Table 2. Summary of straw washing treatments for rice and wheat straw

0	Untreated,	milled (19	mm), sample	e not sub	pjected to v	washing or p	precipitation

Laboratory washed, 100 g whole straw, hand sprayed for 1 min. with tap water

2 Laboratory washed, 100 g milled (19 mm) straw, flushed with tap water, 20 l

Rice straw, naturally rain washed: 6 65 mm cumulative precipita

- 65 mm cumulative precipitation
- 480 mm cumulative precipitation, from soil surface
- 8 480 mm cumulative precipitation, from stubble surface

Laboratory washed, 100 g milled (19 mm) straw, flushed with distilled water, 20 l

<sup>4</sup> Laboratory washed, 50 g milled straw (20 mesh), flushed with distilled water, 7 l

<sup>5</sup> Laboratory washed. 100 g whole straw, submerged in 7 l distilled water, 24 h

Freatment #	Treatment	Rice straw	Wheat straw*
)	Untreated	19.6	13.0
t	Sprayed	19.1	9.5
2	Flushed (tap water)	18.3	5.0
3	Flushed (distilled water)	18.2	4.2
1	Flushed (milled)	17.9	5.2
5	Soaked	17.6	6.2
5	Rain washed (fall)	18.0	
7	Rain washed (spring, on soil)	30.9	
}	Rain washed (spring, on stubble)	21.3	

Table 3. Ash concentrations in samples of untreated and treated straw

\*Imperial Valley.

1500°C to 1350°C due to the limited capacity of the heaters. The average temperature for these shorter tests was therefore lower than that for the 1 h tests. For wheat straw at temperatures above 1000°C, samples were held in a refractory cup, as the rapid burning caused most samples to be expelled from the furnace stage at higher temperatures. These samples were inspected after 20 min as earlier observations indicated longer intervals yielded little qualitative difference.

Another set of experiments was conducted on fuel pellets ignited directly at temperatures between 800 and 1650°C. Pellets were held for 20 min at each temperature, removed and cooled. The severity of the fusion was recorded using six categories constructed to describe the typical appearance of the ash after burning.

Inspection and determination of phase assemblages (crystalline/amorphous) of rice straw samples from treatments 0 and 5 (untreated and soaked) were conducted via scanning electron microscope. Phase compositions were analyzed with a Cameca SX-50 electron beam microprobe.

#### 3. RESULTS

## 3.1. Solid properties

3.1.1. Total ash. Results of ash analyses for the various treatments are listed in Table 3. Average ash content for untreated rice straw was 19.6% dry basis. Total ash is reduced by each of the treatments employed. Hand spraying for 1 min reduced the ash content by 0.5% absolute, although this may be partly the result of fine material washed from the straw. Flushing was somewhat more effective, yielding averages of 18.3 and 18.2% ash for tap water and distilled water respectively. Leaching finely divided rice straw (treatment 4) yielded 17.9% ash, while submerging the straw in distilled water for 24 h reduced the ash to 17.6%. The ash content of the naturally rain washed samples collected after the first precipitation was 18.0%, representing an 8% relative reduction in total ash. Analysis of variance (ANOVA) on the samples for rice straw shows that the ash contents of treated straw samples are significantly different (95% level) from untreated straw samples, but there is insufficient evidence to show that they are significantly different among treatments, although hand spraying appeared to remove less ash than the other treatments.

The results for wheat straw (Imperial Valley source) are remarkable. From an original ash content of 13%, hand spraying for 1 min reduced the ash to 9.5%, while flushing and soaking reduced it to between 4 and 6%. The lowest ash content achieved, 4.2% by treatment 3 (flushing with distilled water), represents a decrease in ash content of 68%. ANOVA on the wheat straw ash concentrations showed three treatment groups to be significantly different from each other (95% level): untreated, hand sprayed, and all other flushing/soaking treatments. Insufficient information was available to show significant differences among the flushing and soaking treatments.

3.1.2. Ash color. An interesting difference between the untreated and treated ash samples is the color of the ash. The untreated ash prepared at 575°C contains both dark and light particles, suggesting carbon (possibly in the form of carbonates) or iron compounds retained in the ash. This persists to much higher temperatures. Ash from treatment 1 (hand spraying for 1 min) takes on less of this appearance. Rice straw ash from treatments 2-6 is pure white at 575°C, a condition which persists to higher temperatures. Rain washed rice straw treatments 7 and 8 (spring harvested straw) appear more uniformly brown when ashed compared to treatments 2-6 (laboratory washed and fall harvested rain



Fig. 2. Higher heating value (dry basis) of untreated and washed rice straw. Numbers next to symbols designate treatment number (refer to Table 2): untreated (triangles), hand sprayed (squares), other washing treatments (diamonds).

washed straw). Treated wheat straw ash samples do not exhibit the clarity of color of the washed rice straw ash samples, but nonetheless had fewer dark inclusions compared to the untreated ash. At higher temperatures, untreated wheat straw ash was observed to become white upon slow heating and fusing, but black upon rapid heating and fusing.

3.1.3. *Heating value*. Heating values have been correlated with ash content,<sup>8.9</sup> and are expected to follow an inverse trend with respect to ash. The measured heating values are consistent in this regard. The treated samples exhibit increasing heating value compared to untreated samples, as illustrated in Fig. 2 for

rice straw and Fig. 3 for wheat straw. The rice straw results (Fig. 2,  $r^2 = 0.457$ ) are more scattered than the wheat straw results (Fig. 3,  $r^2 = 0.884$ ), but the trend is clear in both cases. ANOVA on the results for both rice straw and wheat straw yields significant differences among three treatment groups: untreated, hand sprayed, and all other flushed/soaked treatments.

3.1.4. Elemental composition. Elemental compositions of 4 rice straw samples (treatments 0, 1, 5, and 6) and 2 wheat straw samples (treatments 0 and 5) are listed in Table 4. Total ash contents are somewhat lower in general for the rice straw analyses than for the analyses



Fig. 3. Higher heating value (dry basis) of untreated and washed wheat straw (Imperial Valley). Numbers next to symbols designate treatment number (refer to Table 2): untreated (triangles), hand sprayed (squares), other washing treatments (diamonds).

