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# Influence of leaching pretreatment on fuel properties of biomass



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# ABSTRACT

Modification of fuel compositions can reduce ash fouling and slagging, corrosion, and environmental impacts for thermochemical conversion systems. Leaching was used as a feedstock pretreatment to improve the properties of selected agricultural, forestry, and energy crop biomass, including rice straw, wheat straw, corn stover, switchgrass, Miscanthus, Jose tall wheatgrass, and Douglas fir wood. Crude and leached solids were characterized for changes in ash fusibility, heating value, major element concentrations, and other properties. Leachates were analyzed for major and trace elements and organic species. Ash contents were in all cases significantly reduced although simultaneous inorganic and organic material extraction led to more complex outcomes in fuel properties due to possible changes in the composition of residual solids. Declines in ash concentrations were therefore not always accompanied by increases in heating value or improvements in initial ash melting temperatures, although melt flow temperatures in all cases increased, in some cases by more than 500 °C. The trends in melt behavior are generally predicted from phase equilibria using reduced ash compositions. Sugars (1.5 – 103.5 mg/g dry matter) and organic acids (0.6 - 57.6 mg/g dry matter) constituted the major fractions of the identified organic extracts and may have potential for coproduct recovery.

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# 1. Introduction

Many biomass feedstocks benefit from pretreatment to improve physical and chemical properties for downstream energy conversion, both thermochemical and biochemical [1–5]. Increasing use of sustainable biomass for reducing greenhouse gas emissions and other environmental effects will realize wider demand for energy crop feedstock, agricultural residues, woody materials and the biogenic fraction of urban wastes. For thermochemical conversion at typical combustion and gasification temperatures, the compositions of these feedstocks often lead to high rates of ash slagging and agglomeration, fireside fouling, and with other constituents enhanced corrosion and hazardous emissions. The alkali metals in association with silica and chloride in biomass are of principal concern, but both alkali and chloride are subject to effective removal through solid-liquid extraction, in many cases by simple water washing or leaching. Removal of other constituents is typically more involved, and in most thermal applications water leaching leads to undesirably high moisture contents of the pretreated feedstock that must then undergo dewatering or drying. What is therefore a fairly simple pretreatment of solids generates additional downstream processing cost as well as a leachate that while potentially useful for

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coproduct recovery or thermal and material integration into the energy conversion system, may also increase the need for wastewater treatment or disposal. However, advantages arising from improvements in feedstock properties continue to motivate research and development of efficient and effective extraction pretreatment operations as well as alternative conversion processes to avoid these issues of concern to the more conventional approaches. For these reasons, leaching remains of unique interest for feedstock pretreatment.

Previous studies have investigated the causes of ash slagging and fouling during combustion and other thermochemical conversion of biomass fuels [6–9]. In addition to feedstock selection and furnace or reactor temperature management to mitigate these phenomena, other control techniques have also been suggested including feedstock modification [10-18]. The presence of the alkali metals sodium and potassium in silica-rich melts causes a marked freezing point depression [8, 19]. In addition, chlorine and sulfur present in biomass accelerate the volatilization of alkali metals and may contribute to acid gas and aerosol formation [9,17]. The low ash melting temperatures and volatilization of alkali metals from the ashes of straw and other herbaceous materials lead to the rapid formation of sintered and fused glassy deposits at typical operating temperatures [6,20,21]. The condensation of inorganic vapors and particle deposition on heat transfer surfaces in boilers contributes to fouling [9], and substantial release of chlorine and sulfur accelerates corrosion. Moreover, alkali metals react with bed media in fluidized bed reactors and form liquid-phases on the surfaces of bed particles causing sticking, bed agglomeration, and eventual defluidization [14]. The outcomes of the uncontrolled ash chemistry with these types

of feedstock reduce conversion efficiencies and increase maintenance and product costs for non-slagging reactor designs. Feedstock modification to reduce the concentrations of alkali metals, chloride, sulfur, silica, and other constituents prior to utilization is therefore technically beneficial, although the cost of extraction requires careful analysis and consideration [11–13,22,23].

Leaching biomass with water as a solvent has been shown to improve biomass feedstock properties for high temperature processes, and a number of studies have shown a reduction in the formation of ash deposits [10-18,22-24]. Leaching in most cases removes alkali metals and chlorine bound in water-soluble salts, reducing the ash in biomass and altering the ash chemistry, thereby modifying the slag-forming processes and also typically increasing feedstock heating value by reducing inorganic material dilution as long as there is not a countervailing excess extraction of organic material [5]. Leaching can reduce corrosion and emissions of acidic pollutants and has the potential to reduce the formation of toxic species, such as dioxins and furans, during thermal processing among other environmental benefits [18, 25–29]. In addition to inorganic materials, leaching may also play an important role in the extraction of organic constituents to improve downstream processing or to add value through coproduct recovery [11,30–33]. Fermentation of leachates, for example, might be used to produce ethanol and other fuels and chemicals. Thus, in addition to improving feedstock quality, leaching can provide sugars, lipids, organic acids, alcohols, oils, tannins, polyphenolics, proteins, and others for secondary recovery [11,30,31,34]. In some cases, however, the concurrent removal of organics when attempting to extract inorganic components may lead to undesirable loss of dry matter and hence a reduction in total energy and economic value [11,14,27,30,35,36].

Various methods have been tested for leaching biomass, both as post-harvest unit operations as well as in-field techniques taking advantage of natural precipitation [11,35,37]. Mechanical dewatering following aqueous leaching results in reduced moisture content, but also removes superficial liquid and hence additional soluble inorganic constituents [13]. Different solvents such as acetic and other acids and hot water extractions have also been tried [16,23,31,38]. Depending on the leaching method and the structure of the biomass, significant fractions of alkali metals, chlorine, sulfur and phosphorous can be removed within a short time span of a few minutes with the faster extraction rates making for relatively compact and lower cost equipment although longer periods may be needed for more complete extraction [36,39].

This study was intended to expand the range of data available on the solid–liquid extraction of both inorganic and organic constituents from biomass feedstock using leaching pretreatments. Included are determinations of ion concentrations as well as concentrations of organic acids, carbohydrates, and trace elements, crude and treated feedstock proximate and ultimate elemental compositions, and thermal characterizations for heating value and ash fusibility.

#### 2. Methods

#### 2.1. Sample acquisition and processing

Feedstocks representing a broad variety of energy crop and agricultural and forest residues were selected for this study, including Miscanthus (*Miscanthus x giganteus*), switchgrass (*Panicum virgatum*), Jose tall wheatgrass (*Agropyron elgongatum*), rice straw (*Oryza sativa*), wheat straw (*Triticum sativum*), corn stover (*Zea mays*), and Douglas fir wood (*Pseudotsuga menziesii*). Rice straw (variety M206) was harvested from the Natomas region north of Sacramento, California, in October 2008 following the regular grain harvest. Bales of Yolo County, California, wheat straw from the 2008 harvest were purchased from a commercial supplier (Windmill Feed, Woodland, California). Bales of corn stover from the 2008 harvest in Colusa County, California, were obtained from a private supplier (Broken Box Ranch, Williams, California) in February 2009 after four months in covered storage. Bales of *Miscanthus x giganteus*  were purchased from Mendel Biotechnology, Inc. (BioEnergy Seeds Division, Hayward, California). The Miscanthus was harvested by Idaho National Laboratory at the University of Illinois "SoyFACE" farm, Savoy, Illinois in January 2008. Switchgrass was harvested by hand from the University of California Cooperative Extension field plots in Davis, California, during June 2009. Douglas fir wood chips were obtained from a private supplier (Mallard Creek Inc., Rocklin, California). Douglas fir trees were harvested on the western slopes of the Sierra Nevada mountains between the cities of Chico and Grass Valley, California, in November 2008. The trees were debarked and delimbed prior to chipping. Jose tall wheatgrass, representing a saline irrigated crop grown as phytoremediation biomass on salt-affected soils in the San Joaquin Valley, was harvested and baled at Red Rock Ranch, Five Points, California, also in October 2008.

