

# Post-Harvest Processing Methods for Reduction of Silica and Alkali Metals in Wheat Straw

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## Abstract

Silica and alkali metals in wheat straw limit its use for bioenergy and gasification. Slag deposits occur via the eutectic melting of  $\text{SiO}_2$  with  $\text{K}_2\text{O}$ , trapping chlorides at surfaces and causing corrosion. A minimum melting point of  $950^\circ\text{C}$  is desirable, corresponding to an  $\text{SiO}_2\text{:K}_2\text{O}$  weight ratio of about 3:1. Mild chemical treatments were used to reduce Si, K, and Cl, while varying temperature, concentration, % solids, and time. Dilute acid was more effective at removing K and Cl, while dilute alkali was more effective for Si. Reduction of minerals in this manner may prove economical for increasing utilization of the straw for combustion or gasification.

**Index Entries:** Bioenergy; combustion; gasification; fluidized bed; silica; potassium; chloride; slagging.

## Introduction

Agricultural crop residues are a valuable renewable resource from which to produce biobased products. In 1999, American farmers harvested 53,909,000 acres of wheat (1). The straw from this acreage of wheat represents more than 100,000,000 tons annually. Currently, some of the straw is harvested (baled) for use as livestock bedding or low-grade animal feed. However, these low-value uses provide only a minimal return. Nationally, only about 3.2% of the economic return on wheat is from straw (1). Producers have long recognized the potential economic and environmental benefits in producing bioenergy and bioproducts from excess wheat straw

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residue. However, the silica and alkali metals in wheat straw limit its use for bioenergy and gasification.

Because of slagging, fluidized-bed combustors and gasifiers cannot be operated above the ash fusion temperature of the feedstock, and boilers can only be operated well above or well below the ash fusion temperature (2). Wheat straw contains significant amounts of low-melting ash, which is comprised of mineral oxides including primarily  $\text{SiO}_2$ ,  $\text{K}_2\text{O}$ , and  $\text{CaO}$ , with smaller amounts of  $\text{SO}_3$ ,  $\text{MgO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{TiO}_2$  (3). This mineral ash deposits onto furnace or heat-transfer surfaces in two ways. *Slagging* is deposition of molten or highly viscous ash and occurs in the hottest regions of the combustor or gasifier. In contrast, *fouling* is deposition by condensation of vaporized ash and occurs in the cooler regions. Vaporized KCl is then held in close contact with the metal surfaces of the combustor or gasifier, causing corrosion. Ash fusibility is an important factor in determining whether slagging or fouling will occur.  $\text{K}_2\text{O}$  and other oxides form a eutectic mixture with  $\text{SiO}_2$ , lowering the ash fusion temperature (4).  $\text{K}_2\text{O}$  is of particular importance in the slagging of bio-mass ash owing to its high concentration. For comparison, pure  $\text{SiO}_2$  melts at  $1703^\circ\text{C}$  (5), while a 4:1 (w/w)  $\text{SiO}_2/\text{K}_2\text{O}$  mixture melts at about  $1100^\circ\text{C}$ , a 3:1 mixture at about  $950^\circ\text{C}$ , and a 2.3:1 mixture at about  $850^\circ\text{C}$  (6) (i.e., lower  $\text{SiO}_2/\text{K}_2\text{O}$  ratios lead to lower ash fusion temperatures). While an efficient operating temperature is about  $1100^\circ\text{C}$ , the preferred minimum is about  $950^\circ\text{C}$ , depending on the design (6). Therefore, an effective treatment to remove minerals from straw, thus reducing slagging and corrosion during combustion or gasification, must (1) reduce total  $\text{SiO}_2$  content; (2) increase  $\text{SiO}_2/\text{alkaline oxide}$  ratios, particularly  $\text{SiO}_2/\text{K}_2\text{O}$ ; and (3) increase the  $\text{SiO}_2/\text{KCl}$  ratio.

The cellulose-rich vascular tissues of straw stems contain relatively higher amounts of organic material and fermentable carbohydrates for conversion to bioenergy, biofuels, and chemicals. In contrast, the formerly physiologically active tissues, including the leaves, sheaths, and awns, are heavily impregnated with silica in the epidermal layer, and these tissues also contain higher amounts of noncarbohydrate organic components (i.e., protein, lipids, pigments, pectin, organic acids) than the stems. For cost-efficient utilization of straw and other crop residues for bioenergy or gasification, the undesirable mineral components must be removed. However, the current paradigm for straw utilization includes the necessity to transport all the components of the straw to the point of use. There is no cost-efficient way to remove undesirable components from straw before transportation. This is expensive not only because of the low bulk density of straw, but also because it brings the less valuable components to the manufacturer's gate and creates economic and environmental liabilities.