		Ric	e straw		Wheat st	raw†
Treatment	Untreated 0	Sprayed 1	Soaked 5	Rain Washed 6	Untreated 0	Soaked 5
Fuel (% dry fuel)		· _ · · · · · · · · · · · · · · · · · ·				
Carbon	37.95	39.45	40.06	39.55	42.49	45.67
Hydrogen	4.80	5.11	5.20	5.15	5.12	5.71
Nitrogen	0.52	0.47	0.48	0.60	0.68	0.64
Sulfur	0.09	0.07	0.06	0.06	0.39	0.09
Ash	18.63	17.59	17.10	17.84	12.78	6.45
Chlorine	0.74	0.38	0.06	0.06	2.02	0.21
SiO <sub>2</sub> *	13.84	14.30	15.93	16.34	4.58	3.99
Al <sub>2</sub> O <sub>3</sub>	0.26	0.10	0.17	0.15	0.31	0.18
TiO <sub>2</sub>	0.004	0.012	0.009	0.004	0.019	0.003
Fe2O <sub>3</sub>	0.14	0.13	0.08	0.09	0.12	0.10
CaO	0.30	0.42	0.36	0.37	0.60	0.38
MgO	0.35	0.38	0.15	0.24	0.32	0.15
Na <sub>2</sub> O	0.34	0.28	0.03	0.03	1.34	0.22
K <sub>2</sub> O	2.11	1.31	0.35	0.39	2.35	0.37
P <sub>2</sub> O <sub>5</sub>	0.49	0.30	0.07	0.11	0.19	0.22
SO <sub>3</sub>	0.16	0.15	0.05	0.06	0.70	0.11
Ash (% ash)						
SiO <sub>2</sub>	74.31	81.30	93.13	91.60	35.84	61.79
Al <sub>2</sub> O <sub>3</sub>	1.40	0.59	0.98	0.82	2.46	2.85
TiO <sub>2</sub>	0.02	0.07	0.05	0.02	0.15	0.04
Fe <sub>2</sub> O <sub>3</sub>	0.73	0.74	0.46	0.50	0.97	1.62
CaO	1.61	2.36	2.12	2.09	4.66	5.84
MgO	1.89	2.17	0.86	1.32	2.51	2.37
Na <sub>2</sub> O	1.85	1.57	0.18	0.19	10.50	3.48
K <sub>2</sub> O	11.30	7.45	2.03	2.21	18.40	5.81
$P_2O_5$	2.65	1.68	0.39	0.63	1.47	3.35
SO3	0.84	0.86	0.32	0.36	5.46	1.68
Cl					14.70	0.52
CO <sub>2</sub>					0.12	0.28
Und.‡	3.40	1.21	-0.52	0.26	2.76	10.37

Table 4. Elemental composition of untreated and treated straw

\*ash elements as % dry fuel computed from % ash.

†Imperial Valley source.

‡Undetermined. Blank indicates not measured.

reported in Table 3. The difference is believed to be due to the sampling procedure, in which some fine material was lost from the samples analyzed for major elements. To test this hypothesis, original hammermilled rice straw samples were sieved through 20 mesh and 40 mesh, and the ash contents of each size fraction determined. The results are included in Table 5. The finer fractions yield a substantially larger ash content than the coarse fraction. The lower total ash contents for rice straw seen in Table 4 compared to Table 3 are likely the result of differences in fine material content due to sampling. After noting this difference, more care was used in sampling the wheat straw for

 
 Table 5. Ash content of untreated hammermilled (19 mm) rice straw by size fraction

	Mass fraction	Ash
Fraction	(% dry i	fuel)
>20 mesh	78	19.6
20–40 mesh	16	21.3
<40 mesh	6	26.6
Mass average		20.3

elemental analysis, and total ash concentrations are more consistent between laboratories.

Table 5 also suggests that sampling of the untreated rice straw sample for determination of ash concentration resulted in some loss of fines. The mass average ash content from Table 5 is 20.3%, whereas the sample determination in Table 3 is 19.6%, equal to the ash content for the coarse fraction of Table 5. Given the variability in ash content observed from sample to sample, these may not be significantly different. However, as shown in later analyses (Table 10), improved retention of fines by greater care in sampling led overall to higher ash content determinations. Differences in ash content within treatments may also be partly due to interactions between varying sample composition and ashing temperature. Changes observed when ashing at higher temperatures are noted later. Although the loss of fines from some samples likely influences the compositions, ash fusibility results on whole samples, as discussed later, confirm substantial changes in ash composition due to washing.

		Rice	Straw		Wheat stra	ıw*
Treatment	Untreated	Sprayed	Soaked	Rain washed	Untreated	Soaked
Treatment #	0	1	5	6	0	5
Ash (%, measured)	18.63	17.59	17.10	17.84	12.78	6.45
$SiO_2$ (% ash)	74.31	81.30	93.13	91.60	35.84	61.79
Ash (%, computed)		17.03	14.87	15.11	_	7.40

Table 6. Measured ash content compared with ash content derived from silica conservation.

\*Imperial Valley.

The treatments are striking in the extent to which potassium has been removed. From an untreated concentration of 11.30% K<sub>2</sub>O in the ash, hand spraying for 1 min (treatment 1) reduced the concentration to 7.45%, while soaking (treatment 5) reduced it to 2.03%. This latter value is nearly equal to the potassium concentration in the fall harvested rain washed sample (treatment 6) of 2.21%. Both treatments appear to be quite effective in removing potassium, reducing the total concentration in the fuel by a factor of 5 to 6. For the wheat straw samples, soaking reduced the  $K_2O$ concentration in the ash from 18.40% to 5.81%, a reduction in the fuel concentration by a factor of 6.

Chlorine is also readily leached. Hand spraying rice straw reduced the chlorine concentration in half. Soaking and rain washing were equally effective in removing chlorine. Both treatments reduced the concentration in rice straw from 0.74% to 0.06%, a decrease of 92%. A similar reduction was observed for wheat straw. From an original concentration of 2.02% chlorine in the fuel, soaking dropped the concentration to 0.21%, a 90% reduction.

Sulfur concentration is also reduced by washing, more so for wheat straw than rice straw. From a concentration in rice straw of 0.09% S, soaking decreased the concentration to 0.06%, although there is insufficient data to test whether this is significant. For wheat straw, soaking decreased the concentration from 0.39% to 0.09%. The origin of the sulfur in the wheat straw is not known, but the sulfur was apparently present in a readily leachable form.

Nitrogen does not appear to be much affected by washing. Treatments 1 and 5 for rice straw suggest some decline relative to the untreated sample, but treatment 6 does not. If nitrogen were inert with respect to washing, its concentration would be expected to increase in the washed samples due to the loss of ash. The results are unclear as to influence of washing on nitrogen concentration.

The undetermined fraction of the untreated

rice straw ash composition is somewhat higher than for the washed treatments. Carbonates were not analyzed in these samples, and may be partly responsible for the difference. The carbonate fractions for the wheat straw samples are rather small, however, even though the undetermined fraction in the soaked wheat straw sample is rather high. The rice straw samples suggest some loss of iron due to washing, the wheat straw samples do not. The untreated sample yields 0.12% Fe<sub>2</sub>O<sub>3</sub> in the straw, the soaking treatment yields 0.10% in the straw. The difference is not likely significant.