A 2.73 m<sup>3</sup> forced-convection dryer was used for laboratory airdrying of the freshly harvested rice straw and switchgrass samples. The dryer employed a stainless steel mesh air diffuser screen above an air plenum with unheated ambient air blown upwards through the sample bed. Samples were placed loosely over the screen to about 0.3 m depth, turned 4 times daily, and dried to equilibrium with the laboratory air to achieve moisture contents below 15% wet basis. Douglas fir wood chips were spread and air-dried on the clean laboratory floor under natural convection in 0.15 m deep layers to the same equilibrium moisture content. The wood chips were manually stirred 3 times daily during drying. The air-dried rice straw, switchgrass, and Douglas fir wood samples were sealed and stored in plastic bag indoors under ambient conditions at approximately 22 °C. Bales of wheat straw and Jose tall wheatgrass were stored outdoors under cover while elevated on pallets above the ground. Bales of corn stover and Miscanthus were stored indoors on pallets under ambient conditions.

For processing and analysis, samples of each type of biomass were knife-milled (Pulverisette 19, Fritsch, Germany) through a 2-mm screen. The milled samples were stored air-dry at room temperature (22 °C) in air-tight plastic bags for up to 30 days before analysis and pretreatment.

## 2.2. Sample pretreatment

For each pretreatment experiment, 20 g of air-dried milled sample was batch-leached at room temperature (22 °C) with distilled deionized water in an amount sufficient to yield a 20 L/kg dry matter leaching ratio in simulating a potential industrial process. The experiments were conducted in triplicate for each feedstock. Prior to each experiment, small amounts of sample were oven-dried in an airconvection oven at 103  $\pm$  2 °C to determine moisture content in accordance with ASTM D4442 (2007). For corn stover, switchgrass, Jose tall wheatgrass, Douglas fir wood, and Miscanthus, leaching extractions were carried out for 2 h under agitation with magnetic stir bars at 650-700 rpm. At 20 L/kg, rice straw and wheat straw both swelled to the point of mechanically stalling the stir bars due to the high slurry viscosity. To overcome this, rice straw and wheat straw were soaked for a total of 6 h while manually stirring for 2 min at 30 minute intervals. Each extractor was covered with aluminum foil to reduce evaporative losses during leaching. With batch leaching, changes in the solution properties as the extraction continues may result in differing levels of extraction compared to flow-through processes [35]. The results are therefore specific to this technique.

## 2.3. Feedstock and leachate analyses

At the end of each experiment, the solids and liquid in the batch were separated over a glass microfiber filter (Whatman 934-AH, 110 mm, Whatman, Florham Park, NJ). The electrical conductivity (EC) of each leachate sample was measured (model 30 SCT, YSI Inc., Yellow Springs, OH). From each leachate sample, 40 mL were collected and stored at -20 °C for later analysis. Total solids (TS) in leachate were determined by oven drying a subsample of filtered leachate (20–25 mL) at

60 °C for 48 h followed by 103  $\pm$  2 °C for 15 h. Ash in leachate was determined by loss-on-ignition (LOI) of oven dried samples in an airmuffle furnace (Fisher Model 750-58, Fisher Scientific, Pittsburgh, PA) at 575 °C for 3 h in accordance with ASTM E1755 (2007). Volatile solids (VS) were determined as the difference between total solids and ash.

Both crude and leached biomass solids were analyzed for volatile solids (VS), ash content, constant-volume higher heating value (HHV), proximate composition, ultimate elemental composition for C, H, N, and S, ash elemental composition, and ash fusibility. Ash was determined by loss-on-ignition of oven-dried (103  $\pm$  2 °C) samples in an air-muffle furnace (Fisher Model 750-58, Fisher Scientific, Pittsburgh, PA) at 575 °C for 3 h according to ASTM E1755 (2007). HHV was determined by constant-volume adiabatic calorimetry (IKA C5003/C5001 Calorimeter System, Staufen, Germany) according to ASTM D5865 (2007). Proximate analysis giving volatile matter and fixed-carbon concentrations in addition to ash was conducted according to ASTM D3175 (2007) with volatile matter (VM) determined by pyrolysis at 950 °C and fixed carbon determined by difference. Elemental ash compositions were analyzed using X-ray fluorescence and instrumental neutron activation by Activation Laboratories Ltd., Ancaster, Ontario. Carbon, nitrogen, and hydrogen concentrations were determined using a LECO TrueSpec CHN Elemental Determinator (LECO, St. Joseph, Michigan) with infrared spectroscopic or thermal conductivity detectors (ASTM D5373, 2007). The sulfur concentration was determined using infrared spectroscopy (ASTM D4239, 2007) using a LECO TruSpec Sulfur addon module. In this study, the inorganic fraction was taken to be identical to the ash content. Analyses were conducted in triplicate with the exception of five replicates for HHV.

## 2.4. Ion concentrations

Each leachate was filtered through a 0.2 µm syringe filter to remove particles prior to analysis by high-performance liquid chromatography (HPLC). The filtered leachates were analyzed for anions and cations using a Shimadzu HPLC (Shimadzu, Columbia, MD), consisting of a conductivity detector (CDD-10Avp, Shimadzu, Columbia, MD), two ion exchange columns (Dionex AS22 anion column  $4 \times 250$  mm, and Dionex CS14 cation column  $4 \times 250$  mm, Sunnyvale, CA), two suppressors (Dionex ASRS 300 for anion and Dionex CSRS 300 for cation, Sunnyvale, CA), and a suppressor controller (Dionex RFC-10, Sunnyvale, CA). The cation measurements were performed at 25 °C with a mobile phase of 10 mM methanesulfonic acid at a flow rate of 1.0 mL/min and suppressor current at 30 mA. The anion measurements were performed at 30 °C with a mobile phase of 4.5 mM sodium carbonate/1.4 mM sodium bicarbonate at a flow rate of 1.2 mL/min and suppressor current at 31 mA. The filtered leachates were also analyzed for trace elements using inductively coupled plasma mass spectrometry (ICP-MS) at the Interdisciplinary Center for Plasma Mass Spectrometry, University of California, Davis.

## 2.5. Organic concentrations

As with the ion analyses, leachates were filtered through 0.2  $\mu$ m syringe filters to remove particles prior to analysis for organic compounds by HPLC. Each filtered leachate was analyzed for organic acids, water soluble carbohydrates, and ethanol using the same HPLC with an ion exchange column (Bio-Rad Aminex HPX-87H, 300  $\times$  7.8 mm, Hercules, CA), a refractive index detector (RID-10A, Shimadzu, Columbia, MD), and a UV detector (SPD-20A Prominence, Shimadzu, Columbia, MD). The UV detector was set at 215 nm wavelength and the mobile phase was 5 mM sulfuric acid at a flow rate of 0.6 mL/min. The measurements were performed at 60 °C.

