Renewable and Sustainable Energy Reviews 90 (2018) 223–247

Contents lists available at ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser

A review of the hydrothermal carbonization of biomass waste for hydrochar formation: Process conditions, fundamentals, and physicochemical properties

Tengfei Wang[a,b], Yunbo Zhai[a,b,*], Yun Zhu[c], Caiting Li[a,b], Guangming Zeng[a,b]

[a] College of Environmental Science and Engineering, Hunan University, Changsha 410082, PR China
[b] Key Laboratory of Environmental Biology and Pollution Control (Hunan University), Ministry of Education, Changsha 410082, PR China
[c] Office of Scientific R&D, Hunan University, Changsha 410082, PR China

ARTICLE INFO

Keywords:
Biomass
Hydrothermal carbonization
Hydrochar
Characterization
Mechanism

ABSTRACT

Hydrothermal carbonization (HTC) is a thermochemical conversion technique which is attractive due to its ability to transform wet biomass into energy and chemicals without predrying. The solid product, known as hydrochar, has received attention because of its ability to prepare precursors of activated carbon in wastewater pollution remediation, soil remediation applications, solid fuels, and other carbonaceous materials. Besides the generally lignocellulose biomass used as sustainable feedstock, HTC has been applied to a wide range of derived waste, including sewage sludge, algae, and municipal solid waste to solve practical problems and generate desirable carbonaceous products. This review presented the critical hydrothermal parameters of HTC, including temperature, residence time, heating rate, reactant concentration, and aqueous quality. The chemical reaction mechanisms involved in the formation of hydrochar derived from single components and representative feedstock, lignocellulose, and sludge termed as N-free and N-rich biomass, were elucidated and summarized to better understand the hydrochar formation process. Specifically, hydrochar physicochemical characteristics such as surface chemistry and structure were investigated. Current knowledge gaps, and new perspectives with corresponding recommendations were provided to further exploit the great potential of the HTC technique and more practical applications for hydrochar in the future.

1. Introduction

Biomass represents the biological materials from plants or animals and their derived waste and residues [1]. The utilization of waste biomass as a sustainable resource has been recognized by society mainly due to potential reductions in greenhouse gas emissions (GHGs) [2,3]. It is possible that near zero GHG emissions can be achieved by balancing plant biomass production and utilization in the future [4]. Needless to say, it is critical to search for technologies that are sustainable, non-polluting, and effective. In addressing these concerns, diverse methods of biomass utilization for energy recovery have been found to be economically viable and environmentally friendly. Biomass such as lignocellulose, sewage sludge (SS), and municipal solid waste (MSW) are considered to be an abundant and renewable resource which can be converted into solid, liquid, and gaseous form using biochemical, physicochemical, and thermochemical technologies [1,5,6]. However, there are disadvantages to biomass as a sustainable resource that urgently need to be overcome; for example, its high moisture, low energy content, heterogeneity, low density, and presence of contaminants. In previous studies, common biomass utilization approaches have included pyrolysis, biological conversion, densification to a solid fuel, and hydrothermal processes [7–10]. Pyrolysis is faced with the main obstacle that the high moisture content of biomass requires high heat for vaporization [9]. Moreover, biological conversion processes such as fermentation and anaerobic digestion, despite consuming low energy, require longer timeframes as compared to thermal processes [11]. Subsequently, much attention has centered on hydrothermal conversion processes which have been shown to be more cost-effective as compared to conventional thermal drying [12]. Hydrothermal processes for biomass utilization have both advantages and disadvantages, and these are summarized in Table 1. Of the hydrothermal processes, hydrothermal carbonization (HTC), discovered in 1913 by Bergius [13] was found to mimic the natural process of coal formation that converted cellulose into coal like materials. This artificial coalification process was later re-discovered and has been variously referred to as hot compressed water treatment, subcritical water treatment, wet

* Corresponding author at: College of Environmental Science and Engineering, Hunan University, Changsha 410082, PR China.
E-mail address: ybzhai@hnu.edu.cn (Y. Zhai).

https://doi.org/10.1016/j.rser.2018.03.071
Received 25 December 2016; Received in revised form 13 February 2018; Accepted 22 March 2018

Table 1
Brief approaches of biomass utilization techniques and advantages or disadvantages.

Approaches of biomass utilization	Advantages	Disadvantages	Approach and objective
Pyrolysis	High efficiency and flexibility	Not suitable for high moisture biomass waste	Slow or fast pyrolysis producing biochar, bio-oil and gases like CO, CO_2, CH_4 and H_2
Hydrothermal process	It can be directly applied to biomass with high moisture	Difficult to collect the products and high requirements for equipment	Carbonization, liquefaction and gasification producing hydrochar, bio-oil and gas
Biological conversion	Lower process energy requirements	Period is long	Fermentation or anaerobic digestion producing bio-ethanol and bio-gas
Densified as solid fuel	Lower transportation costs	Energy content is low	Pelletization for fuel pellet or briquette production

torrefaction, and hydrothermal treatment. In recent years, the unwanted solid residue during hydrothermal gasification and liquidation, has received increasing attention [14].