Other elements lost in quantity by washing are sodium and phosphorous. Silica increases substantially in concentration, and appears relatively inert. If used as a tracer under the assumption that silica is not lost by washing, an ash content can be predicted. This is compared to the measured ash content in Table 6. Although the trends are consistent among treatments, the measured ash contents for rice straw treatments 5 and 6 are higher than suggested by the silica contents. This may be the result of inhomogeneities among samples, as a source for additional silica in these treatments is unknown.

3.1.5. Moisture content after washing. Washing adds considerable water to the straw. Upon removal from the soaking treatment and draining for a few seconds, the moisture content of rice straw was 88% wet basis. Spraying left the straw at 83% moisture. Treatments 2, 3 and 4 yielded moisture contents of 82, 83 and 87%, respectively.

## 3.2. Leachate properties

3.2.1. Electrical conductivity of leachate. Incremental EC for 100 g samples of rice and wheat straw leached with distilled and tap water by treatments 2 and 3 are shown in Fig. 4. Incremental leachate EC for treatment 4 is shown for 50 g samples of both straw types in Fig. 5. In the case of the larger particle size (Fig. 4), leachate EC peaks between 1 and 2 l. The peak is relatively narrow,



Fig. 4. Incremental electrical conductivity of leachate from rice straw and wheat straw (Imperial Valley) samples for treatments 2 (tap water) and 3 (distilled water). EC of tap water was 485 µS cm<sup>-1</sup>.

with EC having declined substantially after 4 to 5 l. The secondary peak for rice straw (distilled water) in Fig. 4 is likely the result of some compression of the straw at this point. Additional extraction may result from compression during leaching, but this has not yet been tested in a controlled manner. The peak incremental EC for rice straw in distilled water was 750  $\mu$ S cm<sup>-1</sup>, leaching in tap water appears to induce just a constant shift upwards in EC, equal to the EC of the tap water. The wheat straw leachate achieves a peak value with distilled water of 2,000  $\mu$ S cm<sup>-1</sup>. The peak value with tap water is in the same vicinity, and the results for distilled and tap water are similar between 2 and 41. At higher water volumes, the differential EC returns essentially to that due to the EC of the tap water alone.

3.2.2. Leachate compositions. Ion concentrations in leachate determined by HPLC are listed in Table 7. Also shown are the values for cumulative leachate EC, and the composition of tap water. The leachate compositions for samples washed in tap water are corrected for the ion composition of the water. Mass balances on ions other than bicarbonate show relatively good agreement between loss in total ash and leachate ion mass.

The quality of the leachate analyses was evaluated in several ways. The measured EC was compared to a computed EC determined from the ion concentrations in the leachate. The computed EC was found as:<sup>10</sup>

$$EC = \sum_{i} C_{i} f_{i} \tag{1}$$



Fig. 5. Incremental electrical conductivity of leachate from rice straw and wheat straw (Imperial Valley) samples, treatment 4.

				Table 7. Lead	chate compc	sitions and	d electrica	d conductiv	/ity					
					EC .			lon conce	intration	s (mg l - t)			lon mass	EC
	Treatment	No.	Weight Leached (g)*	Volume Water (L)	measured (μS/cm)	Na+	Υ <sup>+</sup>	, Mg	Ca	HCO3-	CI-	S04 =	Leacned (% fuel)†	$(\mu S/cm)$
						Distilled V	Vater							
Rice straw	Flushed	ŝ	95	20	235	7	11	0.05	12	85	26	pu	2.53	282
Rice straw	20 mesh/Flushed	4	50	7	500	80	165	8	12	208	54	pu	3.75	649
Rice straw	Soaked	5	100	7	1,000	14	226	25	7	452	107	trace	2.82	1,095
Wheat straw	Flushed	ę	76	20	510	56	116	4	12	66	76	-	6.36	658
Wheat straw	20 mesh/Flushed	4	50	7	820	98	232	7	13	125	147	pu	7.46	1,081
Wheat straw	Soaked	S	100	7	1,650	208	469	34	26	477	293	pu	7.80	2,468
						Tap Wa	ter							
	Tap water				485	82	4		9	269	15	pu		485
Rice straw	Hand Spraved	I				101	136	21	13	391	<i>LL</i>	pu		1,023
	Leached1		100	ę		18	133	4	7	122	63		0.78	
Wheat straw	Hand Sprayed	Ι				375	648	48	30	699	583	16		3,976
	Leached		100	m		293	644	31	24	400	568	91	5.41	
Rice straw	Flushed	2			700	66	84	20	13	351	50	0		835
	Leached <sup>‡</sup>		96	20		17	80	4	7	82	36	7	3.61	
Wheat straw	Flushed	0			895	133	101	21	14	345	96	85		1,040
	Leached <sup>‡</sup>		95	20		51	67	5	8	76	81	85	7.82	
*weight of fuel	leached, wet basis.													

conduct	
electrical	
and	
compositions	
Leachate	

On the properties of washed straw

187

Cations	
Ca <sup>++</sup>	2.60
Mg <sup>++</sup>	3.82
K <sup>∓</sup>	1.84
Na <sup>+</sup>	2.13
Anions	
HCO <sub>3</sub> <sup>-</sup>	0.72
CO <sub>3</sub> =	2.82
Cl	2.14
NO <sub>3</sub> -	1.15
SO <sub>4</sub> =	1.54

Table 8. Conductivity facto	s. f <sub>i</sub> (uS	cm <sup>-1</sup> L	$mg^{-1}$ ) f	or ions
-----------------------------	-----------------------	--------------------	---------------	---------

where  $C_i$  is the concentration of ionic species *i* (mg l<sup>-1</sup>) and  $f_i$  is the conductivity factor ( $\mu$ S cm<sup>-1</sup>l mg<sup>-1</sup>) for the same species. The values are listed in Table 8.

The computed values of EC are listed in Table 7. In general the computed and measured values are in fair agreement, although not consistently within the  $\pm 10\%$  recommended.<sup>10</sup> To some extent this may be due to uncertainty in the state of the carbonate ion. The analysis was further checked by completing an anion-cation balance to test for electroneutrality. Differences up to 5% are considered acceptable for the anion concentrations observed. Most of the analyses are within this range, although several approach 20% deviation.

Element balances were also performed where adequate data were available. Total element concentrations were measured in untreated straw, and compared with element concentrations in ash and leachate from treated straw. Results for two rice straw treatments and one wheat straw treatment are listed in Table 9. Full recovery would yield equal element concentrations for each fuel type. In general, the rice straw results show better recovery than the wheat straw results, with the exception of phosphorous. However, phosphorous was more difficult to detect in the leachate. The fate of sulfur in the case of soaked wheat straw is unknown, but the HPLC analysis does not seem to have performed as well in this case compared to rice straw. Several of the elements are found in excess concentration for the soaked treatment compared to the untreated wheat straw. For this reason, the leachate compositions should be considered only semi-quantitative.

