



## Full Length Article

# Hot water extraction as a pretreatment for reducing syngas inorganics impurities – A parametric investigation on switchgrass and loblolly pine bark



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## ABSTRACT

The effects of hot water extraction on the removal of inorganic impurities (N, S, Na, K, Mg and Ca) in biomass that are detrimental to gasification were investigated on switchgrass and loblolly pine bark. As hot water extraction severity increased from 13 to 141 h °C, the extraction liquor pH decreased from 6.0 to 4.5 for switchgrass and 3.6 to 3.1 for pine bark, thus resulting in 20.7–69.6% of ash reduction for switchgrass and 57.0–73.3% for pine bark, respectively. In addition, the nitrogen content which results in ammonia (NH<sub>3</sub>) formation was reduced by 9.3–22.9% for switchgrass and 1.0–6.8% for pine bark following increment of severity. Furthermore, sulfur which leads to hydrogen sulfide (H<sub>2</sub>S) formation was reduced from 48.3 to 62.5% and 5.6 to 17.3% for switchgrass and pine bark, respectively.

The range of potassium, sodium, magnesium and calcium reductions were 94.9–98.8, 47.9–72.4, 58.7–83.5 and 8.5–13.0 for switchgrass and 50.8–67.5, 29.2–60.1, 9.7–50.8 and 3.3–33.0% for pine bark. Finally, statistical analysis was carried out on the statistical significance of the extraction temperature and time as well as their interaction on the removal of inorganic impurities. The extraction temperature, time, and the interaction differed in their effect on liquor pH, ash reduction, mass loss, and reduction of individual inorganics.

## 1. Introduction

Energy and fuel production from renewable feedstocks is a critical research area today because of the forecasted depletion of crude oil reserves and the growing concern of irreversible environmental damage caused by greenhouse gases [1]. In particular, conversion of biomass to biofuel and energy through gasification is attractive as it has the potential to produce mixed alcohols, gasoline and diesel via Fischer-Tropsch (FT) synthesis, gasoline via methanol synthesis as well as energy via internal combustion engine, steam and gas turbines [2]. Currently, the presence of contaminants in biomass derived syngas is considered the primary hurdle for the commercialization of syngas [3]. Among the gaseous contaminants, inorganics have been associated with catalyst poisoning, corrosion, agglomeration, and undesirable emissions during gasification [4,5]. In particular, nitrogen, sulfur, and alkali and alkaline earth metals present in biomass result in ammonia (NH<sub>3</sub>), hydrogen sulfide (H<sub>2</sub>S), and trace metal vapors (K, Na, Ca, and Mg), respectively at concentrations ranging from few parts per million (ppm)

to few thousands depending on the species, operating conditions, and biomass properties [6–9]. Nitrogen in biomass is mainly linking with proteins in living organic tissues [10,11]. During gasification, it is liberated as predominantly as NH<sub>3</sub>, hydrogen cyanide (HCN), molecular nitrogen (N<sub>2</sub>), heavy tars, with a smaller part retained in solid char [12]. Sulfur (S) is found in both organic and inorganic forms in biomass. The organic forms of S are covalently bound to proteins and amino acids, while the inorganic forms can exist as sulfate (SO<sub>4</sub><sup>2-</sup>) and sulfite (SO<sub>3</sub><sup>2-</sup>) [11]. During gasification, sulfur in the biomass is primarily converted to hydrogen sulfide (H<sub>2</sub>S), which causes equipment corrosion and catalyst deactivation in downstream applications [13–15]. The alkali metals (Na and K) in the biomass mainly remained in the form of ionic salts that were not metabolized by the plant [16]. Within the biomass cell structure, alkali metals often exist in free ion form (Na<sup>+</sup>, K<sup>+</sup>) with counterions such as chloride (Cl<sup>-</sup>) or malate (C<sub>4</sub>H<sub>4</sub>O<sub>5</sub><sup>2-</sup>) in the fluid matter [17]. They can also appear in solid salt structures fixed on the cell wall of biomass [17]. A small amount of alkali metals are attached to functional groups in the organic matrix as carboxylates and

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phenoxides [18]. For *in situ* gasification, alkali metals can easily poison catalysts; they also pose challenge to *ex situ* conditioning of syngas or downstream catalytic applications [4,19]. The existence of alkali metals can cause fouling and corrosion in downstream processes as well [20]. Alkaline-earth metals (Mg and Ca) do not usually exist in free ionic form, which is different from the chemical status of alkali metals [11]. Mg and Ca have a tendency to form complexes with organic counterions [18]. These species are regarded as the major inorganic syngas contaminants and their concentrations are strictly restricted depending of the intended syngas application [21]. In fuel synthesis applications through FT and methanol syntheses, the tolerable limit of nitrogen and sulfur contaminants are 20 and 0.01 ppm, respectively. As for gas turbine based power generation applications, concentrations below 50 and 0.02 ppm are desired for nitrogen and sulfur contaminants, respectively [19]. As such, contaminant removal efficiencies greater than 99% are typically required to ensure that inorganic contaminants in biomass derived syngas are below these limits.