# 2.6. Ash fusibility

Ash fusibility results in association with ash chemical compositions are useful for predicting ash fouling and slagging. Instead of conducting the standard pyrometric-cone test (ASTM D1857/E953), the whole fuel ash fusibility testing method developed by Jenkins et al. [11] was employed. The method appears to be more sensitive to the early fusion behavior of biomass, in particular the initial formation of liquid phases as indicated by the initial deformation temperature. Pelleted feedstock samples were tested at 50 °C intervals over the temperature range from 800 to 1550 °C using a Kanthal EPD high temperature melting furnace. Each fuel pellet was 12 mm in diameter and approximately 10 mm in height and weighed 0.6-0.7 g prior to ashing. Each pellet was placed on a pre-fired refractory alumina support and inserted into the furnace, held for 20 min at each temperature under oxidizing conditions with an air flow rate of 10 mL/min, removed and cooled in a desiccator. The physical characteristics of the remaining ash were evaluated according to the rating procedures developed by Jenkins et al. [11]. Due to the large number of analyses, only single samples were evaluated at each temperature.

## 2.7. Statistical analysis

Significant differences between treatments were identified using analysis of variance (ANOVA) and least significant difference with a significance level  $\alpha = 0.05$ . Data were analyzed using SAS software (Version 9.1, SAS Institute Inc., Cary, NC).

## 3. Results and discussion

## 3.1. Moisture content of leached feedstock

The moisture contents of feedstocks after leaching were in the range from 55 to 81% on a wet basis (Table 1). The high moisture in leached biomass would make most of these materials unsuitable for thermochemical conversion without prior dewatering and possibly drying. Downdraft and updraft-fixed bed gasifiers, for example, have maximum feed moisture contents of around 35% and 60%, respectively [40]. Fluidized bed and entrained flow reactors also are restricted to similar feedstock moisture contents, generally below about 30% wet basis. Fuel blending, hydrothermal and supercritical processing, biochemical conversion, and other processes can be employed to overcome difficulties with high moisture content [18,40], but for more conventional combustion and gasification applications water-leaching pretreatments initially produce high moisture feedstock in need of further mechanical dewatering or drying constituting the subject of related research [13,41].

## 3.2. Proximate analysis

#### 3.2.1. Ash content

Leaching significantly reduced the ash contents of all feedstock samples (Table 1). The high electrical conductivity (EC, Table 2) of leachates from wheat straw, rice straw, Jose tall wheatgrass, and corn stover indicates the presence of soluble salts that are substantially leached. Leaching reduced ash concentration in rice straw from above 18 to below 16% of dry matter, similar to results from earlier investigations in which ash declined from 19.6 to 17.6% of dry solids for rice straw soaked 24 h in de-ionized water at a 70 L/dry kg leaching ratio [11]. Leaching also reduced the ash content of wheat straw solids by 2 percentage points (Table 1). By comparison, a study by Jenkins et al. [11] found that the ash content of a wheat straw from the Imperial Valley of California was reduced from 13.0 to 6.2% dry matter by soaking for 24 h in de-ionized water, but this feedstock was produced under saline irrigation typical of that region and not representative of the low salinity conditions prevailing during the production of the feedstock used here.

The ash content of the corn stover feedstock was 8.43% of total dry solids and higher than values reported in some other studies, e.g. 6.73% from Morey et al. [42] and 5.30% from Xiong et al. [43].

# Table 1

Proximate analysis and heating values of crude and leached feedstocks.

	Rice straw		Wheat straw Co		Corn stover S		Switchgrass		Miscanthus		Jose tall wheatgrass		Douglas fir	
Treatment	Crude	Leached	Crude	Leached	Crude	Leached	Crude	Leached	Crude	Leached	Crude	Leached	Crude	Leached
Ash content <sup>a,b</sup> , % dry	18.48 A	15.74 B	8.28 A	6.27 B	8.43 A	3.96 B	5.89 A	4.47 B	8.27 A	5.07 B	8.51 A	4.49 B	0.20 A	0.12 B
Volatile solids, % dry	81.52 A	84.26 B	91.72 A	93.73 B	91.57 A	96.04 B	94.11 A	95.53 B	91.73 A	94.93B	91.49 A	95.51 B	99.80 A	99.88 B
Moisture content, % wet	8.00	81.28	9.00	76.32	7.67	79.12	8.85	78.72	7.32	68.20	11.09	75.07	9.17	54.79
Volatile matter <sup>b</sup> , % dry matter	66.3 A	70.0 B	74.0 A	80.3 B	74.1 A	81.4 B	77.2 A	80.4 B	78.1 A	82.5 B	74.3 A	80.2 B	83.8 A	85.0 B
Fixed carbon <sup>b</sup> ,% dry matter	15.2 A	14.23 B	17.7 A	13.4 B	17.4 A	14.6 A	16.9 A	15.1 B	13.6 A	12.4 A	17.2 A	15.3 B	16.0 A	14.9 B
HHV <sup>b</sup> , MJ/kg dry matter	15.33 A	15.68 B	17.30 A	17.25 A	17.31 A	18.05 B	18.21 A	18.26 A	17.95 A	18.14 A	17.92 A	19.10 B	19.86 A	19.42 B
Volatile matter <sup>b</sup> , % maf <sup>c</sup>	81.3 A	83.1 B	80.7 A	85.7 B	81.0 A	84.7 B	82.0 A	84.2 B	85.2 A	86.9 A	81.2 A	84.0 B	83.9 A	85.1 B
Fixed carbon <sup>b</sup> ,% maf <sup>c</sup>	18.7 A	16.9 B	19.3 A	14.3 B	19.0 A	15.3 B	18.0 A	15.8 B	14.8 A	13.1 A	18.8 A	16.0 B	16.1 A	14.9 B
HHV <sup>b</sup> , MJ/kg maf <sup>c</sup>	18.81 A	18.60 A	18.86 A	18.40 B	18.90 A	18.80 A	19.35 A	19.12 A	19.56 A	19.11 A	19.59 A	20.00 B	19.90 A	19.45 B

Means (n = 3) followed by the same letters are not statistically different within the same sample type at  $\alpha$  = 0.05.

Fixed carbon is determined by difference of ash and volatile matter from 100%.

<sup>a</sup> Ashing at 575 °C for 3 h (ASTM E1755).

<sup>b</sup> Tukey test was used to determine the significance of leaching on each sample.

<sup>c</sup> Moisture and ash free.

The ash content of Miscanthus feedstock in the present study was also in the high range of values reported elsewhere: 1.1% [44], 3.1% [45], and 1.2 to 8.1% [46] dry weight. In the latter study, fall-harvested samples have higher ash contents on average than winter-harvested samples, most likely due to the natural leaching in the field by precipitation that occurs during the winter. Some winter-harvested samples have higher ash contents than the corresponding fall-harvested material, however, indicating other mechanisms at work in addition to inorganic material extraction [46–48]. Multi-year results for combustion quality effects on Miscanthus genotypes led Iqbal and Lewandowski [49] to conclude that field variations in biomass constituents could be divided into controllable and uncontrollable categories, the former including time of harvesting and genotype selection, the latter including weather conditions and aging effects. Concentrations of leachable constituents

#### Table 2

Elemental compositions of feedstocks.

