



# Conversion of industrial biowastes to clean solid fuels via hydrothermal carbonization (HTC): Upgrading mechanism in relation to coalification process and combustion behavior



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## ABSTRACT

The aim of this work was to study the correlation between dynamic mechanisms of carbon structure associated with their upgrading effects with the help of XPS, <sup>13</sup>C NMR and 2D-PCIS methods. Results showed the fuel qualities of biowastes were improved and became comparable to lignite or even bitumite after HTC. The carbon chemical bonds of –C–H and –C–O in biowaste components (mainly protein and polysaccharide) were thermally cracked and enriched in liquid phase in the form of soluble intermediates, which subsequently generated coal-like structures via cyclization as well as polymerization at higher temperatures. The further investigation on thermogravimetric analysis found that the conversion of “–C–H/C–O to aromatic –C–C/C=C” was beneficial for stabilizing their combustion behavior by integrating two stages of biowastes (devolatilization stage and combustion stage) into one stage of hydrochars (combustion stage).

## 1. Introduction

Recently, fossil fuels on which industrial society depends are consuming with a sharp rate of increase (29.75 billion barrels of oil in 2011 and projected to be 34.90 billion barrels in 2030) (Zhao et al., 2014b). The over-exploitation of conventional fossil fuels has been increasingly witnessed due to their potential growing demands, which results in a series of environment problems, including greenhouse effects, photochemical smog and the acidification of aquatic systems (Zhan et al., 2018). For these reasons, a clean and renewable fuels is necessary to replace fossil fuels for the sake of sustainable development of society. Biowastes, known as nontraditional biomass types characterized by their rich organic matter, are generated as by-products from industrial activities and have been considered as an abundant resource (Zhan et al., 2017, 2018; Zhuang et al., 2018). However, the disposal of biowastes is always a global issue due to its inferior characteristics (Zhan et al., 2017, 2018). On one hand, biowastes such as sewage sludge, penicillin mycelia waste and livestock manure usually contain high moisture content, which require a necessary pre-drying process in order to improve their thermal efficiencies (He et al., 2016; Zhao et al., 2014a,b). The increasing operation cost make the economic benefit of

biowaste utilization become unacceptable, especially for the developing countries. On the other hand, various extraneous substances and microorganisms are enriched in biowastes during industrial process, thereby weakening their fuel characteristics in terms of incineration (Zhao et al., 2014b). For instance, biowastes are hard to ignite, unstable and incomplete to burn; moreover, huge amount of gaseous pollutant is generated during the process of combustion as considerable contaminants contained by biowastes (Zhan et al., 2017, 2018).

In attempt to efficiently utilize biowastes as solid fuels, hydrothermal technology has been developed with the aims of upgrading feedstock and recovering energy in the presence of water, which can simultaneously avoid the over-consumption of energy in drying process (Wang et al., 2014). Compared to hydrothermal liquefaction and gasification, hydrothermal carbonization (HTC) is defined as a thermochemical process focused on simulating natural coalification and converting biowastes into coal-like fuel (hydrochar) under moderate temperature (120–350 °C), holding time (5–60 min) and autogenous pressure (2–16 MPa) (Zhao et al., 2014b). Previous literatures stated that two major mechanisms were associated with the upgrading of HTC: dewatering and coalification (He et al., 2013, 2016; Meng et al., 2012; Wang and Li, 2015; Wang et al., 2017; Zhao et al., 2014a,b; Zhuang

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et al., 2018). Meng et al. (2012) investigated the dewaterability of sewage sludge, and indicated the moisture content of hydrothermal sewage sludge was decreased to less than 20% with superior dewatering rate and extent. This finding was in accordance with the results reported by Zhuang et al. (2017a) and Wang and Li (2015), Wang et al. (2017). Furthermore, the volume based heating value and energy density were subsequently increased owing to the significant removal of moisture content (Wang et al., 2014). Apart from the dewatering process, fuel characteristics of biowastes were also elevated via HTC coalification. Zhao et al. (2014a,b) and He et al. (2013, 2016) believed the coalification process not only led to the conversion of “biowastes to low-rank coal”, but also benefited the stabilization of combustion behavior.

Up to now, the dewatering mechanisms of HTC have been systematically studied. Zhuang et al. (2017a) provided understandings related to the relationship between physicochemical structures and dewaterability of hydrothermal sludge, while Wang and Li (2015) and Wang et al. (2017) further elucidated the evolution of water forms (interstitial water, capillary water, immobilized water, etc.) during HTC and its influence on dewatering. In comparison, there were still a lack of knowledge associated with the upgrading mechanisms of coalification process. Although many researches had been studied the effects of hydrothermal upgrading under various temperature region and duration time, most of them just concentrated on improving the fuel characteristics of hydrochar and screening suitable feedstock. Relatively few studies were devoted to clarify the variation of carbon (C) structures or functionalities within coalification process. According to our best knowledge, the content and form of carbon structures were the primary distinction between biomass and coal, which implied that the changes of C-containing surface functionalities, chemical bonds and skeleton structures could strongly impact both fuel properties and combustion behavior of biowastes (He et al., 2016; Zhao et al., 2014b). Gao et al. (2013) examined the C structures of hydrochar derived from swine manure by using  $^{13}\text{C}$  NMR, and found that the alkyl C was dominant in hydrochar. Besides, Harvey et al. (2012) elucidated the highly condensed structures of hydrochar from  $\text{R}-\text{CH}_2-\text{R}$  to  $\text{R}=\text{C}=\text{R}$  by means of two-dimensional perturbation correlation infrared spectroscopy (2D-PCIS). More recently, He et al. (2016) indicated that the increase of aromaticity (aromatic C) was related to the condensation and polymerization of soluble intermediates from organic matter, which improved the coalification degree of biowastes. However, further efforts are required to explore the evolution of C-containing structures during HTC as well as its effects on fuel properties and combustion behavior.