Analyses were conducted on the rinsate from samples of fresh and rain washed rice straw (treatments 0, 6, 7 and 8) obtained by agitating 50 g samples for 2 min in 21 distilled water. The results are listed in Table 10. A sample of wheat straw was also rinsed in this manner. Rinsing of field samples from treatments 7 and 8 was carried out primarily in an attempt to remove soil from the samples which had accumulated on straw left overwinter. The high ash content in Table 10 for treatment 7 (flooded overwinter, sample collected at soil surface) is due to a large amount of soil adhering to the sample. However, all treatments shown in Table 10 indicate that in 2 min inherent elements were evidently leached as well. As mentioned above, total ash concentrations for the untreated and fall rain washed rice straw samples were higher than determined in earlier analyses. Although the ash content for treatment 8 before rinsing is not shown to be different than the untreated rice straw, the sample showed no evidence of fusing other than some sintering when heated at 1500°C. The fresh straw ash was observed to fuse, as was that of treatment 7, the flooded straw with soil contamination.

Ion masses combined with the masses of the settled solid fractions recovered from sieving the rinsate are in fair agreement with total measured mass loss from the original samples, with the exception of the soaked wheat straw. For both of the wheat straw rinsate analyses, Mg was reported in very high concentration, possibly as a result of column contamination. For this reason, Mg has not been listed for these samples. However, even at the concentrations reported, Mg alone cannot make up the

		Rice Straw		Wheat stra	aw*
Treatment #	Untreated	Sprayed	Soaked	Untreated	Soaked
	0	1	5	0	5
Cl	0.74	0.58	0.82	2.02	2.43
Na	0.26	0.26	0.12	1.00	1.74
К	1.75	1.52	1.90	1.95	3.86
Mg	0.21	0.24	0.26	0.19	0.35
Ca	0.21	0.32	0.27	0.43	0.47
Р	0.22	0.13	0.03	0.08	0.09
S	0.09	0.07	0.06	0.39	0.09

Table 9. Total element concentrations for untreated and treated straw (% dry fuel).

\*Imperial Valley.

		F	tice straw	· · · · · · · · · · · · · · · · · · ·	Wheat straw
Treatment	Untreated 0	Rain washed 6	Flooded (stubble) 8	Flooded (soil) 7	Untreated 0
Water Volume (L)	2	2	2	2	2
Rinsate composition (mg/L)					
Na <sup>+</sup>	72	6	3	2	123
Κ+	665	146	85	28	523
Mg <sup></sup>	8	5	30		10
Ca <sup>++</sup>	0	1	1	1	80
HCO3	53	88	61	56	281
Cl	136	25	13	4	nd
NO3-	13	5	nd	3	331
PO4 =	33	nd	nd	nd	nd
SO4 -	293	nd	nd	nd	1,550
EC ( $\mu$ S/cm, measured)	1.150	260	165	65	1,907
EC ( $\mu$ Scm, calculated)	2.205	425	351	113	45.50
Weight rinsed (g dry fuel)	47.83	43.46	45.30	45.54	23.93
Measured weight loss (%)	8.11	4.39	5.85	9.49	5.92
Ion mass in rinsate (%)*	5.33	1.27	0.85	0.42	2.64
Settled mass (%)	2.03	1.87	2.55	6.48	8.56
Total mass leached (%)	7.36	3.14	3.40	6.90	
Ash before rinsing (%)	21.4	20.3	21.3	30.9	
Range	20.4-22.2	19.9-21.1	20.7-22.0	30.4-32.0	
Ash after rinsing (%)	19.8	18.8	20	25.7	
Total ash loss by rinsing (%)	1.6	1.5	1.3	5.2	
Ash content of settled mass (%)	54	55	51	77	
Ash fusibility at 1500°C	fused	unfused	unfused	partial fusion	

Table 10. Rinsate composition, EC, ash and mass balances for rinsed samples of straw

\*% dry fuel, includes HCO3<sup>-</sup>. nd = not detected.

difference between measured and computed weight loss.

Organic matter comprises some portion of the measured loss. This finding is consistent with results from other experiments on leached wheat straw.<sup>7</sup> In addition, silica in the leachate was not analyzed, and may also contribute to the leached mass. Table 6 suggests that although silica could make up some part of the leachate from wheat straw, it cannot alone account for the discrepancy between measured and reconstructed mass. Computed and measured EC values are in fair agreement, but the anioncation balance suggests that the cation concentration is in general too large. This may be the result of improper calibration of the HPLC or contamination of the column. Regardless, the results for both rice and wheat straw show a substantial loss of ash elements in only 2 min. Potassium and chlorine in particular appear to be rather quickly leached. Also apparent is the decreasing alkali concentrations in the rain washed rice straw in progressing from the early fall harvested samples to the spring harvested samples collected at the stubble and soil surfaces. Chloride and most other ions, with the exception of Mg<sup>++</sup>, also show diminishing leachate concentrations. The increase in Mg<sup>++</sup> may be due to increased soil contamination as evidenced by the higher settled fraction, and the higher ash content of this fraction compared to the other treatments.

### 3.3. Ash fusibility

3.3.1. Prepared ash. Pelletized samples of ash from untreated and rainwashed rice straw (treatments 0 and 6) prepared at 575°C were placed in a Kanthal high temperature furnace at temperatures ranging from 800 to 1600°C and observed after 60 min at each temperature. Untreated straw ash was observed to weakly sinter between 900 and 1000°C, was strongly sintered at 1100 and 1200°C, and fully fused at 1300°C, achieving a fluid state by 1400°C. Rain washed samples were unfused below 1500°C. although some weak sintering was observed beginning at 1400°C. At 1600°C, one sample formed a hard sinter. The rainwashed samples exhibited little contraction on heating, while untreated samples were observed to contract upon fusing.

3.3.2. Direct heating of fuel samples. Pellets of both rice and wheat straw were placed directly into the furnace at 1500°C without prior ashing. The behavior of these samples is summarized below.

After 2 min at 1500°C, untreated rice straw was still emitting volatiles and the pellet had swelled and deformed. Fusing of ash was observed at 4 min, with complete fusion attained by 10 min. At this time, the ash had become completely fluid (similar to the state at the fluid temperature in the standard pyrometric cone test).

After 2 min, rice straw prepared by treatment 1, hand spraying, was still emitting some volatiles, and some deformation was evident. By 4 min, the pellets had further deformed into a hemispherical shape which they retained through the remainder of the experiment. These samples did not achieve a fully fluid state at  $1500^{\circ}$ C.

Flushed rice straw samples (treatments 2 and 3) had fully evolved volatile matter within 50 s. After 2 min, pellets increased in height (about 2 times). After 10 min, samples were weakly sintered but not fused. Similar results were seen for samples prepared by treatments 4 (pulver-ized and flushed) and 5 (soaked). The very rapid volatile release was characteristic of all washed samples with the exception of treatment 1 (spraying).