(e.g. K, Cl, Mg) were strongly affected by harvesting time alone while non-leachable constituents (e.g. N, Si, Ca) were influenced by the interactions of harvest time and precipitation [49]. Both samples used here could have included adventitious material in the form of soil typically added during harvesting in addition to inherently higher ash. Early snows, for example, contributed to Miscanthus crop lodging and soil contamination in field trials in Germany [49]. Although leaching reduced the ash content of Miscanthus by 39%, the EC of the Miscanthus leachate was quite low in comparison (321  $\mu$ S/cm, see below), lower than anticipated if the mass differential were due principally to extracted salts. Further, the Miscanthus analyzed in this study was winter-harvested in January after exposure to ice and snow, and some field leaching may have occurred prior to harvest while superficial soil contamination was simultaneously occurring.

	Rice stra	aw	Wheat s	straw	Corn sto	over	Switchg	rass	Miscant	vliscanthus		Jose tall wheatgrass		Douglas fir	
Fuel (% dry fuel)	Crude	Leached	Crude	Leached	Crude	Leached	Crude	Leached	Crude	Leached	Crude	Leached	Crude	Leached	
Ash	18.48	15.74	8.28	6.27	8.43	3.96	5.89	4.47	8.27	5.07	8.51	4.49	0.20	0.12	
С	38.80	39.70	43.50	44.90	43.50	45.80	45.50	46.00	45.00	45.70	44.80	46.40	50.00	49.90	
Н	5.20	5.20	5.70	5.70	5.70	5.80	5.90	5.90	5.80	5.90	5.90	6.00	6.10	6.00	
N	1.04	0.70	0.47	0.32	0.62	0.33	1.09	0.16	0.14	0.06	0.95	0.71	0.44	0.20	
S	0.07	0.04	0.11	ND	0.05	0.03	0.06	0.03	0.03	0.01	0.23	0.06	ND	ND	
0*	36.40	36.10	41.90	42.80	41.70	44.10	41.60	43.50	40.80	43.30	39.60	42.40	43.30	43.80	
Cl	0.46	N/A	0.85	N/A	0.78	N/A	0.21	N/A	0.02	N/A	1.73	N/A	< 0.01	N/A	
Ash composition (	% ash)														
SiO <sub>2</sub>	69.02	85.43	46.32	79.23	39.12	60.64	53.28	76.63	75.58	78.45	35.60	71.53	4.32	4.08	
Al <sub>2</sub> O <sub>3</sub>	0.42	0.38	0.08	0.56	4.68	2.88	0.68	0.32	6.03	3.55	0.28	1.10	2.12	1.52	
TiO <sub>2</sub>	0.02	0.04	0.04	0.05	0.24	0.20	0.08	0.04	0.48	0.31	0.08	0.07	0.16	0.12	
Fe <sub>2</sub> O <sub>3</sub>	0.20	0.26	0.24	0.28	2.27	1.76	0.60	0.36	2.20	1.45	0.48	0.48	2.44	2.72	
CaO	1.84	2.16	1.96	2.10	3.95	4.36	4.08	5.66	2.73	3.78	4.48	4.76	28.4	32.92	
MnO	0.32	0.22	0.05	0.03	0.13	0.12	0.08	0.10	0.29	0.35	0.10	0.10	1.13	1.26	
MgO	1.74	0.72	2.56	1.58	6.15	4.48	6.96	6.49	1.35	1.19	1.84	1.42	5.52	5.88	
Na <sub>2</sub> O	3.39	1.55	3.12	1.72	1.37	1.00	0.84	1.11	0.73	0.55	20.12	6.47	1.68	1.40	
K <sub>2</sub> O	8.25	1.99	25.12	5.85	12.44	13.08	16.00	5.07	3.63	1.87	11.72	4.21	11.36	6.00	
$P_2O_5$	1.28	0.49	0.64	0.28	2.04	1.44	2.20	1.23	1.00	0.62	1.64	1.41	6.44	4.64	
$Cr_2O_3$	0.05	0.04	< 0.01	0.05	0.02	0.04	0.04	0.04	0.01	0.04	0.04	0.03	0.12	0.08	
LOI	11.37	5.82	7.75	6.67	24.65	4.80	9.81	2.79	3.93	6.68	2.49	5.57	24.36	25.66	
Total	97.90	99.10	87.88	98.40	97.06	94.80	94.65	99.84	97.96	98.84	78.87	97.15	88.05	86.28	
Und	2.10	0.90	12.12	1.60	2.94	5.20	5.35	0.17	2.04	1.16	21.13	2.85	11.95	13.72	
Cl	1.94	0.19	7.72	0.57	6.58	1.95	2.09	0.27	0.06	0.02	16.8	1.74	0.15	0.08	
Mass of ion in sam	ple, mg/g	dry matter													
Na	4.65	1.81	1.92	0.80	0.86	0.29	0.37	0.37	0.45	0.21	12.70	2.16	0.02	0.01	
K	12.66	2.60	17.27	3.04	8.71	4.30	7.82	1.88	2.49	0.79	8.28	1.57	0.19	0.06	
Cl	4.60	N/A	8.50	N/A	7.80	N/A	2.10	N/A	0.20	N/A	17.30	N/A	N/A	N/A	
Ca	2.43	2.43	1.16	0.94	2.38	1.23	1.72	1.81	1.61	1.37	2.72	1.53	0.41	0.28	
Mg	1.94	0.68	1.28	0.60	3.13	1.07	2.47	1.75	0.67	0.36	0.94	0.38	0.07	0.04	

\*By difference; ND = not detected; Und = undetermined; N/A = not available; and LOI = loss on ignition at 950 °C in air.

#### Table 3

Means of volatile solids (VS), ash contents, and electrical conductivities (EC) of leachates.

	Extracts, mg/g dry matter						
Sample	VS	Ash	EC, μS/cm				
Rice straw	54.6 (2.4)	41.0 (2.1)	3057 (146)				
Wheat straw	54.6 (0.6)	36.2 (1.2)	3115 (65)				
Corn stover	122.9 (4.2)	35.2 (0.5)	3152 (16)				
Switchgrass	61.5 (4.2)	17.0 (3.9)	1453 (10)				
Miscanthus	19.9 (0.6)	4.5 (0.4)	321 (3)				
Jose tall wheatgrass	153.6 (9.8)	46.4 (2.1)	3935 (57)				
Douglas fir	9.0 (0.4)	1.3 (0.3)	58 (1)				

EC of distilled and de-ionized water: 1.6 µS/cm.

Ashing at 575 °C for 3 h (ASTM E1755).

Volatile solids were determined by loss-on-ignition at 575 °C.

Standard deviations in parentheses (n = 3).

Leaching reduced the ash content of switchgrass by almost a quarter (5.89 to 4.47%). Both values are within the range of ash reported for switchgrass from the study by Sladden et al. [50] that found ash between 4% and 11% depending on the plant variety. Liu and Bi [23] reported ash removal efficiencies for water leaching of switchgrass ranging from about 19 to 36% with ash concentration reductions up to

#### Table 4

Means of ethanol, acid, sugar and glycerol concentrations in extracts of feedstocks.

41% when leaching for 48 h at a leaching ratio of 40 kg water per kg dry sample and particle size reduced to 0.4–0.95 mm.

