



Multiscale characteristics dynamics of hydrochar from hydrothermal conversion of sewage sludge under sub- and near-critical water



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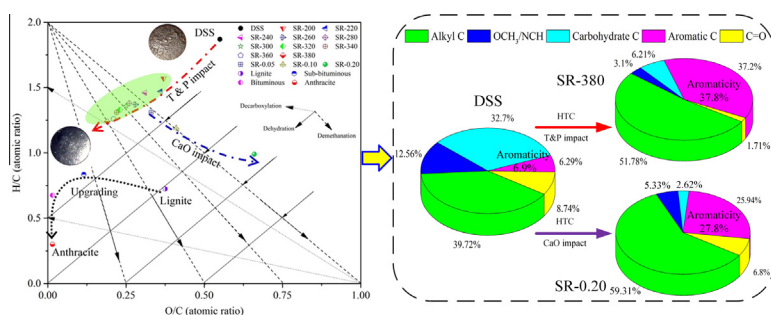
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HIGHLIGHTS

- Sewage sludge was upgraded to hydrochar via three characteristic regimes in HTC.
- Aliphatic C was mainly transformed to aromatic C–C/C–H in subcritical water.
- More N than C–(C,H) was decomposed below 300 °C.
- Considerable aromatic C–(C,H) was transformed to C–(O,N) and C–H at 380 °C.
- CaO favored intense destruction of aromatic C–C/C–H, anomeric O–C–O, C–H, C–(O,N).

GRAPHICAL ABSTRACT



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ABSTRACT

Dewatered sewage sludge was upgraded to hydrochar using hydrothermal conversion in sub- and near-critical water. Three characteristic temperature regimes responsible for the upgrading were identified. Drastic hydrolysis of carbohydrates, amide II or secondary amines occurred at 200 °C while noticeable decarboxylation initiated above 260 °C. Elevated temperature improved porosity but did not induce higher surface area. Aliphatic C was mainly transformed to aromatic hydrocarbon rather than aromatic C–O in subcritical water, whereas COO/N–C=O and aromatic C–O were decomposed to carbohydrate C at 380 °C. Below 300 °C, carbon functionalities in hydrochars were thermally stable and faster decomposition of N than C–(C,H) resulted in dramatic decline of N/C. Above 300 °C, C–H was gradually polymerized to aromatic C–(C,H) which was considerably transformed to C–(O,N) and C–H at 380 °C. CaO favored intense destruction of aromatic C–C/C–H, anomeric O–C–O, C–H and C–(O,N) functionalities but introduced more aromatic C–O and O=C–O.

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1. Introduction

Sewage sludge (SS) is a semi-solid by-product from wastewater treatment plants. At present, generation of SS has been soaring

worldwide, which results from rapid urbanization and increasingly stringent regulations on the discharge of treated effluents (He et al., 2014b). However, because of high moisture content (ca. 80 wt.% after mechanical dewatering) and environmental hazards therein (He et al., 2014a, 2015b), appropriate treatment and re-utilization of SS has attracted great attentions. In terms of wet biomass treatment, hydrothermal conversion (HTC) technology

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has been widely regarded to be more energy-efficient than conventional thermochemical conversion with pre-drying step (Cao et al., 2011), especially for feedstocks with moisture content exceeding 30 wt.% (Changi et al., 2015). Thus, HTC becomes an alternative technology to convert wet SS into cleaner solid fuel with greatly improved dewaterability (He et al., 2013).

Recently, there are tremendous studies on solid fuel generation from hydrothermal carbonization of wet biomass or waste streams, such as SS (He et al., 2013), pulp and paper mill sludge (Mäkelä et al., 2016), wheat straw digestate (Reza et al., 2015a), grindelia and rabbitbrush (Reza et al., 2015b), nut husks (Yang et al., 2015), etc. Although some general characterizations on surface morphologies and functional groups were presented, the majority of these researchers mainly focused on the fuel properties of obtained hydrochar solid fuel. Furthermore, the discussion on the relationship between the characteristics evolution of hydrochar and reaction chemistry involved was limited. Motivated by significant difference in chemical structures between hydrochar from HTC and pyrochar from pyrolysis, Cao et al. (2011) examined chemical structures of swine manure derived chars under different carbonization conditions (i.e. HTC and slow pyrolysis) using advanced solid-state ^{13}C nuclear magnetic resonance (^{13}C NMR). Different from predominant aromatics in pyrochar, they claimed that the alkyl moieties were dominant components in hydrochar and the increased aromaticity was attributed to condensation and polymerization of intermediates from degradation of carbohydrates. More recently, Wikberg et al. (2015) systematically examined the structural and morphological changes of lignin-derived carbonaceous materials during HTC in the presence of various catalysts toward lignin valorization. However, systematic chemical structure characterization of SS derived hydrochar is not well studied.

