Bioresource Technology 266 (2018) 275–283

Contents lists available at ScienceDirect

Bioresource Technology

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

Evaluation of the clean characteristics and combustion behavior of hydrochar derived from food waste towards solid biofuel production

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ARTICLE INFO

Keywords:
Food waste
Hydrochar
XPS
Fuel
TG-FTIR

ABSTRACT

This study investigated the clean properties and combustion behavior of hydrochar from food waste (FW). The hydrochar was characterized by proximate analysis and HHVs, and the chemical forms were investigated by FTIR, XPS (Sulfur), and XANES (Chlorine). TG-FTIR was used to assess the combustion behaviors, and XRF was used to assess the fouling and slagging inclinations. Results showed that increasing temperature from 180 °C to 260 °C enhanced the removal of N, S, and Cl for hydrochar. Especially, aromatic-S and sulfate-S increased in contrast to sulfoxide-S, and more inorganic-S was produced in hydrochar; all samples had mainly inorganic-chlorine. Additionally, the release of HCl, SO_2, and NO of hydrochar combustion were significantly reduced and the SI and FI index decreased to ranges of 0.18–0.16 and 0.32–0.17, respectively. However, hydrochar produced at temperature above 220 °C led increased NO emission possibly due to formation of more pyridine-N and quaternary-N.

1. Introduction

Food waste (FW) is defined as the food residuals generated from households, restaurants, cafeterias and hotels etc (Pham et al., 2015). It reported that approximately 1.3 billion tons/year of the food produced from human consumption were subsequently discharged, lost, degraded or contaminated globally (Girotto et al., 2015). For China, the increased population and fast development of urbanization had brought significant quantities of FW, which brought environmental burdens and risks to human health over the past decades, (Zhou et al., 2015). The FW also represents the major organic fraction of the municipal solid waste, but the high moisture of FW makes it difficult to recover energy and resources. In light of these issues, hydrothermal carbonization (HTC) representing an innovative thermochemical technique is not only sustainable but effective to be an alternative (Wang et al., 2018a; Zhai et al., 2013b). This process is highly attractive due to its suitability to transform wet feedstock into hydrochar with energy or to recover chemicals such as nitrogen and phosphorus (Wang et al., 2017a; Wang et al., 2018b).

Numerous studies have been conducted on the fuel properties of hydrochar obtained from HTC of biomass waste such as lignocellulosic biomass (Hoekman et al., 2011; Wang et al., 2017b), microalgae (Xu et al., 2013), sludge (Chen et al., 2014; Peng et al., 2016), municipal solid waste (Berge et al., 2011), swine manure (Cao et al., 2011). It demonstrated that hydrochar was high valuable carbon-rich material coupled with the loss of hydrogen and oxygen aroused by dehydration and decarboxylation during HTC (Hoekman et al., 2011). These improved properties of hydrochar make it have great potential to the application as solid fuel. For FW, (Kaushik et al., 2014) investigated the hydrochar derived from FW after pre-treatment with enzyme, and the result showed that the calorific values of hydrochar ranged from 17.4 to 26.9 MJ/k. Berge et al. investigated the hydrochar obtained from food waste (Berge et al., 2011). Results showed that increased fixed carbon with decreased volatile matter of hydrochar were obtained as a result of HTC, whilst around 70% carbon can be recovered in the hydrochar employing temperature at 250 °C. Similar results can be found in other studies, which suggested HTC process could enhance the carbon and energy recovery in hydrochar (Liu & Balasubramanian, 2014). In addition, the chemical functional groups and structure contained in hydrochar also changed. Most of oxygen-containing functional groups

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https://doi.org/10.1016/j.biortech.2018.06.093
Received 16 May 2018; Received in revised form 26 June 2018; Accepted 27 June 2018
Available online 30 June 2018
0960-8524/

such as −OH, C═O, and C-O-C from the raw feedstock were weakened by the deoxygenation and dehydration reactions and the hydrochar showed an aromatic and aliphatic structure (Sevilla & Fuertes, 2009b). These performances also can be affected by changing the hydrothermal severity such as temperature and residence time (Gao et al., 2013). Thus, the condensation and aromatization (i.e. high C═C content) in the hydrochar contains high energy concentration and increased heating value (Funke & Ziegler, 2010). HTC extends the potential of conversion of biomass waste with high moisture content into solid fuel, thus providing a sustainable and effective treatment method for FW.

