



Full Length Article

Insights into the evolution of chemical structures in lignocellulose and non-lignocellulose biowastes during hydrothermal carbonization (HTC)

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ABSTRACT

Insights into evolution pathways of chemical structures during HTC are essential in acquiring the mechanisms controlling the structure-reactivity of biowaste-derived hydrochars. In this study, two types of industrial biowastes were selected for HTC experiments, namely, a lignocellulose one (herbal tea waste, HTW) and a non-lignocellulose one (penicillin mycelial waste, PMW). In addition to their fundamental properties, chemical structures of hydrochars were concurrently identified with the help of XRD and Raman (for crystalline and aromatic structure), XPS and ¹³C NMR (for carbon skeleton structures), FTIR and 2D-PCIS (for surface functionalities) technologies. Results found that a more condensed and amorphous structures of biowaste-derived hydrochars was obtained, regardless of the differences in biowaste components. The original structures in biowastes were converted from low-energy states (–C–H/–O/–O) to high energy states (aromatic –C–C/–C=C) via hydrolysis, carbonization and polymerization; nevertheless, the evolution pathways of chemical structures were different from each other. Nucleation growing process was the key mechanism for HTW, while the conversion routes of PMW were more complex than HTW due to the self-rearrangement of amino acids, as well as synergistic reactions between amino acids and reduced sugars.

1. Introduction

To our knowledge, industrial biowastes are universally considered as byproducts/wastes derived from industrial activities, showing significant characteristics of enormous amount and various species with the development of industrialization process in the past decades all over the world, especially in developing countries [1,2]. In fact, the effective disposals of industrial biowastes have faced an increasingly serious issue nowadays due to the environmentally unfriendly substances therein. Most of industrial biowastes (sewage sludge, antibiotic residues, etc.) are contaminated with heavy metals, pathogens and a range of hazardous organic components, thereby posing threats to the soil, plants, animals and humans [1,3,4]. According to preliminary statistics of world health organization (WHO, data from 2016), 12.6 million people have died from living or working in an unsafe

environment caused by unregulated industrial activities, accounting for 23% of all deaths. When accounting for both death and disability, the fraction of the global burden of disease due to the environment is 22%. Consequently, traditional treatments such as landfill, incineration and fertilizer-production are no longer applicable for the sake of human health and environmental protection. However, industrial biowastes can be classified into a type of nontraditional biomass owing to its abundant organic matters introduced during industrial processes, which make the energy utilization become possible [3,5–8]. For these reasons, a feasible and economic technology is necessary for solving the pollution and toxic problems associated with industrial biowastes, and concurrently for recovering their potential energy.

Thermochemical and biochemical conversions are recommended as the appropriate treatment methods due to the dual benefits both in environmental safety and resource reuse. Among them, hydrothermal

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carbonization (HTC) has been developed with the purpose of upgrading biowastes in the presence of water, which can simultaneously avoid the over-consumption of energy in drying process [6,8,9]. Based on the previous literatures, it is commonly accepted that hydrolysis and aromatization are two important reactions during HTC process [10,11]. The former results in the cleavage of linkage bonds in biomacromolecule, and the latter subsequently leads to the formation of coal-like structures [11–14]. Funke et al. [10] stated that aromatic structure showed a strong stability under hydrothermal environment, which could be similarly considered as a basic building block for the formed HTC-coal. Cross-linking condensation of aromatic rings during HTC process could produce the major constituents similar to natural coal, indicating a good comparability between HTC and natural coalification [6,13]. He et al. [6,9,14] and Zhao et al. [7,8] also suggested that HTC was an essential thermochemical process focused on simulating natural coalification and converting biowastes into coal-like fuels (hydrochar) under moderate temperature (120–350 °C), holding time (5–60 min) and autogenous pressure (2–16 MPa). Therefore, HTC is served as a key intermediate step optimizing the chemical structures of solid fuels that is subject to the subsequent combustion or pyrolysis [5,6,15]. The relationship between hydrothermal conditions and chemical structures of hydrochars is a long-term hot research field. A comprehensive knowledge of mechanisms controlling the evolution of biowaste structures and subsequent structure-reactivity is of crucial for the terminal application of hydrochars.