On the other hand, researchers have also extracted and analyzed the formed organic compounds in aqueous phase using GC–MS after HTC of biomass wastes (Reza et al., 2015b; Xu and Lancaster, 2008; Yang et al., 2015), but they failed to form a holistic understanding on the distribution and reaction pathways by examining produced compounds. To date, although there is numerous research on HTC of SS based on simplified reaction network (Yin et al., 2015), little is known regarding reaction chemistry during HTC. This is mainly due to the complexity of SS as well as entire reaction system.

Additionally, despite established main reaction pathways for HTC of individual model compounds, many interactions (e.g. Maillard reaction) of major starting components and reaction intermediates take place simultaneously, which may have great influences on reaction rates and pathways during HTC (Changi et al., 2015). Instead of discussing specified reaction routes for dominant components in biomass wastes, it is more realistic to examine the evolution of major elements (i.e. C, H, and O) and C-containing functional groups to derive plausible reaction chemistry during HTC. From the perspectives of beneficial re-utilization of hydrochar and reaction mechanism or chemistry in HTC, it is of vital importance to get clear knowledge on the evolution of surface structures or morphologies and chemical properties of hydrochars. Moreover, the maximum temperature applied in most hydrothermal carbonization experiments was 260 °C, higher severity of HTC is essential to get more information on HTC of SS under both sub- and near-critical water conditions. Furthermore, since CaO is a

widely used sludge conditioner (He et al., 2015b), its impact on HTC of SS is another concern. More importantly, CaO has been reported to promote H_2 yield and $\text{NH}_4^+/\text{NH}_3$ formation, and inhibit toxic pollutants emission during either HTC or pyrolysis (He et al., 2015a; Liu et al., 2014). Thus, CaO may significantly affect reaction chemistry in HTC of SS, which requires further exploration.

Therefore, we attempt to fill up the knowledge gap on reaction chemistry through examining chemical composition and structure of hydrochar from HTC of SS under sub- and near-critical water in this study. Moreover, influence of CaO conditioner will be explored in detail. Specifically, the main objectives are to (1) visualize H/C and O/C atomic ratios evolution in HTC under various conditions, (2) elucidate the relationship between HTC conditions and surface morphologies of hydrochar, and (3) provide insights into HTC reaction chemistry in terms of transformations of carbon functional groups and chemical structure. Finally, the present study would shed new light on comprehensive understanding on characteristics dynamics of hydrochar toward sustainable management and re-utilization of SS through HTC.

2. Experimental section

2.1. Materials

Dewatered sewage sludge (DSS) with a moisture content of 82.5 wt.% was collected from Ulu Pandan Water Reclamation Plant in Singapore. The DSS sample was stored in 4 °C cold room and used as received for the feedstock in HTC experiments. As for subsequent characterization, DSS sample was oven-dried at 105 °C overnight and ground into fine powders (less than 0.5 mm) using a rotary mill as previously described (He et al., 2014b). The as-prepared DSS dry powders were sealed in dry polypropylene centrifuge tubes and kept in a dry cabinet before usage. The major physicochemical characteristics of DSS are presented in Table 1.

2.2. HTC experiments

HTC experiments were performed in a 1 L stainless steel fixed-head high temperature and high pressure reactor (Parr Instrument Co., USA) as reported previously (He et al., 2015a, 2014b). Initial HTC experiments were designed to understand the impact of temperature and pressure. Typically, 182 g DSS was fed into the reactor vessel and sealed for reaction. After being heated up to desired temperatures and corresponding pressures (i.e. 200 °C and 2.0 MPa, 220 °C and 2.6 MPa, 240 °C and 3.8 MPa, 260 °C and 5.0 MPa, 300 °C and 9.3 MPa, 340 °C and 15.5 MPa, 380 °C and 22.0 MPa), the reaction was maintained for 20 min and quenched quickly to room temperature afterwards using external standing fan and internal cooling coil. In particular, different amount of CaO (i.e. Ca/C molar ratio of 0, 0.05, 0.10, and 0.20) was added in the feedstock under HTC at 380 °C and 22.0 MPa to assess the impact of CaO alkaline conditioner. The gas was released into a gas sampling bag whereas the solid hydrochar was separated from slurry using a vacuum filtration apparatus through 0.45 μm PTFE membrane. The gas and liquid products have been comprehensively analyzed in our previous work (He et al., 2015a). The hydrochar samples were oven-dried at 105 °C overnight and ground into fine powders (less than 0.5 mm) for subsequent

Table 1
Physicochemical characteristics of DSS^a.

Moisture content (wt.%)	HHV (MJ/kg, db)	Ultimate analysis (wt.%, db)					Proximate analysis (wt.%, db)			Fuel ratio FC/VM
		C	H	N	S	O	VM	FC	Ash	
82.5	18.0	39.9	6.2	6.0	5.6	29.1	69.0	9.2	21.8	0.13

^a db, dry basis. HHV, higher heating value; VM, volatile matter; FC, fixed carbon.

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