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Review

Hydrothermal conversion of biomass waste to activated carbon with high porosity: A review

Akshay Jain [a], Rajasekhar Balasubramanian [b], M.P. Srinivasan [c,*]

[a] Department of Chemical and Biomolecular Engineering, National University of Singapore, 117585, Singapore
[b] Department of Civil and Environmental Engineering, National University of Singapore, 117585, Singapore
[c] School of Civil, Environmental and Chemical Engineering, RMIT University, GPO Box 2476, Melbourne, Victoria 3001, Australia

HIGHLIGHTS

- Enhanced resource and energy recovery from biomass waste by hydrothermal treatment.
- Elucidation of the mechanism of hydrochar formation.
- New insights in hydrothermal treatment for enhancing porosity of activated carbon.
- Effect of processing conditions on hydrochar and activated carbon characteristics.

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ABSTRACT

With the awareness of the need for optimal and sustainable use of natural resources, hydrothermal treatment of biomass and biomass waste for energy and resource recovery has received increasing attention. In this context, hydrochars produced by hydrothermal treatment of biomass, which have been traditionally employed as catalyst supports or adsorbents, are now of considerable interest as precursors for activated carbons. Activated carbon produced from hydrochars has been widely used in applications such as energy storage, environmental remediation and resource recovery. Apart from savings in energy and resource conservation, hydrochars are of interest in activated carbon production because they possess unique attributes such as high density of oxygenated functional groups (OFGs) and low degree of condensation which can be tailored to produce activated carbons with specific and desired characteristics. This review aims to integrate the current knowledge on hydrothermal carbonization of biomass waste in the context of resource and energy recovery. Specifically, we bring together recent advances made in this area through a systematic and critical review of the production of activated carbon from hydrochars. Mechanisms involved in the production of hydrochars with different surface characteristics in response to variations in the operating parameters are critically reviewed. The current knowledge gaps and challenges involved in the hydrothermal carbonization of biomass waste are critically evaluated with suggestions for further research.

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* Corresponding author.

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1. Introduction

Biomass being recyclable and abundantly present across the planet has been allotted numerous roles to play for sustainable development. In addition to being a food source and renewable raw material, it can be used for energy production, carbon sequestration and, as an essential element for the production of hydrochars and activated carbons. In the past few years, the use of hydrothermal carbonization for conversion of biomass waste into valuable carbon materials has received considerable attention due to its ability to produce hydrochars with attractive characteristics that promote efficient utilization for a variety of applications such as adsorption [1,2], bio imaging [3,4], catalysis [5–7], activated carbon synthesis [8–10], etc. Utilization of biomass waste for producing hydrochars is attractive because it offers solutions for solid waste management, reduces the cost of raw materials and the properties of the final product can be tailored for different applications.

Basically, hydrothermal carbonization is a thermo-chemical conversion technique which uses subcritical water for the conversion of wet/dry biomass to carbonaceous products through fractionation of the feedstock. Carbonization temperature is dependent on the type of starting materials and its decomposition temperature; a range of 150–350 °C is typically employed [2,10–15]. Hydrothermal carbonization results in efficient hydrolysis and dehydration of biomass and bestows the hydrochar with high OFG (oxygenated functional group) content which makes it an effective precursor for the production of chemically activated carbon [8,16].

Activation of suitable precursors such as lignocellulosic biomass results in formation of highly porous activated carbons whose large surface areas facilitate their performance as adsorbents [17–26]. High porosity is extremely desirable for enhanced performance of adsorbents since it facilitates high mass transfer fluxes and catalyst/adsorbate loading. The tailored porosity and pore size distribution have widened the usefulness of activated carbons to more demanding applications, such as catalysis/electrocatalysis [27–29], separation of multi- sized molecules, energy storage in capacitors [30–34], electrodes and Li-ion batteries [35,36], CO_2 capture or H_2 storage [8,37,38]. Briefly, activation can be done in two ways (i) physical (or thermal) activation using CO_2 or steam at 800–900 °C; and (ii) chemical activation using KOH, $ZnCl_2$, H_3PO_4, etc. typically in the range of 450–650 °C.

Extensive work is being done to enhance the porosity of activated carbons by the use of different chemical activating agents, optimization of the activation conditions such as temperature, ramp rate and gas flow rate [39–42] and the usage of pre-treatment methods such as soaking or stirring [43,44]. In addition, chemical characteristics of the lignocellulosic biomass are of significance and play a substantial role in creation of porosity in activated carbons. Therefore, it is of great importance to understand the role of these characteristics in development of porosity in carbons and thus optimize the process conditions by the use of appropriate pre-treatment processes.

A few studies have investigated the influence of precursor reactivity on the porosity of activated carbons obtained via hydroxide (NaOH and KOH) activation [8,9,40,45–47]. Reactivity of precursors or the OFG content in the precursor is an important indicator of the effectiveness of chemical activation and can thus predict the extent to which porosity will be developed in the activated carbons [8,9,47–49]. In view of these recent developments, hydrothermal carbonization has gained much importance for recovery of carbonaceous materials because of its potential in producing hydrochar with high OFG content and its further use for synthesis of activated carbon with desired properties [50–54].

Recently, Jain et al. reported the hydrothermal pre-treatment of coconut shells that lead to hydrochar with improved reactivity (high OFG content) and significant improvement in mesopore area by as much as 67% [49]. However, the formation of OFG largely depends on the processing conditions of hydrothermal carbonization. To this end, Falco et al. reported an increase in porosity in the corresponding carbons when the precursor was hydrothermally carbonized from 180 to 240 °C due to an increase in carbonyl functionalities up till 240 °C [47,55]. A further increase in temperature to 280 °C led to enhanced chemical stability and structural order in hydrochar which resulted in a decrease in porosity upon KOH activation [47,55]. Furthermore, Jain et al. reported the use of H_2O_2 for enhanced growth of OFG on the hydrochar to further improve the porosity of activated carbons [56]. The role of the structural order of the carbon precursor may play an important role in the final porosity of activated carbons [46,47,57,58].

Numerous studies on hydrothermal carbonization have been carried out to investigate the effects of various operating parameters on the quality and yield of products (solid char, liquid and gas) [11,12,16,52,53,59–65]. The objective of this review is to integrate the current knowledge available on the operating conditions of hydrothermal carbonization to have a deep understanding of their influence on the production of hydrochars from diverse feedstocks. Additionally, we provide an overview of *in situ* chemical treatment of biomass waste during hydrothermal carbonization that affects the characteristics of hydrochars. This integrated knowledge is required to facilitate identification of suitable experimental protocols for synthesis of activated carbons with enhanced and tailor-made properties (Scheme 1). The review also discusses the mechanisms involved in the production of hydrochars in response to variations in the operating parameters (temperature, residence time and substrate concentration) of hydrothermal carbonization. This mechanistic understanding will prove to be useful in tuning the hydrochar properties for the efficient large-scale synthesis of activated carbons. The current knowledge gaps and challenges involved in the hydrothermal carbonization of biomass waste are also discussed with suggestions for further research.