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Hydrothermal carbonization: Fate of inorganics

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ABSTRACT

Hydrothermal carbonization (HTC) is a pretreatment process for making a homogenized, carbon rich, and energy-dense solid fuel, called biochar, from lignocellulosic biomass. Corn stover, miscanthus, switch grass, and rice hulls were treated with hot compressed water at 200, 230, and 260 °C for 5 min. Mass yield is as low as 41% of the raw biomass, and decreases with increasing HTC temperature. Higher heating values (HHV) increase up to 55% with HTC pretreatment temperature. Up to 90% of calcium, magnesium, sulfur, phosphorus, and potassium were removed with HTC treatment possibly due to hemicellulose removal. At a HTC temperature of 260 °C, some structural Si was removed. All heavy metals were reduced by HTC treatment. The slagging and fouling indices are reduced with HTC treatment relative to that of untreated biomass. Chlorine content, a concern only for raw and HTC 200 switch grass, was reduced to a low slagging range at 230 °C, and 260 °C. Alkali index was medium for raw biomass but decreased by HTC.

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1. Introduction

The world is facing two vital challenges in current energy demand: energy supply and sustainability. Limited fossil fuel reserves and their environmental impact intensifies interest in the use of biomass, one of the largest energy resources. Biomass is an alternative, renewable, and sustainable energy source with a large potential to mitigate the energy crisis. About 450 million dry tons of wood, energy crops, and agricultural residues both primary and secondary are available currently in the US and the amount is expected to increase to more than 1000 Mt by 2030 [1]. Feedstock supply and logistics of lignocellulosic biomass, such as wood, rice hulls, straw, and switch grass, are challenging due to low bulk density, low energy density, and high ash content [2–4]. Hydrophilic biomass is subjected to biological deterioration, limiting the practical time for storage, a challenge for seasonally available agricultural residues. A pre-treatment process which can

overcome these limitations of biomass usage for energy is essential.

Hydrothermal carbonization (HTC) is a prominent pretreatment process for biomass enhancement [5–7]. In HTC, biomass is treated with hot compressed water resulting in three products: gases, aqueous chemicals, and a solid product known as HTC biochar. Reaction temperatures are in the range of 200–275 °C, and the pressures are maintained above the saturation pressure to ensure the liquid state of water. The gas product is about 10% of the original biomass, consisting mainly of CO₂, while the aqueous extractive compounds are primarily sugars, acetic acid, and other organic acids [9,30]. The solid product contains about 41–90% of the mass and 80–95% of the fuel value of the original feedstock [8–10]. HTC processes make a solid char with higher energy density that is easily friable and more hydrophobic than the original biomass [11]. The reaction mechanisms are still poorly understood [9,12].

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Plants acquire inorganics, which are necessary for their metabolic pathways, from the soil in which they are grown. Inorganics are in the form of inorganic salts, bound to the organic structure by ionic bonds, or possible covalent bonds in a cross-linked matrix [17]. Woody biomass contains less inorganic content than grasses or agricultural residues [13,14]. Due to their high melting point, the inorganics usually remain in the ash, which usually has a negative impact on biomass firing or even co-firing with coal [15]. During combustion, ash must be removed from the boiler, as it increases the complexity in co-firing as well as lowers the efficiency of boiler. Moreover, sodium, potassium, calcium, and other metals can cause slagging and fouling, resulting in lower power plant efficiency [16,17]. Alkali metals react with silica to form alkali silicates, which soften below 700 °C and thus cause undesirable slagging. They also react with sulfur to make alkali sulfate, which deposits on heat transfer surfaces, reducing the efficiency of the combustion process [18]. Chloride, which is very corrosive for stainless steel, can also react with alkalis and silicates to form an undesirable stable slag [14]. Heavy metals like mercury, lead, arsenic, chromium, copper, zinc, and selenium are scarce in biomass [12]. However, they are concentrated by about an order of magnitude in ash. For these reasons, elimination or at least reduction of inorganic components including heavy metals is important in promoting biomass combustion.