During the HTC process, raw biomass is converted into a lignite-like solid product that is significantly affected by the medium [15]. Because wet biomass requires no predrying prior to HTC, it has been successfully introduced and practically applied. Moreover, water is an inexpensive, environmentally benign, and nontoxic media [16]. Generally, the HTC process occurs at relatively low temperatures (180 − 250 °C) and under autogenous pressure that lowers both the oxygen and hydrogen content of the feedstock through dehydration and decarboxylation [17]. This process is governed by hydrothermal parameters such as residence time and temperature, which determine the reaction severity and degree of coalification of the raw biomass [18,19]. The solid residue derived from the HTC process, defined as hydrochar in this review, exhibits high hydrophobic and friable properties, and hence, is easily separated from the liquid product. The hydrochar demonstrates superior performance relative to the raw biomass in terms of higher mass and energy density, better dewaterability, and improved combustion performance as a solid fuel [9]. Based on the different kinds of biomass used, hydrochar has been widely used for carbon sequestration, soil amelioration, bioenergy production, and wastewater pollution remediation [20]. Unlike the solid products, liquid products require fractionation by extraction when used for bio-oil production. Moreover, research has indicated that the liquid products from hydrothermal treatment are biodegradable on account of their high organic substance [21–23]. Hydrochar has been demonstrated as a high value, carbon-rich material after undergoing hydrothermal treatment to reduce its hydrogen and oxygen content [17]. Importantly, the utilization of these carbon-rich materials is in many aspects a sustainable way to mitigate anthropogenic CO_2 [24]. The sustainability benefits of hydrochar production and its potential applications are summarized in Fig. 1. Firstly, green plants remove CO_2 by photosynthesis; through the HTC process, this CO_2 is bonded to the final carbonaceous structure of the hydrochar, representing an effective approach to diminish CO_2 from the carbon cycle. Furthermore, the bio-oil and hydrochar produced during the HTC process can be employed as biofuel, reducing dependency on fossil fuels and further offsetting CO_2 emissions. Meanwhile, large amounts of human derivative waste biomass including SS, feces, MSW, and lignocellulose can be converted into hydrochar. In terms of carbon migration, the production of hydrochar from human waste can be regarded as strengthening the immobilization of CO_2 from a recalcitrant form of carbon carrier.

In recent years, the potential benefits and applications of hydrochar have received significant attention, both in terms of producing functionalized carbon materials and the various potential applications of hydrochar in the field of energy storage and environmental protection. Since 2009, there has been rapid growth in the number of publications related to the production and application of hydrochar. For example, Libra et al. [25] and Reza et al. [26] summarized the technical and climate change aspects of hydrochar production and discussed the application of hydrochar in soil remediation. Kambo et al. [9] and Zhao et al. [27], respectively, reviewed the characteristics of hydrochar production and highlighted the benefits of waste biomass derived hydrochar as a clean solid fuel from HTC. Current commercial and large-scale applications of the HTC process were reviewed by Okajima et al. [28]. Jain et al. [29] reviewed hydrochar formation mechanisms and identified a high density of oxygenated functional group products in the process. To date, few reviews have focused on detailing hydrochar formation mechanisms, especially in terms of available single components. In particular, there is a need to critically and comprehensively understand the complex conversion of waste biomass during the HTC process, and to explore the research advances, challenges, and future opportunities of thoroughly utilizing the superiority of hydrochar. In this review, we discuss the critical hydrothermal parameters in the HTC process; mechanisms of hydrochar formation in response to single components and typical biomass including lignocellulose and SS (N-free and N-rich biomass, respectively); and the physical, chemical, and structural characteristics of hydrochar. Additionally, we provide some perspective on future research opportunities and applications of hydrochar.

2. Production of hydrochar

2.1. HTC process

The HTC process occurs in the subcritical region as shown in Fig. 2. It is widely known that the characteristics of water change dramatically under subcritical conditions. Temperature increases below 374 °C decrease the dielectric constant, weakening water's hydrogen bonds and producing high ionization constants, which enhance the dissociation of water into acidic hydronium ions (H_3O^+) and basic hydroxide ions (OH^-) [30–32]. Furthermore, the subcritical water itself can boast a sufficiently higher H^+ concentration as compared to liquid water, which is an excellent medium for the acid-catalyzed reaction of organic compounds without added acid [30,33]. Under different temperatures, water properties change dramatically and the field of application for hydrothermal processes are shown in During HTC, the water contained in the biomass or supplied to the process is an excellent solvent and reaction medium [25]. Conditions are mildly controlled at relatively low temperatures (180–250 °C) under autogenous pressure maintained for a specified residence time [17,25]. In recent studies, various feedstocks were selected for HTC, ranging from model substances to actual feedstock including cellulose [36,37], glucose [37], agricultural residue [38], animal manures [39], food waste [40,41], MSW [42], SS [43,44], and aquaculture and algal residues [45]. It is apparent that the HTC process is not restricted to traditional lignocellulosic biomass; feedstocks can be more complex, and these renewable feedstocks represent large quantities of organic matter that require proper treatment to limit pollution of the environment. The products of HTC mainly consist of three components: solid, aqueous solution (bio-oil mixed with water), and a small volume of gas (mainly CO_2). The distribution and properties of these products is heavily influenced by the feedstock and process conditions [46,47]. Solid residue is regarded as the main product of HTC; it can be easily separated from the suspension due to its high hydrophobicity and homogeneous properties [48]. Furthermore,