At the Idaho National Engineering and Environmental Laboratory (INEEL), we are developing an in-field method to selectively harvest the stem fraction in order to reduce the harvested silica and mineral loads. In

this article, we describe tests conducted at the INEEL to further reduce silica and alkali mineral loads in the stem fraction to allow its use for bioenergy production and gasification in fluidized beds and boilers. The objectives of this study were to reduce  $\text{SiO}_2$  content to minimize total slag formation; to reduce  $\text{K}_2\text{O}$ , increasing the ratio of  $\text{SiO}_2$  to alkaline oxides and increasing the temperature at which the slag forms; to remove chlorides, minimizing the potential for corrosion owing to the generation of KCl vapor at metal surfaces beneath slagging and fouling deposits; and to perform these reductions in a manner that can be used economically in both distributed and centralized systems.

## Materials and Methods

### *Wheat Straw*

Westbred 936 wheat straw, a hard red spring variety, was obtained from Grant 4-D Farms (Rupert, ID). All straw utilized in the laboratory studies was produced during the year 2000 cropping season. Twenty large bales of Westbred 936 ( $1.2 \times 2.4$  m [4 ft  $\times$  8 ft] bales) were collected and stored in a stack at the side of the field, using only the protected center bales for the studies. To better handle the straw for the laboratory studies, the large bales were rebaled as needed into smaller  $0.61 \times 1.2$  m (2  $\times$  4 ft) bales containing about 22.7 kg (50 lb) each and placed in covered storage. The straw was rethreshed before use in the mineral removal studies as described by Hess et al. (7) to remove the high-silica plant components including the leaves, sheaths, fines, and nodes. Only the separated straw stems were used in the laboratory studies, except when comparing removal of minerals and silica between whole straw and the stem fraction.

### *Chemical Wash Procedure*

Five to 20 g of air-dried, whole chopped straw or mechanically separated straw stems were weighed to the nearest 0.1 mg into a tared 500-mL wide-mouth polypropylene, Teflon®, or polycarbonate bottle. Sufficient wash solution was weighed into the bottle to achieve the desired % solids for the experiment (4–16 wt%). Wash solutions included distilled water, 0.1–5.0 wt%  $\text{H}_2\text{SO}_4$ , and 0.1–1.0 wt% NaOH. The bottles were shaken at a minimum of 150 rpm for 0.5–24 h at the desired temperature (25, 37, or 50°C). The liquid was then poured off into tared Pyrex beakers. The straw stems were then washed quickly with about 25 mL of distilled water to remove as much of the wash solution as possible without further removing minerals; this liquid was then added to the collected wash liquid. Both the collected liquid fraction and the treated stems were dried at 90–105°C for at least 2 d. The dried samples were removed from the oven, cooled, and their weights recorded. The dried straw samples were finally ground to 60 mesh in a Wiley mill and stored at room temperature for carbohydrate, lignin, ash, and mineral analyses.

## *Analytical Methods*

### *Ashing*

At least 1 gram of dry straw, ground to 60 mesh, was weighed to the nearest 0.1 mg into a dry, tared ceramic crucible. The residue from the collected liquid fraction was also dried and weighed. Ashing was done in a muffle furnace at 550–650°C for 18–24 h. On selected samples, a duplicate or spike such as SiO<sub>2</sub> flour or potassium silicate was added to the straw before ashing to validate silica measurements. Ashing temperatures as high as 940°C were used to determine weight loss as a function of temperature and composition changes from the volatilization of KCl.

### *Mineral Analyses*

#### ENERGY-DISPERSIVE SPECTROMETRY

Mineral analyses were done by energy-dispersive spectrometry (EDS), modifying existing geologic and metallurgical procedures (8). The spectra were measured at 10–20 KeV using a Phillips XL30ESEM Scanning Electron Microscope with a Princeton Gamma Tech Detector (Princeton, NJ). Compositions of minerals in the ash were determined for the elements Si, K, Ca, S, Mg, Mn, Ti, Fe, Al, P, Na, Cl, and O. Except for some carbon that remains after the ashing and some losses of KCl, these elements should account for >95% of the ash. Ashed straw was placed in a thin film onto aluminum disks using double-sided tape, taking care to transfer as much ash as possible onto the taped disks. The disks were then carbon coated to prevent charging. Two or three separate 1.0-mm<sup>2</sup> areas of each disk were scanned to verify homogeneity, depending on whether the measured Si values differed by >1% among measurements. Scanning was done for 5–10 min, with longer times used for samples containing very small distinguishable peaks.

