



Full Length Article

Performance assessment of dilute-acid leaching to improve corn stover quality for thermochemical conversion

John E. Aston^{a,*}, David N. Thompson^a, Tyler L. Westover^b^a Biological and Chemical Processing Department, Idaho National Laboratory, USA^b Idaho National Laboratory, Biofuels and Renewable Energy Technology Department, USA

ARTICLE INFO

Article history:

Received 25 March 2016

Received in revised form 9 August 2016

Accepted 12 August 2016

Available online 30 August 2016

Keywords:

Corn stover

Pyrolysis

Hydrothermal liquefaction

Combustion

Leaching

Ash

ABSTRACT

Lignocellulosic biomass is a sustainable energy source that can help meet the demand for biofuels in the United States. However, the quality and availability of such feedstocks greatly affect their suitability for downstream conversion. This work reports the effects of dilute-acid leaching at various aqueous loadings, temperatures and catalyst loadings (sulfuric acid) on the quality of a traditional biochemical feedstock, corn stover, as a potential feedstock for thermochemical conversions.

At 95 wt% aqueous, dilute-acid leaching was observed to effectively remove 97.3% of the alkali metals and alkaline earth metals that can negatively affect degradation pathways during pyrolysis and result in greater yield of non-condensable gases. In addition, up to 98.4% of the chlorine and 88.8% of the phosphorus, which can cause equipment corrosion and foul upgrading catalysts, respectively, were removed. At 25 °C in the absence of the acid catalyst, only 6.8% of the alkali metals and alkaline earth metals were removed; however, 88.0% of chloride was still removed.

The ratio of alkaline/acidic ash species has been suggested to proportionately relate to slagging in combustion applications. The initial alkali/acid ratio of the ash species present in the untreated corn stover was 0.38 (significant slagging risk). At 95 wt% aqueous, this ratio was decreased to 0.18 (moderate slagging risk). At 0 wt% catalyst and 90 °C, the ratio was decreased to 0.07, 0.08 and 0.06 at 0.5 wt% catalyst at 25 °C, 50 °C and 90 °C, respectively (low slagging risk). Increasing the catalyst loading to 1.0% slightly decreased the measured alkali/acid ratio of remaining ash.

The results presented here show that a water wash or a dilute-acid preprocessing step can improve corn stover quality for pyrolysis, hydrothermal liquefaction and combustion.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

More than one billion dry tons of lignocellulosic feedstocks are expected to be sustainably available in the United States by 2030, an amount that would potentially provide enough chemical energy to replace up to 30% of the United States' current petroleum consumption [1]. However, bioenergy is not yet a mature industry, and as such, an understanding of feedstock quality and its impacts on conversion are not widely understood [2,3].

Three major conversion pathways for lignocellulosic feedstocks are biochemical (alcohol or organic acid fermentation), thermochemical (bio-oil formation through pyrolysis or hydrothermal liquefaction (HTL) or syn gas production through gasification) and combustion. Currently, feedstock quality specifications for

these pathways are largely limited to total ash, organic content and sugar content. These attributes may be used to predict a potential yield, but do not account for inhibitors that affect reactivity, product degradation and/or corrode and foul conversion equipment.

Factors such as these have driven the selection of feedstocks for given conversion pathways. For example, the yield from biochemical conversion of lignocellulosic feedstocks to ethanol is more a function of cellulose and hemicellulose content and less so of ash content; because of this, high-ash herbaceous feedstocks such as corn stover are commonly used [4–6]. Conversely, woody biomass is often used for thermochemical conversions such as pyrolysis and HTL because the low ash content results in high yields with less catalytic poisoning, slagging and equipment fouling [2,7–9]. These considerations notwithstanding, to strengthen and secure the availability of feedstocks for the biofuels industry in the United States and globally, biorefineries must eventually consider adapting for more flexible feedstock availability and quality.

* Corresponding author at: Idaho National Laboratory, P.O. Box 1625, Idaho Falls, ID 83415, USA.

E-mail address: John.Aston@inl.gov (J.E. Aston).

One of the most prominent and widely available lignocellulosic feedstocks is corn stover. However, the relatively high amount of inorganic contaminants found in corn stover, and other agricultural residues, adds expense to the logistics, processing and conversion [10]. Further, many of the ash species that adversely affect thermochemical conversions are physiological, and therefore would require a chemical preprocessing step to be removed.

Existing chemical preprocessing methods that target the removal of physiological ash components are low-severity water and dilute-acid leaching. Water washing at temperatures from ambient to near boiling can remove exogenous ash components such as sodium, alumina, iron and silica introduced via soil entrainment [2]. However, significant removal of physiological ash components, including the bulk of the alkaline earth and alkali metals that are inhibitory to pyrolysis conversions, via their catalysis of secondary cracking of vapors and reduce bio-oil yield and quality, may require dilute-acid leaching [11–15]. Other chemical treatments may also be applied such as simple hot water washing, which may affect deacetylation and lower the pH of the wash media.