Untreated and hand sprayed rice straw samples held for 60 min at 1500°C were completely fused, while samples from treatments 2–6 showed very light sintering. A sample of rice straw from treatment 7 (spring harvested rain washed straw collected from the soil surface after flooding), was fused after 10 min at 1500°C. Samples of rice straw from treatment 8 (collected at the stubble surface after flooding) sintered but did not fuse.

Fuel pellets were also inserted directly into the furnace at temperatures ranging from 800 to 1650°C and held for 20 min. Untreated rice straw sintered beginning at 800°C, and began to fuse at 1200°C. Rice straw prepared by treatment 4 yielded ash that remained unsintered through 1200°C, and did not fuse up to 1650°C. The strength of sintering increased continuously from 1200 to 1650°C. Rain washed rice straw (treatment 6) sintered weakly at 1000°C and began to fuse above 1500°C. This method of testing appeared more sensitive than that using the prepared ash, as sintering was detected in the rain washed samples at a lower temperature when the fuel was burned directly, rather than first ashing at 575°C for 2 h.

Untreated and hand sprayed pellets of wheat straw (Imperial Valley source) emitted volatiles for 2–4 min, in a manner similar to the same treatments for rice straw. Untreated samples fused completely to a black liquid after 4 min at 1000°C. One sample of the hand sprayed wheat straw separated spontaneously into two distinct fused and unfused fractions, but this was not a repeatable effect. The fused fraction was darker in color and had been completely liquid. The other washed samples of wheat straw emitted volatiles very rapidly (45 s), exhibited some swelling, but did not sinter or fuse at  $1000^{\circ}$ C.

Untreated wheat straw samples were found to fuse completely to a hard glassy slag at temperatures between 800 and  $850^{\circ}$ C. Wheat straw prepared by treatment 4 (milled 20 mesh, flushed with distilled water) achieved the highest fusion temperature for this fuel with slag formation apparent at between 1250 and 1300°C. This treatment remained unsintered and unfused up to 1200°C. The other washing treatments (2, 3, and 5) produced ash that sintered at temperatures beginning a little over 1000°C. Samples from treatment 3 (flushed with distilled water) were lightly sintered at 1100°C, while those from treatment 2 (flushed with tap water) exhibited partial fusion at 1100°C.

3.3.3. Loss on ignition at higher ashing temperatures. Samples of rice and wheat straw were ashed consecutively in a muffle furnace at 575, 750, 900, and 1000°C to ascertain how ashing temperature influenced the determination of ash concentration. Results are shown in Figs 6 and 7. Untreated samples show a marked decline in ash content with increasing temperature, suggesting a loss of alkali or other species at higher temperature. The results for untreated wheat straw show a greater decline in total ash compared to untreated rice straw due to the lower silica concentration. Treatment 1, hand spraying, also exhibits this trend, although to a lesser extent. The washed samples from treatments 2 through 6 (2-5 combined in the figures due to their similar behavior) are more refractory, and show very little change in total ash with increasing temperature. The total ash content at 575°C is lower for these treatments, and the trend for the untreated samples at higher ashing temperatures is a convergence with the treated samples at a lower ash concentration. The untreated samples were sintered and fused when ashed at 1000°C. Those from treatments 2-5 and the rain washed rice straw (treatment 6) were not, although as noted above, treated wheat straw samples were observed to fuse at lower temperatures than treated rice straw samples. A decrease in the apparent volatilization of ash elements due to washing suggests a reduction in fouling during combustion of treated straw compared to untreated straw.



Fig. 6. Relative ash concentrations for untreated and treated rice straw after ashing single samples at 575, 750, 900, and 1000°C. Ash concentrations are relative to 575°C. Results for treatments 2–5 are averages over treatments.

3.3.4. Phase assemblages by SEM. Samples of untreated and soaked rice straw ash (treatments 0 and 5) prepared at 1000°C were inspected by scanning electron microscope (SEM), with chemical analyses of various phases carried out using an electron beam microprobe. Inspection under light microscope revealed individual untreated ash particles to be fused with a transparent glassy appearance. When examined in bulk without magnification, this ash had a pink color not readily observed under magnification. The washed straw particles were unfused, having a milky white appearance observed both with and without magnification. Many of these particles appeared unaltered from their state in the original plant material, with cellular details still distinct. Such details were not seen in the untreated samples.

Electron micrographs taken at a magnifi-

cation of  $50 \times are$  shown for both treated and untreated samples in Fig. 8. The untreated sample (Fig. 8a) shows the particles to be completely fused, with the bulk melt phase consisting primarily of Si, K, Ca and Na. Within the main body of the fused particles are Si rich inclusions, possibly crystallized from the melt phase. The treated sample (Fig. 8b) shows the particles to be unfused, with the majority of the particles being composed almost entirely of Si. A few particles include small amounts of K and Al.

At  $1000 \times \text{magnification}$  (Fig. 9a), the untreated straw particles show evidence of apatite (Ca-P) precipitates, as well as crystalline Si rich inclusions within the bulk Si-K glass phase. At  $500 \times$ , particles from the treated sample (Fig. 9b) are seen to consist predominantly of a uniform amorphous unfused Si



□ 575°C 2 750°C ■ 900°C 2 1000°C

Fig. 7. Relative ash concentrations for untreated and treated wheat straw (Imperial Valley) after ashing at 575, 750, 900, and 1000°C. Ash concentrations are relative to 575°C. Results for treatments 2–5 are averages over treatments.



Glassy melt phase (Si, K, Ca, Na)

Si rich crystalline inclusion

(a)



Amorphous Si phase

Si rich with small amounts of K, Al

(b)

Fig. 8. Scanning electron micrographs of rice straw ash prepared at  $1000^{\circ}$ C,  $50 \times$  magnification. (a) Untreated; (b) soaked, treatment 5.

phase. A characteristic "zipper" structure is visible, which can also be observed directly in unheated plant tissue.

## 4. DISCUSSION

Washing clearly can be effective in removing troublesome elements from straw. Treatments 2–6 were also effective in generating ash which did not fuse at temperatures as high as 1600°C for rice straw, although some sintering did occur at these higher temperatures. The simple hand spraying treatment (treatment 1) was less effective in this regard because of the limited time of spraying and the likelihood that not all straw was wetted or leached in the process. At the water application rates used, less than 3 1  $(0.03 \ 1 \ g^{-1})$  of water were applied to each straw bed, and full penetration of the bed may not have been achieved. The EC data in Fig. 4 imply an inadequate leaching in any case. Apparently a more substantial treatment is required. Rinsing treatments in which straw was agitated in water for only 2 min showed significant loss of alkali elements.