The ash content of debarked and delimbed Douglas fir was 0.2% of total dry solids, emblematic of a clean bole wood. Leaching reduced this a further 40%. Results from the study by Wu et al. [22] for the wood fraction of Mallee biomass are similar with ash declining from 0.4 to 0.2% dry weight by water leaching. Link et al. [51] reported 6.73% ash in Douglas fir for whole wood samples, but these include bark with a higher fraction of ash. Liu and Bi [23] found water leaching of pine bark to be ineffective in removing inorganic constituents for starting ash concentrations below 3% dry weight although ash extraction efficiencies under acidic leaching ranged up to 72%. The EC of the leachate from the Douglas fir wood tested here was also low (58  $\mu$ S/cm), indicative of low initial ash content (Table 2) and leaching is not suggested to be a critical pretreatment for this type of feedstock.

## 3.2.2. Volatile matter

Volatile matter (VM) in rice straw was 66.3% of dry matter. This is low in comparison to the other feedstocks due to the much higher ash concentration (Table 1). On a moisture and ash free (maf) basis, volatile matter among all samples was similar at between 81 and 85% dry weight in initial samples. Except for Miscanthus and Douglas fir,

	Feedstocks						
Extracts, mg/g dry matter	Rice straw	Wheat straw	Corn stover	Switchgrass	Miscanthus	Jose tall wheatgrass	Douglas fir
Cellobiose	0.75 (0.04)	0.83 (0.05)	3.04 (0.05)	ND	ND	2.93 (0.03)	0.14 (0.01)
Glucose	7.41 (3.59)	4.60 (0.37)	50.71 (0.76)	14.90 (2.46)	2.88 (0.85)	20.58 (0.22)	0.54 (0.29)
Xylose + mannose + galactose	12.52 (1.76)	8.11 (0.57)	49.76 (1.66)	18.24 (0.56)	4.15 (0.34)	30.17 (1.21)	0.50 (0.12)
Arabinose	0.55 (0.01)	0.56 (0.01)	ND	ND	ND	0.28 (0.01)	0.29 (0.01)
Total sugar	21.23 (2.76)	14.10 (0.99)	103.51 (2.44)	33.14 (3.47)	7.03 (1.08)	53.96 (2.76)	1.47 (0.42)
Lactic acid	3.65 (4.20)	14.81 (0.43)	4.01 (0.17)	1.11 (0.63)	0.76 (0.29)	ND	ND
Formic acid	3.41 (0.60)	5.12 (0.15)	7.73 (1.40)	ND	0.92 (0.38)	11.16 (1.17)	0.64 (0.03)
Acetic acid	2.58 (1.15)	7.78 (0.54)	ND	2.65 (1.24)	0.47 (0.26)	ND	ND
Propionic acid	1.60 (0.70)	29.93 (1.03)	ND	9.76 (0.87)	6.62 (0.70)	ND	ND
Isobutyric acid	ND	ND	ND	ND	ND	ND	ND
Butyric	ND	ND	ND	ND	ND	0.94 (0.55)	ND
Total acid	11.24 (1.71)	57.64 (2.12)	11.75 (1.40)	13.52 (3.60)	8.77 (0.83)	12.10 (1.71)	0.64 (0.03)
Ethanol	5.07 (0.65)	ND	ND	0.80 (0.52)	ND	ND	ND
Glycerol	1.25 (0.22)	0.41 (0.02)	0.55 (0.04)	1.63 (0.30)	0.30 (0.07)	ND	ND

Standard deviations in parentheses (n = 3).

ND: not detected.

#### Table 5

Means of anion and cation concentrations in feedstock leachates.

	Anion extracts, mg/g dry matter									
Sample	F	CH₃COO	Cl	NO <sub>2</sub>	Br	NO <sub>3</sub>	PO <sub>4</sub>	SO <sub>4</sub>		
Rice straw	0.57 (0.05)	0.871 (0.126)	3.92 (0.29)	ND	0.026 (0.002)	ND	3.10 (0.16)	0.62 (0.06)		
Wheat straw	0.19 (0.03)	ND	6.14 (0.27)	ND	ND	0.39 (0.03)	0.45 (0.02)	1.79 (0.05)		
Corn stover	0.29 (0.01)	0.006 (0.001)	7.84 (0.17)	ND	0.038 (0.001)	0.26 (0.01)	1.99 (0.08)	0.32 (0.02)		
Switchgrass	0.30 (0.02)	0.955 (0.098)	1.94 (0.12)	ND	0.013 (0.001)	0.02 (<0.01)	1.09 (0.06)	0.30 (0.04)		
Miscanthus	0.23 (0.03)	0.002 (0.003)	0.10 (<0.01)	ND	ND	0.02 (<0.01)	0.75 (0.03)	0.25 (0.01)		
Jose tall wheatgrass	0.54 (0.01)	ND	16.36 (0.08)	ND	0.450 (0.368)	0.55 (0.02)	0.97 (0.04)	4.10 (0.21)		
Douglas fir	0.03 (<0.01)	0.101 (0.005)	0.02 (<0.01)	ND	ND	ND	0.06 (<0.01)	0.04 (0.01)		
	Cation extra	acts, mg/g dry ma	tter							
Sample	Li		Na	NH <sub>4</sub>	К		Mg	Ca		
Rice straw	0.0025 (0.00	004)	2.82 (0.37)	0.308 (0.009)	13.63	(0.78)	0.32 (0.08)	ND		
Wheat straw	0.0023 (0.00	001)	1.15 (0.41)	0.064 (0.002)	11.44	(0.52)	0.33 (0.03)	ND		
Corn stover	0.0003 (<0.	0001)	0.16 (0.01)	0.108 (0.013)	14.33	(0.37)	1.94 (0.08)	1.08 (0.07)		
Switchgrass	0.0001 (<0.	0001)	0.11 (0.01)	0.093 (0.001)	6.26	(0.32)	0.96 (0.03)	0.06 (0.02)		
Miscanthus	ND		ND	0.037 (0.002)	1.30	(0.05)	0.13 (0.01)	0.20 (0.04)		
Jose tall wheatgrass	0.0126 (0.00	004)	10.03 (0.19)	0.114 (0.002)	6.31	(0.05)	0.41 (0.04)	0.22 (0.21)		
Douglas fir	0.0001 (<0.	0001)	0.03 (0.01)	0.008 (<0.001	) 0.24	(<0.01)	0.01 (<0.01)	0.01 (0.01)		

Standard deviations in parentheses (n = 3).

ND: not detected.

leaching significantly increased the volatile matter by up to 5% and correspondingly reduced fixed carbon (Table 1), suggesting that leaching also changed the mass fraction and composition of organic compounds in the leached solids for these feedstocks. The study by Wu et al. found similar elevations in the volatile matter of Mallee wood, leaf, and bark fractions although ash in bark increased with leaching [22]. The results from Deng et al. [24] again show similar elevations in volatile matter with leaching for wheat straw, rice straw, corn stalk, cotton stalk, candlenut wood, and rice hull using water temperatures up to 363 K (90 °C). These are accompanied by declines in ash concentration although ash in rice hull is not substantially reduced due to the high concentration of silica that comprises most of the ash in this feedstock.