EDS standards, prepared from reagent-grade silicates, oxides, and chlorides, and ashed at the same temperatures used for the samples, were used to prepare calibration curves to correct the internal quantitative EDS values for matrix effects. In addition, Standard Reference Materials, including coal fly ash (SRM #1633 and #2690) and soil (SRM #2710), both from the National Institute of Standards and Technology (Gaithersburg, MD), were also used to check the accuracy of the instrument and the quantification software. Finally, several random straw samples were also analyzed by inductively coupled plasma (ICP) analysis (9) to validate the EDS results. Oxide compositions were calculated from the elements based on standard stoichiometric ratios.

#### INDUCTIVELY COUPLED PLASMA

Mineral analysis by ICP (9) was done to validate EDS results (>1 wt% K and Ca, <1 wt% P, K, S, Mg, Fe) and quantify trace elements (<0.1 wt%), particularly the composition of straw micronutrients in the ash, such as Cu, Zn, Mn, and B. Straw samples and standard reference material/calibration standards used for the EDS analyses were shipped to Western Labs (Parma,

ID) for ICP analyses. Western Labs measured P, Ca, K, Cu, Zn, B, Fe, and Mn using standard methods (10).

#### Carbohydrate and Lignin Analysis

Carbohydrate and lignin compositions of untreated and treated straw samples were determined by quantitative saccharification using the method of Saeman et al. (11). Carbohydrate analyses were done by high-performance liquid chromatography using a Bio-Rad HPX-87P carbohydrate column. The acid-insoluble fraction, which contained lignin, extractives, and acid-insoluble ash (primarily  $\text{SiO}_2$ ), was ashed at 550–650, and Klason lignin with extractives was calculated by weight difference.

## Results and Discussion

The organic and ash compositions of the untreated baled straw and untreated mechanically separated straw stem fraction are given in Table 1. Mechanical separation reduced the total ash and  $\text{SiO}_2$  concentrations of the harvested fraction by 23 and 44%, respectively, thereby reducing overall slagging potential (7). However, mechanical separation concentrated the alkali metals relative to  $\text{SiO}_2$ , reducing the  $\text{SiO}_2/\text{K}_2\text{O}$  and  $\text{SiO}_2/\text{KCl}$  ratios. Although reduction of total  $\text{SiO}_2$  is important for overall reduction of potential slag formation, in terms of modifying the eutectic properties and thereby raising the ash fusion temperature, removal of  $\text{SiO}_2$  is detrimental without also removing proportional amounts of K, since it decreases the  $\text{SiO}_2/\text{K}_2\text{O}$  ratio in the ash.

Washing straw with aqueous liquids removed both organic and mineral matter. Most of the removal occurred in the first 4 h of washing. The ratio of organic losses to inorganic losses was similar with all of the wash solutions; that is, no particular wash solution was more selective for dissolution of organic components or minerals. Rather, the minerals appeared to be released along with organic material, such that very short or very long washes released approximately the same ratio of organic and inorganic components of the straw.

Three wash solutions—distilled water, dilute  $\text{H}_2\text{SO}_4$ , and dilute NaOH—were used separately to remove minerals from separated stems and from chopped whole straw. General comparisons of the effects of these washes on  $\text{SiO}_2/\text{K}_2\text{O}$ ,  $\text{SiO}_2/\text{KCl}$ , and the loss of heating value, at 25, 37, and 50 are shown in Figs. 1–3. Acid washing of straw removed most of the K by dissolution and gave the highest  $\text{SiO}_2/\text{K}_2\text{O}$  ratios. Some acid washes removed sufficient K to raise the  $\text{SiO}_2/\text{K}_2\text{O}$  ratio above the desired minimum ratio of 3.0. The highest removal of K and Cl from straw stems occurred with a 0.2 wt% acid wash at 50°C (Fig. 1). This acid wash increased the  $\text{SiO}_2/\text{K}_2\text{O}$  ratio from 0.9 to 3.2 and the  $\text{SiO}_2/\text{KCl}$  ratio from 0.5 to 71.3 (Fig. 2), significantly reducing corrosion potential. For this calculation, it was assumed that all Cl was present as KCl. The concentration of  $\text{SiO}_2$  in the distilled water- and acid-washed stems remained constant even though other mass was lost. Thus, both water and acid removed some  $\text{SiO}_2$ , but its

Table 1  
Organic and Inorganic Compositions of Whole Westbred 936 Straw  
and Mechanically Separated Straw Stem Fraction

