



Research paper

Using a chelating agent to generate low ash bioenergy feedstock



Charles Warren Edmunds, Choo Hamilton, Keonhee Kim, Stephen C. Chmely^{**},
Nicole Labbé^{*}

Center for Renewable Carbon, University of Tennessee, 2506 Jacob Drive, Knoxville, TN 37996-4542, United States

ARTICLE INFO

Article history:

Received 5 May 2016

Received in revised form

1 November 2016

Accepted 3 November 2016

Available online 10 November 2016

Keywords:

Biomass

Ash

Inorganics removal

Chelating agent

ABSTRACT

Inorganic elements present in lignocellulosic biomass and introduced during harvesting and handling of the feedstock negatively affect biomass conversion to fuels and products. In particular, alkali and alkaline earth metals act as catalysts during thermochemical conversion, contribute to reactor degradation, and decrease the yield and quality of the reaction products. In this study, we investigated an approach to reduce ash content of switchgrass. Several reagents (chelating agents ethylenediaminetetraacetic acid (EDTA) and citric acid, as well as acetic acid, sulfuric acid, and water) under various extraction times (5, 10, 15, and 20 min) were tested using a microwave-assisted extraction method. After the extraction, mass loss, total ash, individual inorganics, and concentration of sugars in the hydrolyzates were measured. EDTA afforded the highest inorganics removal, with near complete extraction of alkali and alkaline earth metals K, Ca, and Mg, and high removal of S and Si. Citric acid and sulfuric acid removed similarly high amounts of K, Ca, and Mg as EDTA, but less Mg, P, S, and Fe. Additionally, extraction with water resulted in near complete removal of K; however, more modest removal of other inorganics was observed compared to other treatments. The mass loss was significantly higher in the sulfuric acid extractions due to hydrolysis of the structural carbohydrates, while EDTA resulted in little carbohydrate degradation due to the more neutral pH conditions. This study illustrated the benefits of extracting with chelating agents, as opposed to mineral acids, to remove inorganics and improve biomass quality.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Lignocellulosic biomass is a promising feedstock for renewable fuels, and carbon-containing products such as platform and fine chemicals and materials. The conversion of lignocellulosic biomass to fuels and products occurs via pathways that require some combination of engineering systems and catalytic technologies (either biological, chemical, or both) [1,2]. Whereas lignocellulosic biomass can be considered in broad terms as a source of “renewable carbon,” in reality, it is a much more complex mixture of organic (cellulose, hemicellulose, lignin, and other extractable compounds) and inorganic (ash) components. In fact, the latter typically has a detrimental effect on the technology implemented to bring about conversion of the former into fuels, chemicals, and other products [3,4].

For instance, thermochemical conversion routes of

lignocellulosic biomass, including pyrolysis and gasification, require rapid and intense heating of feedstock materials (500–1400 °C) to initiate fragmentation and depolymerization reactions [1]. However, the presence of ash during this heating step contributes to decreased reactor efficiency by promoting slagging and fouling on reactor surfaces [3]. Additionally, product selectivity and yield is often affected by the presence of alkali and alkaline earth metals in the ash via siphoning of conversion products through undesirable autocatalytic reaction pathways [2,4]. Ash content also has a marked effect on downstream processes, where inorganic components can react detrimentally with catalyst systems that are responsible for additional upgrading reactions [5].

Ash content varies by biomass type and anatomical fraction, but in general, agricultural and herbaceous biomass (straws and grasses) have the highest ash content and debarked woody biomass has the lowest [6]. Technical projections for thermochemical conversion of lignocellulosic biomass conducted by the U.S. Department of Energy (DOE) assume a delivered ash content of less than 1% in biomass feedstock [7]. While best management practices can lower entrained ash content in biomass feedstock (e.g. through the reduction of introduced ash from superfluous soil, debarking,

^{*} Corresponding author.

^{**} Corresponding author.

E-mail addresses: schmely@utk.edu (S.C. Chmely), nlabbe@utk.edu (N. Labbé).

delaying harvest time [8], or feedstock blending [9]), an additional and advanced preprocessing step to remove physiological ash could be necessary for many bioenergy crops.

One such treatment involves rain-washing, where biomass is left in the field to be exposed to precipitation before it is harvested [10]. This technique removes substantial amounts of ash constituents, particularly K and Cl [11]. However, results are highly variable as they are dependent on the amount of precipitation and other factors [10]. As such, post-harvest water leaching or rinsing has been investigated to remove inorganic constituents [4,10,12–17]. This technique is facile and readily removes water-soluble inorganics such as K, Na, Ca, Cl, and Mg. For example, Turn et al. [18] utilized a mechanical press and a tap water rinse to afford a 45% reduction in the ash content of banagrass. In addition, Carrillo et al. [14] demonstrated a 20% reduction in ash content of sorghum by soaking the material in tap water. Finally, Liu et al. [19] reported that using distilled water is effective for removing up to 40% of the inorganic constituents of switchgrass. However, washing with pure (or municipal) water does not remove water insoluble inorganics, and its efficacy greatly depends on a number of factors, including leaching time, water-to-biomass ratio, water temperature, and biomass particle size.

A variety of acid washes have been studied to elucidate their ability to decrease feedstock ash content. The addition of strong acids such as nitric, sulfuric, and hydrochloric acid, as well as weak acids such as hydrofluoric, phosphoric, oxalic, nitric, and acetic acid to wash greatly decreases biomass ash content [17,19–26]. However, these treatments generate a waste stream that must be neutralized. In addition, many of these acids contain the very elements that comprise detrimental biomass ash, including N, S, P, and Cl. Finally, the use of acid as a pretreatment can lead to the hydrolysis of cellulose and hemicellulose, which will lead to a decrease in the carbon content of the biomass feedstock [27].