Therefore, there are two main purposes for this study. The first one is to develop a HTC process that can be employed to effectively reuse biowastes as an alternative clean fuels; the second one is to fill the knowledge gap on the upgrading mechanism of coalification process during HTC.

## 2. Material and methods

### 2.1. Feedstock preparation

The biowastes used in this study were three typical industrial wastes from China: 1) penicillin mycelia waste (PMW) from a medicine production enterprise at Hebei province; 2) sewage sludge (SS) from a wastewater treatment plant at Guangdong province; and 3) peat waste (PW) from Changbai mountain at Jilin province. After collecting, all biowastes were directly dried at  $105\text{ }^\circ\text{C}$  overnight, and then ground, screened and re-dried so as to obtain samples with the same particle size of 0–300  $\mu\text{m}$ . Afterward, the dried samples were sealed in a drying vessel prior to analysis and experiment. The basic characteristics of biowastes were showed in Table 1.

**Table 1**  
The basic characteristics analyses of samples.

Samples	Proximate analysis (wt%, db)			Ultimate analysis (wt%, db)					HHV (MJ/kg)
	VM	FC	Ash	C	H	S	N	O <sup>a</sup>	
PMW	78.5	13.5	8.0	44.6	6.6	0.5	7.3	33.0	19.06
SS	39.2	4.2	56.5	21.6	3.7	0.5	3.4	14.3	9.67
PW	37.3	12.6	50.4	24.8	3.2	0.2	1.5	19.9	11.55

  

Samples	Composition analysis (wt%, daf)			
	Protein	Carbohydrate	Lipid	Crude fiber <sup>b</sup>
PMW	49.47	42.69	7.84	< 0.4
SS	33.97	62.62	3.41	< 0.2
PW	21.13	75.89	2.98	/

<sup>a</sup> By difference.

<sup>b</sup> Crude fiber is defined as part of carbohydrate.

### 2.2. HTC experimental procedure

A 250 ml stainless steel autoclave reactor (SLM250, Senlong Co. Ltd, China) equipped with a magnetic drive stirrer was used for HTC of biowastes. In each batch experiment, 10 g of sample powder mixed with 100 ml pure water was loaded into the vessel and sealed. Subsequently, the reactor was placed into a muffle furnace and flushed with high purified argon (99.999%) for 10 min in order to remove residual air inside the reactor. After that, the reactor was heated from room temperature to preset temperature (rang from  $120\text{ }^\circ\text{C}$  to  $300\text{ }^\circ\text{C}$  at intervals of  $60\text{ }^\circ\text{C}$ ) under autogenous pressure and held for 30 min. The influence of duration time on HTC was concurrently investigated by changing the duration time (30 min, 60 min and 120 min) at  $300\text{ }^\circ\text{C}$ . Meanwhile, the heating rate was set at  $5\text{ }^\circ\text{C}/\text{min}$  and the magnetic stirrer was rotated at a constant speed of 300 rpm throughout the whole hydrothermal process so as to ensure the even heating of mixture inside. At the end of carbonization process, the reactor was removed from furnace and quenched to ambient temperature rapidly. Afterward, the mixture was filtered by  $0.45\text{ }\mu\text{m}$  filter membrane to separate solid product (hydrochar) from liquid phase. The hydrochar, a type of clean solid fuel, was further dried and screened with 80mesh sieve before analysis.

### 2.3. Chemical and physical analysis

#### 2.3.1. Fundamental characteristics

Proximate analysis of solid samples was performed according to the American Standard for Testing and Materials (ASTM) methods. The test methods for Ash and volatile matter (VM) were D3174 and D3175 respectively, while the proportion of fixed carbon (FC) was calculated by difference. The elemental analysis was carried out in a Vario E1 cube elemental analyzer (Elementar Co. Ltd, Germany), and the fraction of oxygen was also determined by difference based on dry basis. The energy content of solid samples was assessed via the higher heating value (HHV) in a calorimetric bomb (IKA C2000, Germany). Regarding FTIR analysis, the mixture of sample and KBr (at a ratio of 1:200) was ground and pressed into pellet for each run. Then, these pellets were immediately measured on a Bruker Vertex 70 spectrophotometer in the range of  $400\text{--}4000\text{ cm}^{-1}$  with 64 accumulated scans at a resolution of  $4\text{ cm}^{-1}$ . The relative absorption bands of functional groups for the FTIR spectra were listed in Supplementary materials on the basis of previous researches (He et al., 2013; Hu et al., 2017; Smidt and Meissl, 2007; Xin et al., 2015).

#### 2.3.2. X-ray photoelectron spectroscopy (XPS)

The X-ray photoelectron spectroscopy (XPS) analysis was performed to record the C 1s spectra of biowastes and its derived hydrochars on a Thermo Scientific ESCALAB 250Xi spectrometer, which was equipped

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