Component	Component (wt%) <sup>a</sup>	
	Westbred 936 whole straw	Westbred 936 stem fraction
Glucan	32.1	37.2
Xylan	19.3	19.4
Galactan	1.0	0.9
Mannan	4.5	3.0
Arabinan	2.1	1.6
Lignin with extractives	20.3	18.9
Other <sup>b</sup>	9.5	10.3
Ash (wt%) <sup>c</sup>	11.2	8.7
SiO <sub>2</sub>	2.6	1.3
K <sub>2</sub> O <sup>d</sup>	1.7	1.2
KCl <sup>d</sup>	5.2	5.2
CaO	0.6	0.2
SO <sub>3</sub>	0.4	0.3
MgO	0.3	0.2
P <sub>2</sub> O <sub>5</sub>	0.2	0.1
FeO	0.04	0.05
Na <sub>2</sub> O	0.06	0.04
MnO <sub>2</sub>	0.005	0.003
CuO	0.0005	0.0005
B <sub>2</sub> O <sub>3</sub>	0.005	0.005
Al <sub>2</sub> O <sub>3</sub>	0.0002	<0.005
TiO <sub>2</sub>	<0.005	0.0001
ZnO	0.0007	0.004
Total	100	100

<sup>a</sup>Based on 100% dry wt of material.

<sup>b</sup>Other organics are attributed to uronic acid, protein, and so on, and to recovery errors in carbohydrate analysis technique.

<sup>c</sup>Oxide contents estimated by mass balance from elemental composition as determined by EDS.

<sup>d</sup>Potassium assumed to first combine with available chlorine, and then apportioned as oxide.

removal was offset by the removal of organic matter, and the concentration in the washed stems remained the same. Alkaline washing dissolved up to 20% of the SiO<sub>2</sub> and slightly lowered the final SiO<sub>2</sub> concentration in the straw. However, the SiO<sub>2</sub>/K<sub>2</sub>O ratio was lowered because a less-than-proportional amount of K was removed.

The effect of wash solution and temperature on loss of heating value is shown in Fig. 3. For these calculations, all components of the organic matter were assumed to be of equal heating value per unit weight. In gen-

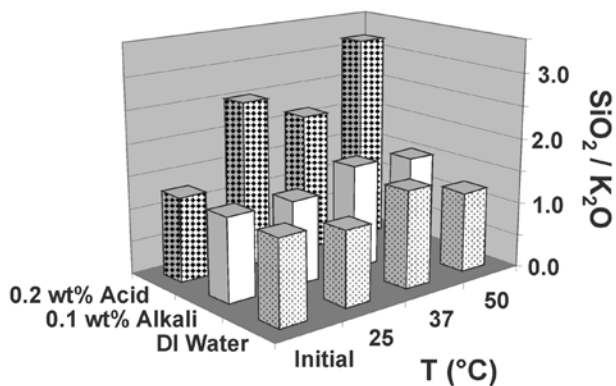


Fig. 1.  $\text{SiO}_2/\text{K}_2\text{O}$  ratio after acid, alkali, or water washing of straw stems at various temperatures. DI, distilled water.

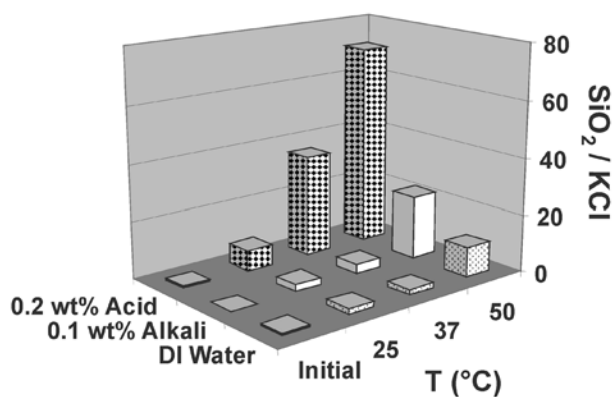


Fig. 2.  $\text{SiO}_2/\text{KCl}$  ratio after acid, alkali, or water washing of straw stems at various temperatures. DI, distilled water.

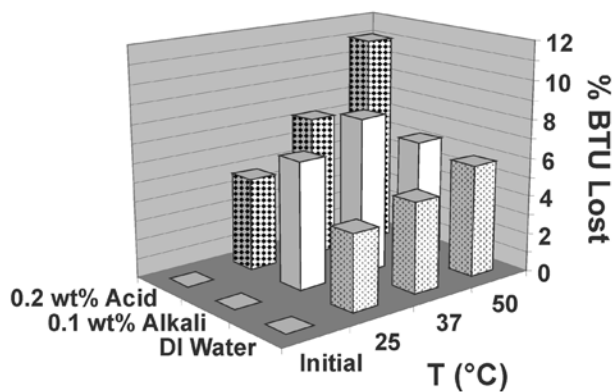


Fig. 3. Loss of heating value as function of acid, alkali, and water washing of straw stems at various temperatures. DI, distilled water.