Traditionally, syngas inorganic contaminant reduction has been achieved through downstream gas cleanup [13,19]. While effective commercial gas cleanup technologies exist, recent technoeconomic analyses show that gas cleanup accounted for the highest share of the total capital investment in gasification related applications [22]. In recent years, pretreatment techniques have been explored to reduce inorganic content and improve the quality of biomass prior to pyrolysis conversion [23–30]. Among these treatments, hot water extraction is particularly attractive as it does not require the addition chemicals, unlike other chemical pretreatment, and can be optimized to minimize carbon loss [31]. Originally intended for extractives and hemicellulose extraction, hot water extraction consists of biomass immersion in water and subsequent heating up to 180 °C with autogenous pressure development. During this process, acid groups are released thus rendering the extract acidic. The acidity of the extract can be tuned through controlling the hydrolysis of these groups by regulating the severity of the extraction using temperature and time [32,31]. However, the potential beneficial impact of pretreatment techniques on reducing inorganics of concerned (N, S and metals) in gasification have drawn less attention [33]. The pretreatment methods can be very different for pyrolysis and gasification due to the downstream processes requirements for their dissimilar conversion products (bio-oil and syngas, respectively). Consequently, this study aims to explore the impact of hot water extraction (HWE) as an inorganic reduction pretreatment on biomass nitrogen, sulfur, and select metals (Na, K, Mg and Ca).

## 2. Materials and methods

### 2.1. Biomass preparation and characterization

Biomass types investigated in this study were switchgrass (*Panicum virgatum*) obtained through the University of Tennessee Biofuels Initiative (UTBI) and loblolly pine (*Pinus taeda*) bark obtained from Auburn University. The samples were grounded and sieved to particle size below 40 mesh (425 μm) to ensure that all samples have a uniform size distribution [34]. Proximate analyses of moisture, ash, volatile matter and fixed carbon were performed on each biomass sample according to standard methods ASTM E871-82(2013) [35], ASTM E1755-01(2015) [36] and ASTM E872-82(2013) [37], respectively. Ultimate analysis of C, H, N, and O were conducted using a Perkin Elmer CHN analyzer. Fixed carbon was determined by difference between the volatile matter and ash values. The inorganic elemental composition of each biomass was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) with an Optima 7300 DV spectrometer (Perkin Elmer). Prior to ICP-OES analysis, approximately 0.5 g of each biomass sample was microwave digested using 4 mL of concentrated nitric acid (HNO<sub>3</sub>, 70% w/w), 3 mL of concentrated hydrochloric acid (HCl), and 0.2 mL of hydrofluoric acid (HF, 51%) at temperatures between 160 and 210 °C for 20 min [38]. After digestion, the

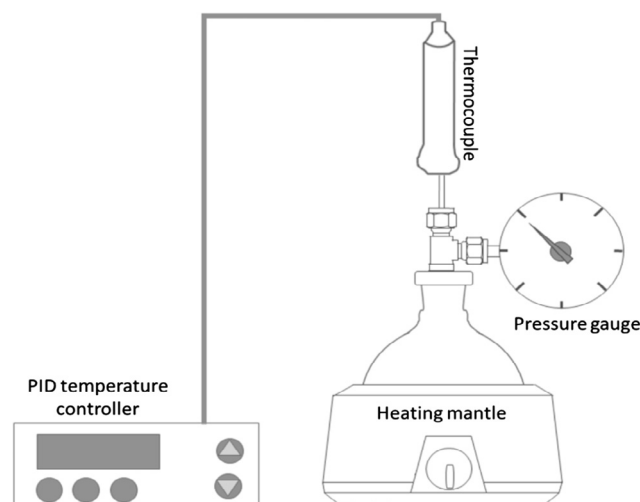


Fig. 1. Schematic representation of the hot water extraction experimental setup.

solution was diluted to 50 mL with Milli-Q H<sub>2</sub>O and filtered with 0.45 μm PTFE filters prior to ICP-OES analysis. All compositional and elemental analyses were performed in triplicate.

### 2.2. Hot water extraction

The HWE extraction vessel consists of a 200-mL heavy-wall round bottom flask with a screw cap fitted with ¼ in. compression fittings for a thermocouple and pressure gauge ports (Fig. 1). The extraction temperature was monitored and controlled by a PID (proportional–summation–difference) temperature controller with continuous data logging. In this experiment, the extraction severity (16–141 h °C for switchgrass and 13–128 h °C for pine bark, respectively) was determined by computing the time integral of the experimentally measured temperature recorded by a PID controller using a Matlab script. The script carried out a numerical integration routine to convert the temperature–time plot into a single severity value. This approach enabled to capture the contribution of the overall extraction of ramping from room to extraction set point temperature as well as to use natural temperature fluctuations observed in experiments.

For each HWE experiment, approximately 5 g of each biomass sample were thoroughly mixed with deionized (D.I.) water at 1:20 biomass to water ratio, on weight basis. This ratio was chosen to ensure that (i) there is ample liquor for further analysis and (ii) that the thermocouple was fully submerged even during vigorous agitation which led to the formation of a vortex in the slurry. After reaching the appropriate extraction temperature (60, 80, 100, 120 and 140 °C), the mixture was held there for a desired extraction time (15, 30 and 45 min). The reactor was then allowed to cool, and the slurry was filtered to recover the undiluted filtrate for pH measurement. The residual extracted biomass was thoroughly rinsed with 100 mL of D.I. water to remove any deposited inorganic elements on the surface and dried at 80 °C overnight. All HWE extraction and compositional and elemental analyses were performed in triplicate.

### 2.3. Characterization of hot water extraction products

The pH, total dissolved solids (TDS), inorganic elemental composition, and total organic nitrogen (TN) were measured on the undiluted liquor collected after filtration of the HWE slurry. ICP-OES analysis of the liquor followed the same approach used in determining biomass inorganic elemental composition and described in 2.1. TN analysis was performed on a TOC-L analyzer attached with TNM-L unit (Shimadzu Corp., Japan) after filtration of liquor samples using 0.2 μm filter to remove any suspended particles. The filtrates were subsequently diluted

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