## 3.3. Heating value

Changes in heating value (higher heating value at constant volume. HHV) from leaching were mixed among the different feedstocks (Table 1). Increases in the heating value of leached solids in comparison to feedstock are generally associated with an excess fractional extraction of ash compared with organic matter yielding lower dilution by ash. Alternatively, more effective removal of organic matter compared with ash can result in a decline in heating value, or if the extractions are relatively balanced the heating value may be largely unaffected even though significant mass loss from the sample has occurred. Compositional changes within the residual organic fraction can additionally affect heating value. Corn stover, for example, increased in heating value from 17.31 to 18.05 MJ/kg dry matter due presumably to the excess removal of inorganic components (ash concentration decline from 8.43 to 3.96% dry weight) leaving a higher organic matter concentration. Leaching only slightly increased (2%) the mean HHV of rice straw with results similar to earlier studies [11]. Although leaching appeared to have a limited effect on the HHV of rice straw, the change was statistically significant. Wheat straw saw a non-significant reduction in heating value from 17.30 to 17.25 MJ/kg despite a 24% reduction in ash content, in contrast to some prior findings showing an increase for the high-ash variety mentioned above from 17.10 to 18.10 MJ/kg dry matter [11]. Leaching appeared to have no significant effect on the HHV of switchgrass and Miscanthus. The higher heating value of the Miscanthus feedstock was 17.95 MJ/kg and within the range reported by a number of others [45,48,52] from 16 to 19 MJ/kg including feedstock produced during phytoremediation trials of heavy metal contaminated soils. The HHV of Douglas fir wood (19.10 MJ/kg) was the highest among the feedstocks tested due in large part to its low initial ash concentration.

## 3.4. Elemental concentrations

Ultimate and ash elemental analyses reveal significant changes in the concentrations of constituent elements due to leaching (Table 2). While leaching did not much alter the major C and H element concentrations from feedstock to leached solids, N and S were in all cases reduced, reflecting benefits to be derived in terms of acid gas and pollutant formation. All samples except Miscanthus had high nitrogen

**Table 6** Conductivity factors (μS cm<sup>-1</sup> L mg<sup>-1</sup>) for ions [53].

Ions	Factors
Na <sup>+</sup>	2.13
K <sup>+</sup>	1.84
$Mg^{2+}$	3.82
Ca <sup>2+</sup>	2.60
Cl <sup>-</sup>	2.14
NO <sub>3</sub>	1.15
$SO_4^{2-}$	1.54
HCO <sub>3</sub>	0.72

concentrations that would be expected to contribute to elevated NO<sub>x</sub> formation during combustion and high ammonia production during gasification. Crude Jose tall wheatgrass had a higher sulfur concentration (0.23% dry matter) than other feedstocks, suggesting elevated SO<sub>x</sub> or H<sub>2</sub>S formation during conversion; however sulfur was substantially extracted by leaching.

Among the seven feedstocks, Douglas fir had the least amount of Na (0.02 mg/g) and K (0.19 mg/g) consistent with forest production. Fir was followed by Miscanthus with Na at 0.45 mg/g and K at 2.49 mg/g (Table 2). Jose tall wheatgrass had higher Cl concentration than other feedstocks with implications for all the deleterious effects noted above during thermochemical conversion processes; however, leaching was able to remove up to 95% of Cl as determined by differences between original feedstock concentrations and subsequent analysis of chloride



**Fig. 1.** (a) EC difference between measured and calculated values, (b) cation–anion balances, and (c) difference between ion sum and measured EC. Error bars are one standard deviation.

in leachate. Six hours of leaching under agitation were sufficient to remove 61% of Na, >99% of K, and 85% of Cl from rice straw. By comparison, a study from Jenkins et al. [11] found that soaking whole rice straw in de-ionized water for 24 h removed 38% of Na, 90% of K, and >99% of Cl, consistent with the results of Deng et al. [24] who also observed higher removal efficiencies for Cl than K for a rice straw feedstock. The results here reverse the rankings for K and Cl, but both are substantially leached. Mixing and size reduction add cost in the leaching process, and particle size and solids-to-solvent ratio also affect the time required for complete leaching. Investigations characterizing the leaching kinetics, evaluated separately, are important to the economic optimization of the process.

Leaching extracted about 60% of Na, 66% of K, and 72% of Cl from wheat straw. By comparison, Jenkins et al. [11] found that soaking wheat straw for 24 h in de-ionized water removed 83% of Na, 84% of K, and 90% of Cl. In contrast, the experiments of Deng et al. [24] for wheat straw yield higher removal for K than for Cl. Differences in feedstock origin and composition likely contribute to differences in the extraction yields, although differences in leaching time may in this case also have an effect. Corn stover and switchgrass leachates had much less Na than rice and wheat straws, but had moderate amounts of K, 8.71 and 7.82 mg/g dry matter, respectively (Table 2). Overall, leaching removed major fractions of K, Na, and Cl from all feedstocks, however, only up to 12% of Ca was removed by water with the exception of corn stover for which 45% of Ca was removed. Similarly, 62% of Mg was extracted from corn stover while up to 43% was extracted from the other feedstocks.

#### 3.5. Organic matter in leachates

Leaching removed a substantial fraction of organic matter from most feedstocks, especially corn stover (123 mg/g) and Jose tall wheatgrass (154 mg/g, Table 3) representing a loss of up to 15%. Ethanol was detected only in leachates from rice straw and switchgrass with yields of 5.07 and 0.80 mg ethanol per gram original dry matter (Table 4). The amount of total sugars extracted from corn stover was the highest of all feedstocks with half (51 mg/g) identified as glucose. Glycerol was detected except in Jose tall wheatgrass and Douglas fir leachates, but the amounts were small, ranging from 0.30–1.63 mg/g dry matter. Among all feedstocks, wheat straw leachate contained the greatest yield of total organic acid (57.64 mg/g dry matter) with 52% as propionic acid and 15% as lactic acid (Table 4). Acids and sugars extracted from feedstock might potentially be recovered and used in other downstream processes after leaching. Of the total organic mass in leachate, only 43% was specifically identified by the type of compound for Jose tall wheatgrass, while 94% was identified for corn stover. Rice straw, switchgrass, and Miscanthus had between 68 and 79% of mass identified by compound. The unidentified fraction may include phenolic compounds, vanillic acid, syringic acid, and ferulic acid that have been detected in wheat straw leachate generated from warm aqueous leaching. In a study by Sun et al. [31], hot water (80–95 °C, pH 6–8) extraction of wheat straw resulted in a fractional yield of extractives ranging from 0.48 to 0.62% of original dry weight and identified a number of compounds including free fatty and other acids, sterols, waxes, di- and triglycerides, and steryl esters in total accounting for 70 to 77% of the

#### Table 7

Concentrations of major and trace elements in leachate samples.