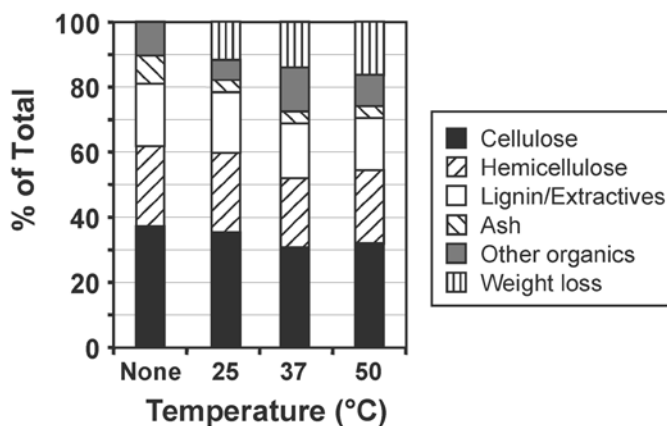


Fig. 4. Mass balances with increasing temperature for unwashed and washed straw stems using distilled water at 4% solids for 4 h.

eral, higher wash temperatures resulted in greater loss of mass in acid washes, with smaller increases in the base and water washes. Increases in acid concentration increased the amount of minerals removed but did so at the expense of heating value since organic matter was also removed; about 80% of the mass removed in the acid washes was organic (not shown). These losses, amounting to 6–11%, indicate that there are trade-offs between the cost of the lost heating value and the benefits of reducing minerals through use of the treatment. These trade-offs will depend on a number of factors, including boiler/gasifier design, operating conditions, feedstock, and cost of the downtime required to remove slag from the heat-transfer surfaces, and will vary significantly among power generation/gasification facilities.

The effects of temperature on the organic component mass balances for the tests in Figs. 1–3 are shown in Figs. 4–6. The mass balances for the distilled water washes are shown in Fig. 4. There were generally higher losses of organics with increasing temperature, as expected, since this treatment is analogous to an autohydrolysis at low temperature. There were only small losses of both cellulose and hemicellulose, with losses of organic matter principally from the “other organics”—uronic acids, proteins, and so on—which were not measured in the compositional analyses. No change was seen in lignin contents, as was expected. There were few differences in overall ash removal with increasing temperature, although inspection of Fig. 2 shows that more KCl was removed at higher temperatures.

The mass balances for the 0.1 wt% NaOH washes in Figs. 1–3 are shown in Fig. 5. For the alkali washes, there were similar weight losses of organic matter at all temperatures tested. There were no significant losses of lignin at any of the temperatures tested. This was somewhat surprising given the alkaline nature of the washes; evidently, either the temperature



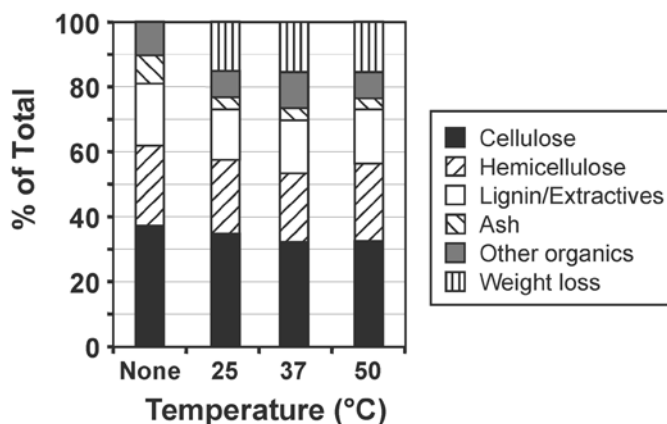


Fig. 5. Mass balances with increasing temperature for unwashed and washed straw stems using 0.1 wt% NaOH at 4% solids for 4 h.

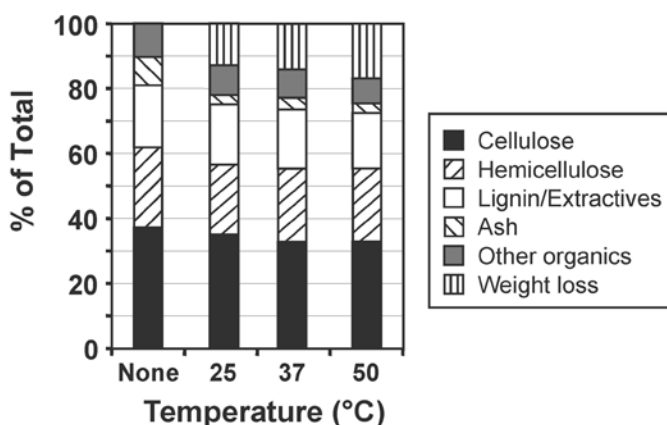


Fig. 6. Mass balances with increasing temperature for unwashed and washed straw stems using 0.2 wt% H<sub>2</sub>SO<sub>4</sub> at 4% solids for 4 h.

or pH was not high enough to effect significant lignin removal. In the alkali washes, there were only small losses of hemicellulose and cellulose, while the overall ash removal was similar at all temperatures tested. Again, inspection of Fig. 2 shows higher removal of KCl at higher temperatures. Figure 6 shows the mass balances for the 0.2 wt% acid washes. There were increased losses of organic matter with increased temperature, with greater hemicellulose losses occurring in the 25 to 37°C step than in the 37 to 50°C step. Cellulose removal mirrored the hemicellulose removal with increasing temperature, while higher losses of “other organics” occurred in the 37 to 50°C step. Ash removal also increased with increasing temperature, and there were no significant losses of lignin.