One key concern is the pollutant emissions which may stimulate the attention on the evolution of the nitrogen (N), chlorine (Cl) and sulfur (S) contained in hydrochar producing pollutants as gas release such as NO_x, HCl and SO_2 during the combustion process. At present, HTC has shown its advantages to minimize the pollutant elements to some extent. As for nitrogen, it contained in feedstock mainly as protein, which was converted into liquid products by hydrothermal deamination, a major way for the ammonia release after HTC. Yu et al. suggested approximately 65–70% of nitrogen in the low-lipid microalgae was converted into water soluble compounds through hydrothermal process when temperature was higher than 220 °C with time longer than 10 min (Yu et al., 2011). However, Kruse et al. compared the nitrogen evolution in three biomass including carrot green, the algae chlorella pyrenoidosa and straw, and result showed the chemical nature of nitrogen varied with the feedstock; the nitrogen was not completely removed in hydrochar using beech wood impregnated with cysteine as feedstock due to incorporation of nitrogen in hydrochar aroused by Maillard reaction (Kruse et al., 2016). Falco et al. investigated the mixture of glucose and microalgae during HTC and result indicated more stable nitrogen groups, namely quaternary-N and pyridine-N, were formed in hydrochar than that of solo microalgae, especially at higher temperature (Falco et al., 2012). A similar result can be founded in Wang et al.'s study, which showed HTC of FW at high temperature enhanced the protein conversion in FW but more stable nitrogen forms like pyridine-N and quaternary-N were produced in hydrochar (Wang et al., 2018b). Nevertheless, current researches about the effect of HTC on the Cl behavior focus on the MSW which has high poly vinyl chloride plastics (Jin et al., 2013). Few study focused on the Cl conversion during HTC of FW. It is generally accepted that the hydrochloric acid, a water-soluble inorganic chlorine, was the major product from the dechlorination during HTC, which decreased the formation of dioxin or HCl during the combustion process of hydrochar (Hwang et al., 2006). In Prawisudha and coworker's work, organic chlorine concentration in the MSW generated from poly vinyl chloride reduced 80% because of the transformation into water-soluble inorganic chlorine which could be easily water-washed and dewatered from hydrochar (Prawisudha et al., 2012). Up to now, studies on the effect of HTC on sulfur in hydrochar were limited. Two recent studies using HTC as method to treat the low quality coals showed that organic sulphur could be converted to inorganic sulphur, which could result in a low SO_2 emission (Wu et al., 2015).

Hence, based on the description above, a systematic study on how the HTC effects on the fuel properties and clean properties including the N, S, and Cl within hydrochar from FW is lacking, and deep insights are needed for the combustion characteristics. In this study, a multiscale characterization of the hydrochar from FW was conducted by the fuel properties and chemical functional groups with FTIR. The effect of HTC on the removal efficiency of N, S, and Cl element under different temperature was investigated combined with the corresponding chemical forms in hydrochar employing XPS and XANES, respectively. Finally TG-FTIR system was used to evaluate the combustion properties and gas release of hydrochar by comparison with FW, and the fouling and slagging inclinations were estimated.

2. Materials and methods

2.1. Materials

The FW in present study was obtained from the cafeterias of Hunan University in Changsha, China. The feedstock contained a variety of cooked food (e.g., meat, seafood, vegetables, rice, noodles and gravy), condiments (e.g. salad dressing, ketchup, cocktail sauce) and chopsticks. In consideration of processing limitations, the plastic materials and bones were separated out. Prior to the HTC process, the feedstock was thoroughly homogenized and followed by storing in a plastic box before the experiments.

2.2. HTC procedures

The HTC of FW experiments were conducted in a 500 mL 316 stainless steel autoclave equipped with a PID controller and autostirred. In brief, around 20% of FW (as-received solid) was loaded in the reactor and sealed. The reactor was then heated at a rate of approximately 4 °C/min to reach the preset temperature (180–260 °C) and kept for 60 min under stirring at 100 rpm. After desired reaction time, the reactor was cooled down to room temperature. To ensure reproducibility, HTC process were conducted for twice. The reaction mixture consisting of liquid product and solid residue was collected and then separated by a vacuum filtration apparatus. The solid residue was dried at 105 °C overnight. After that, the hydrochar samples were weighed and milled to particles less than 200 μm and stored in plastic bags.

2.3. Analysis methods

Elemental compositions including C, H N and S of the solid samples were conducted by an Elementar Vario EL cube (Germany). The HHVs was defined as the equation: HHVs = 0.339C + 1.443(H-0.125O) − 0.0224(9H) + 0.0093S + 0.001464N (Peng et al., 2016). The proximate analysis of the pellets was analyzed according to the Chinese Standard Practice for the Solid biofuels (GB/T28731-2012). The total chlorine content analysis in the dry solid hydrochar was analyzed by using traditional Eschka method according to Chinese standard (GB/T 358-2014). A colorimetric method, according to (Baethgen & Alley, 1989), was used to determine the ammonium (NH_4^+-N) concentrations of the liquid product. The nitrate (NO_3^--N) concentrations was determined using nitration of salicylic acid method (Cataldo et al., 2008). For determining the total nitrogen (TN) content, the Kjeldahl-N concentrations in the liquid product calculated from the NH_4^+-N after the samples were digested on the basis of the Chinese standard method (GB11891-1989). The organic nitrogen (ON) was determined as the difference between TN and the sum of NH_4^+-N and NO_3^--N. The soluble protein in the aqueous phase was analyzed using bicinchonininc acid method with BCA Protein Assay Kit. The elements (N, S and Cl) removal efficiency (R) was defined as the followed equation:

$$R = 1 - \frac{\text{Total content of element in hydrochar}}{\text{Total content of element in feedstock}} \quad (1)$$

X-ray photoelectron spectroscopy (XPS) measurements of the samples were conducted using an ESCALAB 250Xi model. Constant pass energy of 20 eV with an energy step size of 0.1 eV was used to collect the spectra, using Al Kα X-ray as source. The surface functional groups were performed by a FTIR-8400S Spectrometer (USA) in the 400–4000 cm^{-1} region with 100 scans. For every experiment, a disk from the mixture of the sample powder with KBr was prepared. The Cl edge X-ray absorption near edge structure (XANES) were carried out at 4B7A using synchrotron radiation (medium X-ray beamline 2050–5700 eV, BSRF, Beijing, Institute of High Energy Physics, Chinese Academy of Sciences) to investigated the chlorine forms in the hydrochar. Reference Cl components including NaCl, 3-chloropropion acid