



# 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

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

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of feedstock reduce conversion efficiencies and increase maintenance and product costs for non-slugging 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 elongatum*), 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 air-drying 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 air-convection oven at 103 ± 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

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