The effects of additional parameters, including % solids, acid concentration, and the use of whole straw vs straw stems, on the organic compo-

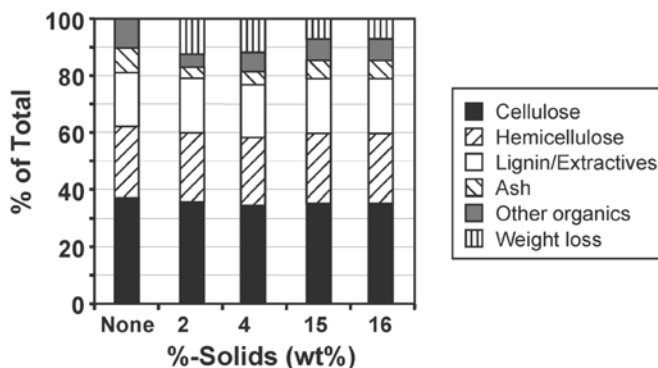


Fig. 7. Mass balances with increasing % solids for unwashed and washed straw stems using distilled water at 25° for 4 or 24 h.

nent mass balances are shown for selected experiments in Figs. 7–9. The values of  $\text{SiO}_2/\text{K}_2\text{O}$ ,  $\text{SiO}_2/\text{KCl}$ , and the percentages of the ash represented by  $\text{SiO}_2$ ,  $\text{K}_2\text{O}$ , and  $\text{KCl}$  are given in Table 2 for these experiments. Figure 7 compares a 24-h, 15 wt% solids wash and a 4-h, 16 wt% solids wash of straw stems. Note that distilled water is a slightly more aggressive solvent than tap water because it has been demineralized; thus, the distilled water washes indicate the maximum removals possible using water. Equilibrium was reached by 4 h in all washes. The effect of % solids (solids loading) in the distilled water washes is also shown in Fig. 7. Increasing the % solids resulted in decreased removal of both organic matter and minerals. This occurred whether the straw remained submerged in the bulk liquid or was only partly submerged (15% solids). This indicates that the process is solubility limited as long as the straw is submerged and may become liquid-solid contact limited at solids loadings as high as 15% solids.

It was also observed that the differences between mineral removal at low and elevated temperatures (37 and 50°C; not shown) were not as great at higher mass loadings, since solubility limits the amount of material that can be dissolved, rather than the more aggressive solvent characteristics secured at the higher temperature. Washing with water removed 11.1% of the mass of straw in a 4% fully submerged suspension, while only 6.8% mass was removed in a 15% partially submerged suspension. The ash concentration of unwashed straw was reduced to 4.6% in the 4% solids water wash, but to only 6.7% in the 15% solids wash. A continuous wash that lowers the effective “loading” even further would overcome the solubility limitations and may result in higher mineral losses than experienced in these batch experiments. However, acidic or alkaline washing in a continuous process may present some difficulty in removing the residual wash fluid from the straw if residual  $\text{SO}_4$  or Na is not desirable. In the specific case of Na, this would definitely not be desirable, since both Na and K contribute to the eutectic composition and lower the ash fusion temperature. The straw

Table 2  
SiO<sub>2</sub>/K<sub>2</sub>O, SiO<sub>2</sub>/KCl, and Percentage of Ash Represented  
by SiO<sub>2</sub>, K<sub>2</sub>O, and KCl for Washes Shown in Figs. 7–9