Element	Detection limit	Rice straw	Wheat straw	Corn stover	Switchgrass	Miscanthus	Jose tall wheatgrass	Douglas fir
Concentration	1, μg/L							
Li	0.09	6	24	29	14	10	474	1.3
В	10	387	616	583	189	282	11,309	29
Na	93	203,733	69,393	15,821	18,348	2734	597,400	439
Mg	0.36	72,907	77,133	156,013	142,100	22,460	43,613	679
Р	41.1	53,293	15,750	52,347	69,307	31,773	23,540	1148
Ca	332	3799	34,967	94,640	19,628	34,667	77,193	2169
Ti	1.61	6	ND	4.64	4.90	14.67	2.94	ND
V	0.02	2.9	1.0	2.5	0.49	2.1	2.8	0.13
Cr	0.07	14	13	5	7	5	5	0.22
Mn	0.16	11,894	574	2375	913	3066	1478	67
Fe	0.42	1683	102	205	243	678	155	13
Co	0.04	10	1.2	10	5	4	2.4	0.49
Ni	0.12	31	8	26	87	16	11	0.51
Cu	0.14	80	48	131	112	48	101	0.43
Ga	0.14	0.25	ND	0.27	ND	0.54	ND	ND
Ge	0.06	0.45	0.26	0.19	0.12	0.59	0.65	ND
As	0.29	61	12	13	9	18	12	10
Se	16.38	ND	ND	ND	ND	ND	85	ND
Rb	0.08	1448	527	172	391	64	151	16
Sr	0.20	62	512	958	181	102	734	17
Zr	0.15	0.97	ND	ND	ND	1.60	ND	ND
Nb	0.02	0.18	0.04	0.05	0.05	0.08	0.04	ND
Mo	0.05	21	7.1	3.1	1.1	0.67	25	0.05
Cd	0.04	0.31	0.57	1.5	0.47	1.4	1.5	0.25
Sb	0.08	1.1	1.5	0.48	3.2	1.1	ND	4.3
Те	1.05	ND	1.4	ND	ND	1.8	1.6	ND
Cs	0.04	0.99	1.1	0.41	0.50	0.27	0.51	0.09
Ba	0.10	96	322	279	73	194	35	21
Ce	0.01	0.92	0.59	2.0	0.55	4.0	0.88	0.07
Nd	0.02	0.23	0.19	1.0	0.17	2.2	0.32	0.05
W	0.003	0.97	0.72	0.96	0.89	0.82	2.7	0.15
Re	0.01	0.01	0.02	0.03	ND	ND	4.9	ND
Th	0.03	8	0.11	0.74	0.53	1.1	0.71	0.21
U	0.02	0.05	0.14	ND	ND	0.28	0.44	ND
mg/g dry ma	tter							
Na		2.59	1.17	0.23	0.32	0.05	11.09	0.01
Mg		0.93	1.30	2.30	2.50	0.40	0.81	0.01
Ca		0.05	0.59	1.39	0.35	0.62	1.45	0.04

ND: The concentration is lower than the detection limit.

extract. Phenolic compounds in the same extracts were present in fairly low concentrations ranging from 0.9 to 3.6% dry weight with syringaldehyde, vanillin, and vanillic, *p*-coumaric, ferulic, cinnamic, fumaric, and *m*-toluic acids comprising a major share. He et al. [32] analyzed water extractable organic matter from alfalfa, corn, soybean, clover, vetch, lupin, and wheat shoot samples as well as from dairy manure after milling air-dried samples to 2 mm and batch leaching in chilled (4 °C) water at 40 L/kg for 18 h with periodic agitation. Using spectroscopic techniques they observed significant soluble carbohy-drates along with organic acids, amino acids, peptides, and phenolic compounds in addition to various mineral phases.

Although leaching yielded organic coproducts, excessive organic matter removal might reduce the energy and economic value of the feedstock due to a reduction in the total dry weight after pretreatment [11,30,35]. Without coproduct recovery, extraction of organics would increase biological and chemical oxygen demand of leachate for wastewater treatment if needed [33], incurring additional cost [36,39].

### 3.6. Electrical conductivity and ion concentrations in leachates

Electrical conductivities (EC) of leachates exceeded 3000  $\mu$ S/cm for rice and wheat straw, corn stover, and Jose tall wheatgrass (Table 3). As noted above, the low EC for Miscanthus may be indicative of adventitious material in the sample rather than extraction of inherent constituents. The low EC for Douglas Fir wood is consistent with the low ash content of the feedstock and overall lower ion concentrations compared to the other feedstocks (Table 5). The EC of leachate from Jose tall wheatgrass was the highest among all feedstocks as a result of its origin in remediation of salt affected soils and production under highly saline conditions.

The quality of the leachate results as measured by HPLC was evaluated by comparing the measured EC to a computed EC determined from the ion concentrations in the leachate. The computed EC was determined by [53]:

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

where  $C_i$  is the concentration of ionic species *i* and  $f_i$  is the conductivity factor for the same species (Table 6). Aside from corn stover and Jose tall wheatgrass, the computed values are outside the  $\pm$  10% recommended allowable deviation of [53] (Fig. 1a). In general, the measured EC values were higher than the calculated EC values, a result similar to that of Deng and Che [33] who attribute the differences in part to the neglect of organic ions. In this case it may also be due to the absence of  $HCO_3^-$  among the analytes due to the selected column and mobile phase for this study. The anion-cation balance in leachate was calculated to test for electroneutrality (Fig. 1b). Except for the Jose tall wheatgrass leachate, the differences between anionic and cationic charges are also outside the  $\pm 5\%$  recommended [53]. The cationic charge was larger than anionic charge in most of the leachates, similar to other results [11,33]. Jenkins et al. [11] suggested calibration errors or column contamination as possible contributors while as noted above Deng and Che [33] suggest the presence of unquantified organic anions in the leachate. In the present study, the deviation is again believed to be due in part to the absence of HCO<sub>3</sub><sup>-</sup> measurements in the leachate samples. The reported concentrations of HCO<sub>3</sub><sup>-</sup> in wheat straw and rice straw leachates from the study of Jenkins et al. [11] were used here to estimate a corrected anion-cation balance. The differences in anion-cationic charge for wheat straw and rice straw were reduced from 32% and 22% to 18% and 6% respectively. Additional corrections from organic ions [33] might further reduce the error.

The analysis was also checked by comparing the measured EC with the ion sums. In general, both the anion and cation sums should

be about 1% of the measured EC value. The acceptance criterion is [53]:

 $0.9EC \le 100 \times anion (or cation) sum, meq/L \le 1.1EC.$  (2)

Overall, the application of the criterion in Eq. (2) to the cation sum yields a result close to the  $\pm 10\%$  recommended except for wheat straw and Douglas fir (Fig. 1c). Both of these factored cation sums were significantly lower than the EC values suggesting the presence of undetermined species. The anion sums for the leachates all fall well below the recommended value, again indicating the absence of HCO<sub>3</sub><sup>--</sup> measurements and the possible presence of undetermined organic ions.

#### 3.7. Trace elements in leachates

The leachates were analyzed for trace elements using ICP-MS and only results above the detection limits are tabulated (Table 7). Some element concentrations (for Na, Mg, and Ca) were converted to mg/g dry feedstock to compare with the analyses done by HPLC on leachates reconstructed to original dry weight basis (Table 5). Overall, the concentrations of Na in leachates analyzed by ICP-MS were similar to the results from the HPLC. For concentrations of Ca in switchgrass, Miscanthus, Jose tall wheatgrass, and Douglas fir leachates, the results from ICP-MS were higher than results from HPLC, potentially as a result of low concentrations of Ca in leachates with lower sensitivity for the HPLC in comparison with the ICP-MS. The concentrations of K exceed the ICP-MS detector limits and are not reported in Table 7. Otherwise, alkali metals (Li, Na, Rb) and alkaline earth metals (Mg, Ca, Sr, Ba) were readily detected with ICP-MS as were other elements including B, P, Ti, Cr, Mn, Fe, Co, Ni, Cu, and As. These concentration results along with site-specific



Degree of fusion [11]:

 Fuel pellet vertically extended to column of soft ash, no apparent sintering, column has open and rough surface, pellet free of refractory support

- Pellet vertically extended, weak sintering of particles, column has open and rough surface, pellet free of refractory support
- 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 2mm
- Ash vaporized or absorbed into refractory support with no measurable thickness

**Fig. 2.** Fusibility of crude and leached feedstock ash from whole fuel fusibility experiments (50 °C temperature intervals from 800 to 1550 °C). All samples held at temperature for 20 min with air flow rate at 10 mL/min. Degree of fusion [11]: 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.

environmental regulations determine the safety of the leachates for downstream application or disposal [30].