Although much focus has centered on removal of inorganic constituents from biomass feedstocks, very little of it pertains to the use of chelating agents for ion removal. This is perhaps surprising, given the prevalence of chelating agents in myriad industrial processes that require the removal of metal ions [28]. Chelating agents interact strongly with metal ions and alter their solubility (and therefore, concentrations) in solution. In contrast to many strong and weak acids, there are a number of industrially relevant chelating agents that are biodegradable such as nitrilotriacetic acid (NTA) [29]. In addition, common chelating agents typically have a buffering effect, and therefore pH-dependent hydrolysis of cellulose and hemicellulose would be negligible. In fact, Reza et al. [26] recently described a mild hydrothermal preprocessing technology that reduces the ash content of dry corn stover by 77% using sodium citrate, a common industrial chelating agent. This process was shown to have no effect on the holocellulose fraction, although an increase in Na ion concentration was noted due to the presence of this ion in the chelating agent (up to 3 mol Na per mole of citrate ion). Chelating agents show promise as a means to reduce the metal ion concentration of biomass feedstocks.

Ethylenediaminetetraacetic acid (EDTA) was selected for this study due to its prolific industrial, agricultural, and domestic usages including soil remediation, phytoremediation, addition to agricultural fertilizers, and its addition to detergents and cosmetics [28,30]. EDTA is a hexadentate chelating agent that contains two Lewis-basic amino and four Brønsted-basic carboxylate moieties. EDTA has shown a wide affinity for chelating many metal ions, and is particularly effective in forming stable water soluble complexes with divalent and trivalent cations [29,31]. Previous work has shown EDTA is effective for the removal of heavy metals from biomass. For example, EDTA was shown to remove significant amounts of Cr, Cu, and As from chromated copper arsenate (CCA)

treated wood [32], and was employed to remove Pb from *Salvinia minima* used in phytoremediation [33]. By maintaining slightly basic to near neutral pH conditions, EDTA eliminates the risk of acid catalyzed hydrolysis of biomass carbohydrates. In addition, alkaline conditions can increase the reactivity of lignin in relatively low temperature conditions [34]; thus, slightly basic conditions may enhance the removal of lignin-bound inorganics [26]. To our knowledge this is the first description of using EDTA for the extraction of inorganics from lignocellulosic biomass for enhancing feedstock properties for thermochemical conversion.

Accordingly, we report on the temperature- and time-dependent demineralization capacity of two industrially relevant chelating agents: EDTA and citric acid (the conjugate acid of sodium citrate) for the removal of inorganic ash components from dried and milled *Panicum virgatum* (switchgrass) grown in Eastern Tennessee, USA. We use microwave-assisted rapid heating in an effort to shorten the extraction times and maximize inorganics removal. We also compare these results to the extraction ability of sulfuric acid, acetic acid, and deionized water using the same conditions. In addition to measuring the inorganic composition of raw and extracted switchgrass, we also use dry mass loss, CHN analysis, and hydrolyzed sugars to determine the effect of each treatment on the carbon content of the same. These results indicate the comparable effectiveness in using chelating agents to reduce the inorganic content while simultaneously retaining the original carbon content of an important renewable carbon feedstock.

2. Materials and methods

2.1. Biomass and other reagents

The switchgrass (*Panicum virgatum* L.) cv. Alamo which was used in this study was field-grown near Vonore, TN and harvested in 2012. The switchgrass was processed at Genera Energy Inc. (Vonore, TN) where it was comminuted by using a tub grinder and then delivered to the University of Tennessee where it was stored under climate controlled conditions prior to experiments. The material was further processed using a Wiley mill (Thomas Scientific, Swedesboro, NJ) to a particle size of 0.425 mm. All other reagents used in this study were commercially available and used as received.

2.2. Ash, inorganics, and CHN analysis

Total ash content was determined in triplicate by complete combustion at 575 °C using a Fisher Scientific Isotemp Programmable Muffle Furnace 750 according to protocols developed by the U.S. Department of Energy's National Renewable Energy Laboratory (NREL) [35]. Inorganic composition was determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES). Ground material (0.5 g) was digested using a Multiwave 3000 microwave digester from Anton Paar (Richmond, VA) with HNO₃ (4 cm³; trace metal grade, 67–70%), H₂O₂ (3.0 cm³; 35%), and HF (0.2 cm³, 48%; 4%) was added to the solutions to complex any remaining HF and to facilitate dissolution of the precipitated fluorides. The reaction solution was then diluted to 50 cm³ with DI water and filtered using PTFE 0.45 μm syringe filters before analysis by the Optima 7300 Dual View ICP-OES (Perkin Elmer, Shelton, CT). Plasma was produced using 15 L/min argon gas and a radio frequency (RF) power of 1500 W, and instrument calibration was achieved using commercially available National Institute of Standards and Technology (NIST) certified calibration standards (SPEX CertiPrep) to build a calibration curve prior to analysis. In addition, carbon, hydrogen and nitrogen content were determined in triplicate using a CHN

Download English Version:

<https://daneshyari.com/en/article/4996398>

Download Persian Version:

<https://daneshyari.com/article/4996398>

[Daneshyari.com](https://daneshyari.com)