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#### Review

## Minireview of potential applications of hydrochar derived from hydrothermal carbonization of biomass

June Fang<sup>a</sup>, Lu Zhan<sup>a,b</sup>, Yong Sik Ok<sup>c</sup>, Bin Gao<sup>a,\*</sup>

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#### ABSTRACT

This review provides a brief overview of the potential applications of hydrochar and its derivatives. It first summarized the key processes of hydrothermal carbonization (HTC) of biomass and basic properties of the resulting hydrochar. Most of the efforts of this review is then on reviewing the potential applications of hydrochar in various fields including environment, energy, adsorbent and medical applications. It also discusses different modification and activation methods to produce hydrochar-based engineered carbon materials for enhanced performances in those applications, particularly with respect to their application as low-cost adsorbents for the removal of heavy metals, organics, phosphate and pathogens.

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E-mail address: bg55@ufl.edu (B. Gao).

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<sup>&</sup>lt;sup>a</sup> Department of Agricultural and Biological Engineering, University of Florida, Gainesville, FL 32611, USA

b Shanghai Key Lab for Urban Ecological Processes and Eco-Restoration, School of Ecological and Environmental Sciences, East China Normal University, Shanghai 200241, China

<sup>&</sup>lt;sup>c</sup> Korea Biochar Research Center & School of Natural Resources and Environmental Science, Kangwon National University, Chuncheon 24341, Republic of Korea

Corresponding author.

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#### Introduction

Many studies have suggested that biomass can be thermally processed into biochar, a solid by-product that has been used for a variety of applications such as contaminant remediation, fuel, and amending soil for carbon sequestration purposes as well as to improve fertility and water retention [1–5]. Biochar is typically produced through pyrolysis, where dried biomass is heated in the absence of oxygen at relatively low temperatures [6–8].

In recent years, hydrothermal carbonization (HTC) has been considered as an alternative method of processing biomass for value-added products [9-12]. The solid product created during HTC is called hydrochar in order to distinguish it from biochar [13-15]. During HTC, biomass is heated in an oxygen free environment in the presence of subcritical water and autogenous pressure in the range of 2-10 MPa [16,17]. The HTC is known to have several advantages such as lower energy consumption and less emission over pyrolysis. Feedstocks with a high moisture content yield low amounts of solid material after drying, which makes them insufficient sources for pyrolysis [17]. Therefore, a greater variety of feedstocks could be considered for processing into hydrochar since drying the feedstock is not necessary for HTC [15]. Another advantage is that HTC yields higher amounts of char and uses lower amounts of energy than pyrolysis. This is partially due to the fact that the feedstock does not need to be dried, as well as lower operating temperatures for HTC compared to pyrolysis [13,18]. The HTC and pyrolysis generally use temperatures between 200–300 °C and 300–600 °C, respectively [19]. The lower operating temperature of HTC is due to the activation temperatures of the chemical reactions that occur when the biomass is heated in the presence of liquid. When biomass is heated during HTC or pyrolysis, the physical structure is altered through reaction mechanisms such as hydrolysis, dehydration, decarboxylation, aromatization and re-condensation [20]. While these reactions occur during both pyrolysis and HTC, hydrolysis is the predominant reaction during HTC, which has a lower activation energy than the other decomposition reactions [13].

Despite the fact that hydrochar can be used for the same purposes as biochar [21], it is still necessary to test their effectiveness in these applications and compare it to biochar. This is because the physicochemical properties of the hydrochars could be dramatically different from that of the biochars [13,15,18]. This review compiles studies that have so far been conducted on the production and application of hydrochar and identifies knowledge gaps and future considerations in hydrochar research. An overview of the properties of hydrochar that distinguish it from biochar is

also provided to give some insight on how hydrochar may be advantageous or disadvantageous for different applications.

#### **Hydrothermal carbonization**

Overview of chemical reactions during HTC

During the hydrothermal carbonization (HTC), biomass undergoes structural rearrangement by degrading into solid, liquid and gaseous products [22,23]. The solid product (hydrochar) has a chemical composition and physical appearance that are different from the feedstock (Fig. 1). The difference in chemical composition is explained by the reaction mechanisms that occur during HTC, which include hydrolysis, dehydration, decarboxylation, aromatization and re-condensation [11,20,24]. Although these processes generally occur in this order, they do not operate in a successive manner; instead, they occur simultaneously during HTC and are interconnected with each other [20].

Out of all of these processes, hydrolysis has the lowest activation energy being the first step to be initiated during HTC [24,25]. Hydrolysis breaks down the biomass chemical structure through cleavage of ester and ether bonds of bio-macromolecules with water molecules. This process creates (oligo-)saccharides and fragments of lignin that enter the liquid phase [13,24]. The lignin fragments are then hydrolyzed into phenols, but the saccharides can continue to initiate other chemical pathways and products during HTC. The products created through these other mechanisms can also undergo hydrolysis [18,24,26].

Dehydration is the process where water is removed from the biomass matrix, causing hydroxyl groups to be eliminated. Decarboxylation is the removal of CO<sub>2</sub> from the biomass, eliminating carboxyl groups in the process [14,27]. Aromatization occurs because of dehydration and decarboxylation. Double bonded functional groups such as C=O and C=C replace the single bonded hydroxyl and carboxyl groups in the biomass matrix [9,28]. The furfural compounds generated by these two mechanisms then undergo hydrolysis, which further breaks them down into acids, aldehydes, and phenols. The acids that are generated then catalyze the release of inorganic elements from the biomass matrix [29,30].

The compounds created during the previously described mechanisms can undergo re-condensation if they are highly reactive. Lignin fragments are highly reactive and condense easily, as well as aromatized polymers from cellulose degradation [31,32]. The re-condensation of HTC degradation products leads to the formation of hydrochar [13]. Degradation products from



Fig. 1. hydrochar produced from wood sample (Euc Amplifolie).

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