The incremental EC measurements made during the flushing treatments (2 and 3) suggest

that for these treatments extraction is reasonably complete after application of 4 l per 100 g. This may be compared with the application rate based on natural precipitation to a uniformly spread straw layer in the field. For rice straw, with a yield of 6 t ha<sup>-1</sup>, an application of  $0.04 \ 1 \ g^{-1}$  (4 l/100 g) is achieved by 24 mm of rainfall. Rice straw (treatment 6) receiving 65 mm precipitation prior to analysis was well depleted in alkali species and chlorine, a result



Ca, P rich (apatite) phase

Bulk Si, K rich glass phase

Si rich inclusions





(b)

Si rich amorphous phase

Fig. 9. Scanning electron micrographs of rice straw ash prepared at 1000°C. (a) Untreated,  $1000 \times$ ; (b) soaked, treatment 5,  $500 \times$ .

which is consistent with the results of the laboratory washing treatments. The ash from this straw showed no evidence of fusing at the highest temperatures of the furnace. When left overwinter in the field, potassium, sodium, and chlorine can be leached from the straw into the soil or runoff, which constitutes a means of recycling these elements. The field samples also show that contamination from soil caused by flooding can reduce the benefits derived from leaching. Reliance on natural leaching processes may lead to uncertainty in the quality of the fuel supply, assuming that straw can be harvested in an acceptable manner after overwintering in the field and that organic matter loss does not constitute an unacceptable loss of fuel value.

Washing was effective in removing potassium, sodium, and chlorine. Concentrations of sulfur were also reduced by washing. Total ash concentrations in rice straw were reduced by about 10%, and by about 68% for wheat straw for well washed samples. That potassium can be readily leached from straw has been observed previously, although not with respect to the benefits to fuel utilization. Amarasiri11 found that 40% of potassium was removed from rice straw in 15 min of submergence. Garland's leaching experiments<sup>7</sup> for the CELLS project with hydroponically grown wheat straw showed a recovery in leachate of over 80% for potassium, and 60 to 80% for P and Mg at  $0.12 l g^{-1}$  total leach rate. Zn and Cu were also recovered at high levels (>80%). Nitrogen recovery was not determined directly, but based on nitrate levels in the leachate, Garland concluded that nitrogen leaching was substantial, contrary to the findings here. Amarasiri<sup>11</sup> found that nitrogen loss was insignificant in the samples he analyzed. Nitrogen in hydroponically produced crops may be more readily leached, although the reasons for this are not clear. The removal of chlorine is particularly attractive due to its perceived role as a facilitator in alkali deposition, as a contributor to corrosion, and as an agent of toxic emission formation.

The difference in fusibility behavior for the washed wheat straw compared to washed rice straw is consistent with the ash compositions of Table 4. An inspection of appropriate phase diagrams<sup>12</sup> shows that although substantial amounts of ash have been leached from wheat straw, the concentrations of alkali species is still sufficient to cause the melting temperature to remain below that for well washed rice straw.

The  $K_2O$ -CaO-SiO<sub>2</sub> phase system is shown in Fig. 10, and reveals the substantial differences in compositions among the types of fuel samples. Indicated on the figure are the compositions for the six samples listed in Table 4, normalized to the three species. The rice straw treatments shift the composition to the right in the silica rich corner of the diagram, towards higher silica concentration and higher fusion temperatures.

The trend in fusion temperatures shown is consistent with the furnace experiments described above. For wheat straw, the untreated composition (W0, Imperial Valley source) appears in a region of low melting temperatures. Soaking (W5) also moves the composition to the right in the figure, but not as far as for rice straw. The fusion point is indicated to be in the range of 1200 and 1300°C, which is somewhat higher than observed in the furnace although similar to that obtained for treatment 4 with wheat straw. Figure 10 also shows that in traversing the range between 60 and 80% silica, washing could result in a decrease in fusion temperature, if the washing is done poorly. This may be the case with hand spraying (treatment 1) for wheat straw, although an analysis of the composition has not yet been performed.

Because of the low CaO concentration in the ash, the phase relationships can also be observed in the simple two oxide system for K<sub>2</sub>O-SiO<sub>2</sub> or Na<sub>2</sub>O-SiO<sub>2</sub>, Fig. 11. In some respects, normalization on the basis of just the alkali metals and silica better reproduces the observed behavior in the furnace experiments as far as fusion temperature is concerned. The steep increase in fusion temperature past 80% silica is quite apparent, as are the double minima in the K and Na relationships between 50 and 80% silica. The wheat straw from the Imperial Valley source contains high concentrations of both K and Na, which serve to keep the fusion temperature low unless leached at extremely high levels. Thus, whereas rice straw shows substantial benefit due to washing because of its initially high silica concentration, wheat straw is rather less beneficially altered.

The wheat straw from the Imperial Valley source was produced under saline irrigation and contains high concentrations of chlorine and alkali metals, sodium in addition to potassium. The composition may not be particularly representative for this reason. The effects of leaching were further tested on a wheat straw from an alternate source produced under fresh water irrigation. This straw was obtained from



Fig. 10. K<sub>2</sub>O-CaO-SiO<sub>2</sub>phase diagram showing normalized compositions for rice and wheat straw. R = rice straw, W = wheat straw (Imperial Valley source), Y = wheat straw (Yolo County source), numbers following letters refer to treatment number (refer to Table 2). Placement is by composition only, temperatures are only in approximate agreement with furnace experiments.

Yolo County, in northern California, with the composition shown in Table 11. The straw has a chlorine concentration an order of magnitude lower than the Imperial Valley straw, and  $K_2O$  and  $Na_2O$  are lower by 22 and 80% respectively. SiO<sub>2</sub> is higher by 47%. The only treatment applied to this straw was to flush it with distilled water by treatment 4 (with a somewhat larger particle size of 3 mm). The composition of the flushed straw has not yet been analyzed. The ash content at 575°C is listed in Table 11 and is 32% lower than the untreated straw.

Relative ash concentrations at different ashing temperatures for the untreated and treated Yolo County wheat straw are shown in Fig. 12. At 1000°C, the untreated straw yields 87% of the weight in ash compared to  $575^{\circ}$ C. The treated straw yields 95% relative ash for all three temperatures above  $575^{\circ}$ C, and again appears relatively refractory.