Condition	SiO <sub>2</sub> /K <sub>2</sub> O	SiO <sub>2</sub> /KCl	SiO <sub>2</sub> , K <sub>2</sub> O, and KCl (wt%)
4–24 h, 25°, stems, H <sub>2</sub> O wash, vary solids—ratios for Fig. 7			
Unwashed stems	0.9	0.3	92.9
2 wt% solids, 4-h wash	1.3	32.8	88.0
4 wt% solids, 4-h wash	1.2	4.7	78.5
15 wt% solids, 24-h wash	2.4	3.3	84.2
16 wt% solids, 4-h wash	2.4	3.3	84.2
4 h, 4% solids, 25°, stems, acid wash—ratios for Fig. 8			
Unwashed stems	0.9	0.3	92.9
0 wt% H <sub>2</sub> SO <sub>4</sub>	1.2	11.7	85.7
0.2 wt% H <sub>2</sub> SO <sub>4</sub>	1.3	>75 <sup>a</sup>	83.9
0.4 wt% H <sub>2</sub> SO <sub>4</sub>	2.4	>75	93.5
1.0 wt% H <sub>2</sub> SO <sub>4</sub>	2.8	>75	90.6
24 h, 10% solids, 50°, whole straw, acid—ratios for Fig. 9			
Unwashed whole straw	1.3	0.5	96.4
0 wt% H <sub>2</sub> SO <sub>4</sub>	1.3	35.6	59.0
0.2 wt% H <sub>2</sub> SO <sub>4</sub>	2.3	13.2	63.0
0.4 wt% H <sub>2</sub> SO <sub>4</sub>	2.6	5.6	86.1
1.0 wt% H <sub>2</sub> SO <sub>4</sub>	ND <sup>b</sup>	ND <sup>b</sup>	ND <sup>b</sup>

<sup>a</sup>Cl was not detected by EDS in this sample, so the approximate Cl detection limit was used to calculate the minimum possible SiO<sub>2</sub>/KCl ratio.

<sup>b</sup>ND, not determined.

stems absorbed about 3.7 times their weight of water, and chopped whole straw absorbed 4.2 times its weight. Thus, residual SO<sub>4</sub> or Na might be difficult to remove efficiently without significant further water washes.

Mass balances for washing of straw stems at 25°C with dilute acid at various acid concentrations are shown in Fig. 8, while Fig. 9 shows the same for whole straw at 50°C. Higher acid concentrations were required to reach the same SiO<sub>2</sub>/K<sub>2</sub>O ratios for whole straw as reached for stems at 50°C (not shown). Still, SiO<sub>2</sub>/K<sub>2</sub>O ratios obtained with whole straw approached the minimum acceptable level of 3.0. However, the whole straw contains larger amounts of silica (separated from the stem fraction in the selective harvest), and therefore has greater slagging potential. Both the mineral and organic content removed increased with higher acid concentrations. The highest K removal without excessive loss of organic matter was achieved at 50°C with 0.2 wt% H<sub>2</sub>SO<sub>4</sub> in a 4% straw suspension (*see* Fig. 2). The SiO<sub>2</sub>/K<sub>2</sub>O ratio

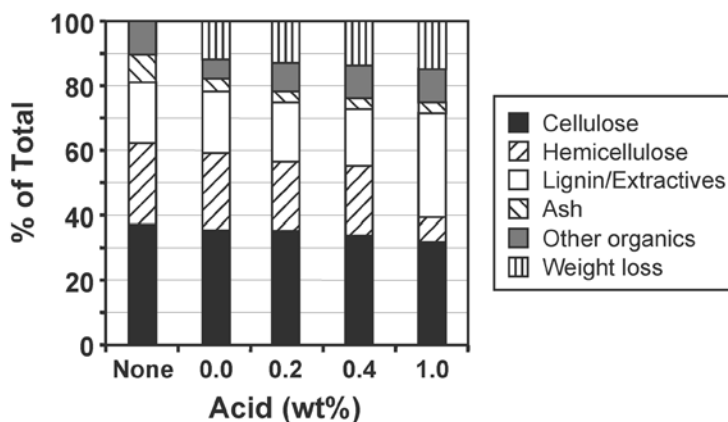


Fig. 8. Mass balances with increasing acid concentration for unwashed and washed straw stems using dilute H<sub>2</sub>SO<sub>4</sub> at 25° for 4 h, at 4 % solids.

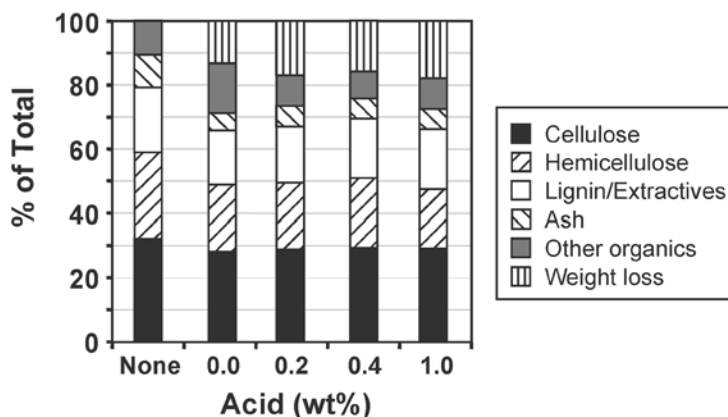


Fig. 9. Mass balances with increasing acid concentration for unwashed and washed of whole chopped straw using dilute H<sub>2</sub>SO<sub>4</sub> at 50° for 24 h at 10% solids.

achieved in this run was approached with whole straw (SiO<sub>2</sub>/K<sub>2</sub>O of 2.8) at 10% solids, which was not achievable with stems alone at 10% solids. This may be because the whole straw starts at a higher SiO<sub>2</sub>/K<sub>2</sub>O ratio than stems alone, since the mechanical stem separation concentrated the alkali metals relative to the silica in the stems. In any event, lowering the solids content would probably produce washed straw with an SiO<sub>2</sub>/K<sub>2</sub>O ratio above the desired minimum of 3.0.