Chemical structures of hydrochars include but not limit to carbon skeleton, crosslinks of aromatic polymer, surface porosity, functional groups and ultimate components [13,14,16,17]. All of these characteristics can be changed significantly via HTC, thereby influencing the reactivity and fuel properties of hydrochars. For example, He et al. [6,14] reported that the increase of aromaticity was related to the condensation and polymerization of soluble intermediates from organic matters, which enhanced the coalification of biowastes. Harvey et al. [17] also investigated the primary reactions in HTC, and elucidated the more condensed structures of hydrochar from $R-CH_2-R$ to $R=C=R$ by means of two-dimensional perturbation correlation infrared spectroscopy (2D-PCIS). This variation of carbon bonds was further confirmed by the results of Xin et al. [18]. Additionally, Keiluweit et al. [16] revealed the dynamic molecular structures of plant-derived bio-char across a temperature range of 100–700 °C, indicating the progressive transformations of transition, amorphous, composite and turbostratic phase in carbon skeleton structures. More recently, Wei et al. [11] used sewage sludge as feedstock and highlighted that polycyclic aromatic components were the final products of coke, leading to the similar

properties to low-rank coal. However, fundamental understandings for the evolution pathways of chemical structures in relation to various biowaste-derived hydrochars are still lacking.

The primary objective of this study is to fill up the knowledge gap on the evolution routes of chemical structures in various biowaste-derived hydrochars during HTC process. Two biowaste types are taken into account for biowastes variability: a lignocellulose one (Herbal tea waste, HTW) and a non-lignocellulose one (Penicillin mycelial waste, PMW). The specific goals of this study are to: 1) identify the difference of biowastes in components and thermal properties; 2) discuss the fundamental characteristics of hydrochars derived at various temperatures; 3) investigate the variation of chemical structures, including aromatic and crystalline structures (characterized via XRD and Raman analysis), carbon skeleton structures (characterized via XPS and ^{13}C NMR analysis) and surface functionalities (characterized via FTIR and 2D-PCIS); 4) establish two comprehensive evolution diagrams for lignocellulose and non-lignocellulose industrial biowastes during hydrothermal process.

2. Materials and methods

2.1. Feedstock preparation

Two industrial biowastes used in this study was well characterized by their intrinsic components: lignocellulose (HTW) and non-lignocellulose (PMW). HTW was collected from a traditional Chinese medicine enterprise in Guangdong province, and PMW was sampled from an antibiotic production enterprise in Hebei province. Samples were directly dried at 105 °C for 24 h, and then followed by a series of pretreatments including mechanical-pulverizing, sieving and re-drying. Afterwards, dry samples with the same particle size of 0–300 μm were obtained and stored in a drying basin prior to experiments. The basic properties of biowastes were displayed in Table 1.

2.2. HTC experimental procedure

HTC of biowastes was performed in a 250 ml steel autoclave reactor (SLM250, Senlong Co.Ltd, China) which was depicted in Fig. S1, and the detailed experiment procedure was referred at our previous studies [2,4]. Operating temperatures for HTC were ranged from 120 °C to 300 °C at regular intervals of 30 °C in this study; meanwhile, the heating rate and holding time were fixed at 5 °C/min and 30 min respectively so as to avoid secondary interferences. The magnetic stirrer was rotated at a constant speed of 300 rpm throughout the whole hydrothermal

Table 1
Properties of lignocellulose and non-lignocellulose biowastes.

Sample	Proximate analysis $w_d/\%$			Ultimate analysis $w_{daf}/\%$					HHV/(J/g)		
	VM	FC	A	C	H	O	N	S			
HTW	68.73	17.37	13.90	52.36	7.86	36.44	3.04	0.30	19367		
PMW	78.06	15.42	6.52	47.90	7.59	35.97	7.95	0.59	19061		
Composition analysis ($w_{daf}/\%$)											
Protein			Carbohydrate			Lipid			Crude fiber		
14.67			80.60			4.73			> 20.30		
49.47			42.69			7.84			< 0.40		
Ash analysis (expressed as w/% of metal oxides)											
SiO ₂	Al ₂ O ₃	MgO	Na ₂ O	Fe ₂ O ₃	P ₂ O ₅	CaO	K ₂ O	TiO ₂	ZnO	CuO	SrO
21.98	7.92	7.66	0.40	4.82	4.56	20.78	7.64	0.44	0.09	0.03	0.08
0.39	0.14	3.62	2.85	0.50	30.82	22.64	19.15	0.01	0.09	0.02	0.03

Note: VM, volatile matters; A, ash; FC, fixed carbon; O (oxygen) was calculated by difference based on dry ash-free base; HHV, higher heating value; Crude fiber is defined as part of carbohydrate.

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