The untreated Yolo County straw begins to sinter at 750°C, and is fused by 1000°C. This is consistent with the expected fusion temperature based on the ash composition as shown by the locations (Y0) in Figs. 10 and 11. The composition is to the right of the second minimum in the Na<sub>2</sub>O- and K<sub>2</sub>O-SiO<sub>2</sub> phase systems, unlike the composition for the Imperial Valley straw. Leaching for the Yolo County straw then has an immediate effect of shifting the composition towards higher fusion temperatures. The ash fusion behavior of the washed Re

100

Na

80

RC



60

Yolo County straw was closer to that of the rice straw than the Imperial Vallcy wheat straw. Volatiles came off very rapidly (within 45 s) when heated. A light sintering of particles was observed to occur between 1200 and 1300°C. A

Table 11. Composition of wheat straw from Yolo County source

	Untreated	Flushed
		Fuel (% dry fuel)
Ash (575°C)	10.71	7.26
Chlorine	0.19	
SiO <sub>2</sub> *	7.23	
Al <sub>2</sub> O <sub>3</sub>	0.23	
TiO <sub>2</sub>	0.01	
$Fe_2O_3$	0.13	
CaO	0.33	
MgO	0.31	
Na <sub>2</sub> O	0.22	
K <sub>2</sub> O	1.54	
$P_2O_5$	0.15	
SO <sub>3</sub>	0.54	
	Ash (% ash)	
SiO <sub>2</sub>	67.54	
Al <sub>2</sub> O <sub>3</sub>	2.14	
TiO <sub>2</sub>	0.10	
Fe <sub>2</sub> O <sub>3</sub>	1.22	
CaO	3.08	
MgO	2.88	
Na <sub>2</sub> O	2.05	
K <sub>2</sub> O	14.38	
$P_2O_5$	1.41	
SO <sub>3</sub>	5.02	
Undetermined	0.18	

\*Ash elements as % dry fuel computed from % ash. Blank indicates not measured. harder sintering was observed at 1400°C, but fusing of the particles to a compact glassy slag did not begin until above 1600°C. Leachate EC peaked after 0.5 l at 3125  $\mu$ S cm<sup>-1</sup> and leaching was mostly complete after 2 l (0.04 l g<sup>-1</sup>). The peak EC was similar to that obtained for rice straw (Fig. 5).

To summarize the effects of washing on the three fuels, the extent of ash fusion was characterized by assigning one of six values based on the appearance of the ash after heating to temperature. The values increase in relation to the severity of sintering and fusion, and are described in Table 12. The severity rating ranges from no detectable sintering (degree 1) of the ash from the original fuel pellet, to a fully fluid state with substantial disappearance of ash (degree 6). The behavior of untreated ash as well as washed ash from the three fuels is illustrated by degree in Fig. 13. The washed results are for well washed straw, poorer washing results in behavior intermediate to the untreated and treated results shown, with the possible exception of the Imperial Valley wheat straw noted earlier.

Figure 10 shows that the composition of untreated Imperial Valley wheat straw lies very near the composition yielding minimum melting temperature. Soaking yields a composition to the right of the initial composition, along a path in which the fusion temperature is very little altered due to change in composition by loss of potassium or calcium until achieving at least 80% silica. The figure suggests another route by which fusion temperature could be increased, that is, by the addition of CaO to the system. This is the rationale behind adding lime (or limestone) to reduce agglomeration in fluidized beds. However, commercial boiler experience<sup>3,4</sup> reveals little benefit of this technique in reducing fouling from straw fuels, apparently because of the limited reaction between the added and inherent elements.

These washing results suggest a number of options for improving the quality of biomass fuels through leaching. Several possibilities are schematically shown in Fig. 14. The easiest process conceptually is to leach by natural precipitation, later harvesting the fuel. As indicated above, there are several potential constraints. Timeliness could be a key constraint, in that the timing of the precipitation is largely unpredictable. Both field preparation and the operation of the facility acquiring the fuel would become subject to

Temperature (°C)

1700

1500

1300

1100

900

40



Fig. 12. Relative ash concentrations for untreated and treated wheat straw (Yolo County source) after ashing single samples at 575, 750, 900 and 1000°C. Ash concentrations are relative to 575°C.

considerable uncertainty in the weather. Such uncertainty might not cause undue concern where proper management is applied. Protecting the fuel from soil contamination and excess loss of organic matter may be more difficult. With rice straw, windrowing the straw behind the grain harvester, a procedure that was abandoned in favor of straw spreading to permit faster drying for field burning, might provide a means of satisfying the constraints of a field leaching system. A higher precipitation level would be required to achieve the same leaching volume obtained with spread straw, however. For wheat, which is normally harvested in the late spring and early summer, relying on rain washing in an arid climate like that of California is not feasible, as the precipitation rates during this part of the year are extremely low. Nor would waiting 9 months over winter likely prove feasible.

Straw could be mechanically washed at the field or at the consuming facility. If washed at the field, spreading after washing would likely be required to dry the straw to an acceptable level for handling and transport. Leachate from the process could be more readily disposed by return to the field, a process that would occur naturally at any rate, although distributed over the field (and not subject to regulation). The source of the water for leaching at the field could be problematical, however.

If leached at the plant site, straw drying and leachate disposal are of greater concern. As indicated in Fig. 14, drying might not be required were the fuel simply blended at low concentration with a supplemental fuel, such as wood. The plant would then serve principally as a means of disposal for the straw. As this is not the objective behind the production of energy crops, dewatering and perhaps drying would be required where the material is intended as fuel. Thermal energy for drying might come from residual enthalpy in the facility stack gas. In the case of sugar cane bagasse, the dewatering is accomplished by the sugar extraction mills, and the economic cost of dewatering is not directly applied to the bagasse as fuel. This would not be the case for a fuel washing and dewatering system for straw or similar materials. The cost of handling would be borne entirely by the fuel, unless other incentives, such as air emission offset credits, could provide subsidy.

Table 12. Degrees of fusibility describing appearance of straw ash upon heating.

Degree of fusion	
1	Fuel pellet vertically extended to column of soft ash, no apparent sintering, column has open and rough surface, pellet free of refractory support
2	Pellet vertically extended, weak sintering of particles, column has open and rough surface, pellet free of refractory support
3	Pellet contracted to spherical shape, strong sintering of particles, closed but rough surface, slagged to refractory support
4	Pellet contracted to smooth closed spherical shape, slagged to refractory support
5	Ash fully melted into flat shape with thickness less than approximately 2 mm
6	Ash vaporized or absorbed into refractory support with no measurable thickness.



Fig. 13. Fusibility of untreated and treated straw ash by degree. Flushed treatment refers to treatment 4, rain washed straw is treatment 6. Severity values are described in Table 12. All samples held at temperature for 20 min.

Thermal drying might not be required where mechanically dewatered fuel was blended with a dryer fuel, as long as the dewatered fuel achieved a moisture below the autothermal limit (generally 55–65% moisture wet basis). The addition of a moist fuel might serve to reduce combustion temperatures, thereby reducing the fouling as well. The economics of such a system require careful analysis, however.



Fig. 14. Network of possible options for washing straw or other biomass materials to remove undesirable elements.

Numerous methods for washing the fuel can be conceived. As the hand spraying treatment tested here shows, however, a casual treatment is not likely to be successful. Regardless of method, water consumption and leachate disposal are of concern. To minimize the water consumption, leachate recycle can be employed. To what concentration leachate can continue to be recycled has not been evaluated. Leaching in tap water at 485  $\mu$ S cm<sup>-1</sup> was almost as effective as distilled water in the experiments described here. In combination with a membrane for removal of salts and other materials, leachate recycling may reduce the fresh water makeup considerably, albeit with additional parasitic load for the power plant. Such leachate concentration may also reduce the cost of leachate disposal. What products may be retrieved from the leachate stream has not been explored.