Generally, cellulose and hemicellulose concentrations were not significantly affected by dilute-acid washes with acid concentrations up to 0.4%. However, Fig. 8 shows significant loss of hemicellulose in a 1% H<sub>2</sub>SO<sub>4</sub> wash. A 5 % H<sub>2</sub>SO<sub>4</sub> wash (not shown) resulted in complete loss of both cellulose and hemicellulose. In these experiments, the mass balances indi-

cated a shift from cellulose and hemicellulose to an acid-insoluble fraction, generally referred to as Klason lignin in the quantitative saccharification technique (10). It is believed that significant  $\text{H}_2\text{SO}_4$  remained within the straw lignocellulosic matrix during the  $105^\circ\text{C}$  drying step. Thus, as water was removed, the  $\text{H}_2\text{SO}_4$  was concentrated, eventually reacting with the polysaccharides at the elevated temperature and converting them to acid-insoluble organic matter. Assuming that the acid-insoluble organic matter was still combustible, the total heating value content may not be significantly affected, since the decomposition products were not lost, but converted to the "lignin" category in Fig. 8. Hence, it is clear that acid concentrations of 1 wt% and higher should not be used if recovery of intact carbohydrates is desired.

The effect of size reduction is demonstrated in Fig. 9. Since this chopped (1.9 cm and smaller fragments) straw had not been physically separated, the initial mineral (ash) content was higher at 11.2%. Size reduction increased the contact surface area and the mass that could be fully immersed. Ash removal on washing was not improved, indicating that solubility constraints were of greater importance than surface contact. The chopped whole straw was washed in water and various dilute- $\text{H}_2\text{SO}_4$  solutions at 6.7 and 10 wt% solids. The mass lost after washing was 14.1% for the chopped straw at 6.7% loading. This was comparable to previous tests, in which 15.3% loss for straw stems at 4.5% loading was observed. The inorganic mineral concentration was reduced from 11.2 to 6.4% in the chopped whole straw, and from 8.7 to 4.2% in the unchopped straw stems.

It seems clear from the data presented herein that acid is preferred as a wash solution for removal of alkali minerals from straw for use in fluidized-bed combustors or gasifiers or in boilers. Future work includes testing acid-washed whole straw and physically separated straw stems in a fluidized-bed combustor to determine the combustion and slagging properties of the washed straw. In addition, we would like to test the effect of adding CaO or MgO after washing, since CaO and MgO can modify the eutectic composition and thereby increase the ash fusion temperature further (2). While CaO or MgO could be directly added to the straw without washing to achieve an increase in ash fusion temperature, washing the straw removes large amounts of K, and thus less CaO and MgO would be required to significantly alter the ash fusion temperature. Data from these tests, and estimation of eutectic compositions and ash fusion temperatures, will help in the application of these separations to fluidized-bed combustion and gasification of biomass and combustion in boilers. The acid-washed straw will also be tested for ease of drying and densification as part of a distributed bioenergy system.

## Conclusions

Mechanical separation of straw reduced ash and  $\text{SiO}_2$  concentrations in straw by removing leaves and sheaths and leaving primarily stems. However, this concentrated K relative to  $\text{SiO}_2$ , reducing the  $\text{SiO}_2/\text{K}_2\text{O}$  and

SiO<sub>2</sub>/KCl ratios, which are important indicators of slagging and corrosion potential. Chemical washes removed much of the soluble K and up to 11% of the organic matter. Dilute acid removed both K and Cl but little SiO<sub>2</sub>, while dilute alkali removed up to 20% of the SiO<sub>2</sub>, and lesser amounts of K or Cl than did acid. Elevated temperatures increased both the mineral removal rate and with sufficient bulk liquid, the amount removed. The highest SiO<sub>2</sub>/K<sub>2</sub>O ratio achieved was 3.2, obtained using a 4-h, 0.2 wt% H<sub>2</sub>SO<sub>4</sub> wash at 50°C in a 4% straw stem suspension. Increasing the solids loading minimized loss of organics but also reduced mineral removal. Washing improved SiO<sub>2</sub>/K<sub>2</sub>O and SiO<sub>2</sub>/KCl ratios for both physically separated straw stems and whole straw.

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