Based on different mechanisms involved in ash deposit on the heat transfer surface, two general types of ash deposition have been defined as slagging and fouling [18]. Slagging is the formation of molten or partially fused deposits on furnace walls or convection surfaces exposed to radiant heat. Fouling is defined as the formation of deposits on convection surfaces such as superheater and reheaters [17]. The viscosity of the coal ash slag determines the affects on its erosivity, and the diffusivity of ions within the slag which affects its corrosivity [35].

Slagging and fouling tendencies in coal combustion have been well studied for years. Different correlations have been suggested based on the ash composition of coal. Slagging index, fouling index, alkali index, ratio-slag viscosity index, and chlorine content are the common indices for coal [19]. The

ash compounds may be separated into two groups based on their melting point. The first group has lower melting temperatures and typically contains Fe_2O_3 , CaO , MgO , Na_2O , or K_2O . The other group of higher melting temperature compounds includes SiO_2 , Al_2O_3 , and TiO_2 . Phosphorus sometimes is added into the former group, since P_2O_5 has a relatively high melting point. The slagging index is the measure of scale produced from those two groups in presence of sulfur, while the fouling index is almost identical but includes the sodium and potassium oxides influence. The alkali index is the amount of sodium and potassium oxides present per GJ of solid fuel. The slag viscosity index is the percentage of silica present in the metal oxides. Several indices, along with ratings, are defined in Table 1.

The main goal of this work is to characterize HTC biochar of grassy biomass and agricultural residues. Inorganic analysis of HTC biochar is reported and describes quantitatively. Heavy and trace metal leaching has been examined. Probable slagging and fouling behavior of untreated and HTC treated biomass have been determined by calculation of several indices, using elemental analysis of ash.

2. Material and methods

2.1. Material

Four types of lignocellulosic biomass were evaluated by HTC in this study. Corn stover and miscanthus were provided by Idaho National Laboratory. Corn stover was harvested in Emmetsburg, Iowa during October, 2011. Miscanthus was harvested in Urbana, Illinois during September 2011. Rice hull was harvested in Gridley, California during September 2008, and switch grass was harvested in Fallon, Nevada in October 2007. Corn stover, miscanthus, and switch grass were comminuted to 18 mm by Bliss hammer mill model 4460 (Ponca City, OK). Harvested biomass were dried in a warehouse by free air circulation for a month and stored in plastic container in a dry storage until further use. To promote a more homogeneous biomass reactant and provide effective sub-

Table 1 – Slagging, fouling, alkali, and ratio-slag indices, Cl content, definition and their limits [14].

Slagging/fouling index	Expression	Limit
Slagging index	$I_s = (B/A) \cdot S^d$ $S^d = \% \text{ of S in dry fuel}$	$I_s < 0.6$ low slagging inclination $I_s = 0.6 - 2.0$ medium $I_s = 2.0 - 2.6$ high $I_s > 2.6$ extremely high
Fouling index	$I_f = (B/A) \cdot (\text{Na}_2\text{O} + \text{K}_2\text{O})$	$I_f \leq 0.6$ low fouling inclination $0.6 < I_f < 40$ medium $I_f \geq 40$ high
Alkali index	$I_A = (\text{Na}_2\text{O} + \text{K}_2\text{O})$ in kg/GJ	$0.17 < I_A < 0.34$ slagging/fouling probable $I_A \geq 0.34$ slagging/fouling is certain
Slag viscosity index	$I_v = (\text{SiO}_2 \cdot 100) / (\text{SiO}_2 + \text{MgO} + \text{CaO} + \text{Fe}_2\text{O}_3)$	$I_v > 72$ low slagging inclination $65 \leq I_v \leq 72$ moderate $I_v < 65$ high
Chlorine content	Cl as received (%)	$\text{Cl} < 0.2 - 0.3$ low slagging inclination $0.2 < \text{Cl} < 0.3$ medium $0.3 < \text{Cl} < 0.5$ high $\text{Cl} > 0.5$ extremely high

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