If nothing else, these results should indicate the substantial ability to control the flow of various elements in a well designed system. The results are applicable, at least in part, to the coupling of biochemical and thermochemical conversion systems. Handling herbaceous materials through a fermentation system, with residual solids utilized for thermal and electrical power generation, would seem technically superior to a simple system employing washing only. The economics associated with both concepts requires careful review. Anecdotal evidence from power plant operators in Denmark<sup>4</sup> suggests that rain washed wheat straw used as fuel directly in furnaces does not foul as readily as fresh straw. In the interim, prior to the implementation of more advanced systems, washing would appear to offer a means to burn straw and other such fuels in a manner so as to mitigate fouling, and possibly corrosion, of furnaces and boilers. Issues surrounding the economic feasibility of the approach require further development.

## 5. CONCLUSION

Washing rice and wheat straw with water was effective in removing substantial amounts of alkali metals, chlorine, and sulfur. The removal of such elements was beneficial in increasing the fusion temperatures of straw ash in laboratory furnace experiments. Ash which normally sintered or fused at temperatures between 900 and 1000°C for rice straw was not observed to fuse at temperatures as high as 1600°C for well washed samples, although some sintering occurred above 1100°C. Fusion temperatures for one source of wheat straw ash were increased from 800°C or less to between 1000 and 1250°C by washing. Wheat straw from another source which fused completely at 950°C was not observed to fuse at temperatures up to 1600°C, but only sinter. Although fusibility results do not provide a direct measure of potential fouling, when combined with weight loss measurements at different ashing temperatures that indicate a more refractory character to washed straw ash, a reduction in fouling is implied.

Natural rain washing was nearly as effective for rice straw as the better laboratory washing treatments in removing alkali metals and chlorine, and in delaying the onset of ash fusion, at least for samples collected prior to flooding of the field and contamination of the straw with soil. Hand spraying for 1 min was less effective in removing elements compared to more thorough washing techniques.

Measurements of the electrical conductivity of the leachate shows that the extraction of elements is mostly complete after addition of 0.04 1 g<sup>-1</sup> without compression and without recycle using either distilled or tap water (EC 485  $\mu$ S cm<sup>-1</sup>). An application at this rate is equivalent to 24 mm of precipitation on uniformly spread straw in the field. For rice straw, washing left the ash consisting primarily of silica. Inspection of untreated rice straw by SEM of samples heated at 1000°C for 2 h reveal complete fusion with crystallized Si rich and apatite rich inclusions. Washed samples are unfused, consisting primarily of amorphous silica with many original cellular structures remaining undisturbed. Volatile matter release rates were substantially faster with washed samples than with untreated samples, but the specific reasons for this were not identified.

Differences in observed ash fusibility behavior between washed rice and wheat straw are consistent with differences in ash composition based on phase relationships for alkali-silica systems. Phase relationships also indicate that incomplete washing of wheat straw could result in a *decrease* in fusion temperature compared to untreated straw. The potential influence on fouling behavior is so far unknown. The composition of rice straw and a wheat straw grown with fresh water (as opposed to saline water) irrigation suggests that only beneficial results from washing should be observed.

Washing with water appears to offer an approach to remove troublesome elements from fuel and so avoid excessive fouling and possibly reduce corrosion. The economic potential of the technique has not been tested and requires further analysis. Timeliness in harvesting, field preparation, and plant operation, along with avoidance of fuel contamination with soil materials represent constraints to the application of the technique using natural precipitation. Straw dewatering and drying along with leachate treatment and disposal are constraints to the application of the technique at the conversion facility. Leachate recycle and separation (e.g. by membranes) of removed elements require further study. No full-scale evaluation of washed straw has been conducted, and conclusions concerning the benefits to be derived are speculative based on the results of these laboratory experiments.

#### REFERENCES

- T. R. Miles, Jr. and T. R. Miles, Alkali deposits found in biomass power plants—a preliminary investigation of their extent and nature. Summary report for the National Renewable Energy Laboratory, NREL Subcontract TZ-2-11226-1, Golden, CO (1995).
- Baxter L.L. (1993) Ash deposition during biomass and coal combustion: a mechanistic approach. *Biomass and Bioenergy* 42, 85-102.

- L. L. Baxter, T. R. Miles, T. R. Miles, Jr., B. M. Jenkins, G. H. Richards and L. L Oden, Transformations and deposition of inorganic material in biomass boilers. In M. G. Carvalho (ed), Second Int. Conf. on Combustion Technologies for a Clean Environment, 1: Biomass II, pp. 9-15, Commission of the European Communities, Lisbon, Portugal (1993).
- B. M. Jenkins, L. L. Baxter, T. R. Miles, T. R. Miles, Jr., L. L. Oden, R. W. Bryers and E. Winther, Composition of ash deposits in biomass fueled boilers: results of full-scale experiments and laboratory simulations. ASAE Paper No. 946007, ASAE, St Joseph, MI (1994).
- T. R. Miles, T. R. Miles, Jr., L. L. Baxter, B. M. Jenkins and L. L Oden, Alkali slagging problems with biomass fuels. *First Biomass Conference of the Americas*, Burlington, VT (1993).
- T. R. Miles, T. R. Miles, Jr., R. W. Bryers, L. L. Baxter, B. M. Jenkins, and L. L. Oden, Alkalis in alternative biofuels. FACT 18, Combustion modeling, scaling, and air toxins, pp. 211-220, ASME, New York (1994).
- 7. J. L. Garland, Characterization of the water soluble component of inedible residue from candidate CELSS

crops. NASA Technical Memorandum 107557, National Aeronautics and Space Administration, John F. Kennedy Space Center, FL (1992).

- B. M. Jenkins and J. M. Ebeling, Correlation of physical and chemical properties of terrestrial biomass with conversion. *Energy from Biomass and Wastes IX*, Institute of Gas Technology, Chicago, IL (1985).
- 9. B. M. Jenkins, Physical properties of biomass. In Biomass Handbook, Chap. 5.2, O. Kitani and C. W. Hall (eds). Gordon and Breach, New York (1989).
- 10. American Public Health Association, Standard Methods for the Examination of Water and Wastewater, 18th Edn. Joint publication of the American Public Health Association, American Water Works Association, and the Water Pollution Control Federation, Washington, DC (1992).
- S. L. Amarasiri, Paper 12: Sri Lanka. In Organic Recycling in Asia, FAO Soils Bulletin 36, pp. 119–133. Food and Agriculture Organization of the United Nations, Rome (1978).
- E. M. Levin, H. F. McMurdie and F. P. Hall, *Phase Diagrams for Ceramists*. The American Ceramic Society, Inc., Columbus, OH (1956).