## 3.8. Ash fusibility

The importance of ash fouling and slagging to the operation of thermal systems generates substantial concerns around the measurement and prediction of ash fusibility. Results of the whole fuel ash fusibility tests on crude and leached feedstocks are shown in Fig. 2. Ratings range from 1 (unsintered, no detectable liquid phase) to 6 (ash fully melted with volatile loss). For Douglas fir, the fusibility method as originally developed on whole feedstock samples is sufficiently insensitive due to the very low ash content that results are not included in the figure.

Crude rice straw sintered beginning at 850 °C, began to fuse at 1050 °C, and melted to a spherical state by 1200 °C. Leached rice straw remained unsintered through 1200 °C and did not fuse before 1550 °C. The results of rice straw are in accord with previous results found by Jenkins et al. [11] with a leaching ratio of 70 L/kg, indicating that the lower water use here was sufficient to capture the same benefits in increasing the fusion temperatures. Wheat straw sintered at the lowest furnace temperature (800 °C) with substantial melting (stage 3) by 900 °C. A glassy slag (stage 4) formed at 950 °C, results generally consistent with those of Jenkins et al. [11] and Deng et al. [24] although in the

latter case the softening temperatures of the pre-ashed wheat straw samples are higher than the equivalent temperatures observed here.

The corn stover ash also began to sinter at 800 °C, producing a complete melt phase (stage 5) by 1200 °C. Typically the whole fuel samples exhibit liquid phase formation at lower temperatures than the pyrometric cone tests of ASTM Standard D1857, but begin to align for the hemispherical and fluid temperatures of the standard method. Morey et al. [42] noted initial deformation temperatures for corn stover of around 1054 °C with hemispherical and fluid temperatures of 1149 and 1207 °C, respectively, close to the onset temperatures observed here for stages 4 and 5 melting. The results of Deng et al. [24] for corn stalk, however, align beginning at the initial deformation temperature. Leaching of corn stover did not substantially alter the fusion behavior (Fig. 2) despite the ash content being reduced to less than half of the original (8.43 to 3.96%), the reasons having to do with the composition of the ash described below. Leaching did improve the fusibility ratings of switchgrass and Jose tall wheatgrass. The Miscanthus tested here had relatively good initial fuel quality with a high (1100 °C) sintering temperature. Leaching would therefore be of less importance for thermal processing although it did extend the melting ranges for stage 3 and above.

As a simple prediction of the effect of leaching on ash fusibility, normalized compositions using only the ash elements K, Ca, and Si were compared against ternary phase equilibria (Fig. 3 [54]) in a manner



Fig. 3. Liquidus surface of the ternary system K<sub>2</sub>O–CaO–SiO<sub>2</sub> [54] showing normalized compositions for all crude and leached samples. Placement is by composition only, liquidus temperatures read from the figure (total melting) are only in approximate agreement with fusibility experiments. (RS: rice straw; LRS: leached rice straw; WS: wheat straw; LWS: leached wheat straw; CS: corn stover; LCS: leached corn stover; SG: switchgrass; LSG: leached switchgrass; MS: Miscanthus; LMS: leached Miscanthus; JTWG: Jose tall wheatgrass; LJTWG: leached Jose tall wheatgrass.)

similar to Jenkins et al. [11]. Experimental trends with leaching are in general matched by compositional shifts within the phase space. The limited change in melt behavior for Miscanthus, for example, is evident in the small shift within the high silica corner of the phase diagram (MS to LMS, Fig. 3). The normalized ash compositions of both crude (SiO<sub>2</sub>: 19%, K<sub>2</sub>O: 50%, CaO: 31%) and leached (SiO<sub>2</sub>: 23%, K<sub>2</sub>O: 35%, CaO: 42%) Douglas fir wood were outside the range of the phase diagram and so are not shown.

Due to the low calcium concentrations among the grasses (Table 2), the melting properties can also be estimated using the simple binary phase systems (K<sub>2</sub>O–SiO<sub>2</sub> or Na<sub>2</sub>O–SiO<sub>2</sub>) (Fig. 4 [54]). Due to the complex melt behavior of these mixtures, leaching can under some conditions reduce the feedstock quality rather than improve it if alkali extraction is inadequate. A careful analysis of the leaching process should be undertaken to ascertain potential effectiveness. For example, the liquidus temperature of crude wheat straw is below 950 °C with 62% SiO<sub>2</sub> on a normalized basis as shown in Fig. 4. Leaching resulting in only partial removal of alkali to yield 70% SiO<sub>2</sub> would lead to an unfavorable depression in melting temperature to 800 °C, at least for dry ash conversion systems where slag formation is to be avoided. Simple estimates of ash fusion temperature provided by either the binary or ternary phase diagrams are approximate at best. Other constituents can also affect the melt behavior, and more advanced thermodynamic calculations may be needed for design predictions [55].

#### 4. Conclusions

Among the suite of biomass feedstocks tested (rice straw, wheat straw, corn stover, switchgrass, Miscanthus, Jose tall wheatgrass, Douglas Fir wood), water leaching removed substantial fractions of inorganic (1–46 mg/g dry matter) and organic (9–154 mg/g dry matter) materials. Aside from the resulting initial high moisture content (55 to 80% wet basis) of residual solids, leaching consistently achieved an overall improvement in fuel properties despite a relatively low leaching



**Fig. 4.** Traces of the liquidus temperature of the binary systems  $K_2O-SiO_2$  and  $Na_2O-SiO_2$  [54] showing normalized compositions for all crude and leached samples. Placement is by composition only, temperatures are only in approximate agreement with fusibility experiments. (RS: rice straw; LRS: leached rice straw; WS: wheat straw; LWS: leached wheat straw; CS: corn stover; LCS: leached corn stover; SG: switchgrass; LGC leached switchgrass.)

ratio (20 L water/kg dry matter) at ambient temperature. Ash contents were in all cases significantly reduced although for both Douglas fir wood and Miscanthus leaching is not viewed as being of particular utility for combustion or other thermal conversion applications due to the low ash content or relatively good starting composition of the ash. Simultaneous inorganic and organic material extraction leads to more complex outcomes among other fuel properties, for example heating value was largely unchanged after leaching rice straw, wheat straw, switchgrass, and Miscanthus although ash concentrations declined 15 to 39%, a result consistent with a changing organic composition. Similarly, leaching did not increase the initial ash melting temperatures for corn stover and Miscanthus although it did extend the temperature range to the fluid point, reducing the potential for severe ash slagging at typical operating temperatures. Leaching significantly increased the melting temperatures for the other herbaceous feedstocks. These trends in melt behavior are generally predicted from mineral phase equilibria using reduced compositions for the major ash species. Sugars and organic acids constituted the major fractions of the extracted organic matter and potentially serve as coproducts from the leaching system; however, further identification of organic extracts may be necessary to fully resolve deficiencies observed among anion balances for all feedstocks.

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