The research presented here tested the efficacy of water washing and dilute-acid leaching as a potential preprocessing method to improve the feedstock quality attributes of multi-pass corn stover for thermochemical conversion. Equilibrium water washing and two concentrations of an acid catalyst (sulfuric acid) were tested at three different aqueous loadings and temperatures. The effects on soluble convertible material, ash, ash composition and nitrogen content are reported here and discussed with respect to their relevance to pyrolysis, HTL and combustion.

2. Materials and methods

2.1. Sample collection

Approximately 400 kg of multi-pass corn stover harvested in Boone County, Iowa (2012) was procured and stored at approximately 8 wt% moisture in a dry and covered condition until use. The stover was ground to pass a 1-in. (25.4 mm) screen using a Vermeer BG480 Hammer Mill (Pella, Iowa). After being milled, the stover was mixed in an overflow bin and stored in four super sacks. An eight-way star splitter was used to individually split the four super sacks of ground stover. After the first splitting, the splits from the four super sacks were recombined and mixed. The splitting and mixing process was repeated two additional times. The mixed stover was then divided into smaller aliquots of approximately 6.1 kg. These aliquots were then mixed and split to create samples with masses of approximately 0.35, 0.87 and 1.75 kg to provide 98 wt%, 95 wt% and 90 wt% aqueous loading (i.e., 2 wt%, 5 wt% and 10 wt% solids) for the water and dilute-acid leaching experiments. The aqueous loading by wt% represents the wt% of the final leaching media that is comprised of water and the sulfuric acid catalyst.

Table 1
Experimental matrix showing the conditions tested.

Catalyst [H ₂ SO ₄]			
Variables	Minimum	Mid-point	Maximum
Catalyst loading (wt%)	0.0	0.5	1.0
Temperature (°C)	25	50	90
Aqueous loading (wt%)	90	95	98

2.2. Leaching protocol

An acid catalyst, sulfuric acid, was used to improve the removal of alkali metals and alkaline earth metals. Table 1 shows the test matrix used to determine the effects of catalyst concentration, temperature and aqueous loading on the removal of organics during leaching.

Experiments were completed with a single replicate at each set of conditions, and an additional 9 experiments were completed to estimate experimental error. These included minimal leaching conditions (i.e., 0 wt% catalyst, 25 °C and 90 wt% aqueous), moderate leaching conditions (0.5 wt% catalyst, 50 °C and 95 wt% aqueous loading) and severe leaching conditions (1.0 wt% catalyst, 90 °C and 98 wt% aqueous), each in triplicate. These experimental sets were carried out for twenty-four hours to achieve equilibrium conditions, which were verified by allowing separate experiments to continue for up to 72 h. Even at the most mild conditions tested, 25 °C, 90% aqueous and 0 wt% catalyst, the longer experiments did not result in total ash, potassium, sodium, magnesium, calcium, silica, iron or alumina measurements that were statistically different than the shorter tests, as evaluated by the calculation of 95% confidence intervals (data not shown). Additionally, from the initial untreated sample pool, six randomly selected samples were characterized to measure base-line ash composition for comparison against leached material.

Leaching media were prepared by adding acid catalyst (H₂SO₄, Sigma Aldrich) and deionized (DI) water to the required volumes, dependent upon the desired aqueous loading, in a 30-l aluminum pot. The leaching solution was then heated on hot plates to temperature for each experiment. The temperature was measured using calibrated thermocouples. While the solution heated, a randomly-selected split sample of untreated corn stover was placed inside a concentric cylindrical aluminum wire cage inside another 30-l aluminum pot. Mixing was achieved using a 3.5" magnetic stir bar rotating within the open center of the concentric cage. When the leaching medium had reached the desired temperature, the solution was added to the pot/cage assembly and placed on a hot plate to maintain temperature.

After 24-h, the cage assembly was removed and placed into a stainless-steel pot containing 12 L of DI water, agitated, and washed for 45 min. This step was repeated once more. In each instance of corn stover being transferred from a leachate or wash solution, the solution was filtered subsequently through American Standard Test Sieves with 420 μm and 75 μm mesh, (Humboldt, Elgin, Illinois), and the collected corn stover particulates were returned to the bulk sample. Materials used in the handling of the sample were washed thoroughly between samples. The wash solution was then filtered using the same method and collected material was returned to the bulk solids.

2.3. Preparation of leached material for analytic applications

The leached and washed corn stover was dried in an oven at 105 °C for 48–72 h to reduce the moisture to below 2 wt%. The dried samples were ground to pass a 2-mm screen using a Thomas Wiley Laboratory Knife Mill (Model 4, 1 horse power; Thomas Scientific, New Jersey). The ground material was then divided into smaller representative samples for nitrogen and ash composition analysis. A Retsch ZM200 Ultra Centrifugal Mill (Haan, Germany) equipped with either a 0.2-mm screen or a 0.08-mm screen, respectively, was used to grind the samples for these analyses.

2.4. Total ash and nitrogen analysis

Samples ground to pass a 0.2-mm screen were analyzed for proximate (total ash) and ultimate (nitrogen content) by the

Download English Version:

<https://daneshyari.com/en/article/6476074>

Download Persian Version:

<https://daneshyari.com/article/6476074>

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