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Correlations between hydrochar properties and chemical constitution of orange peel waste during hydrothermal carbonization

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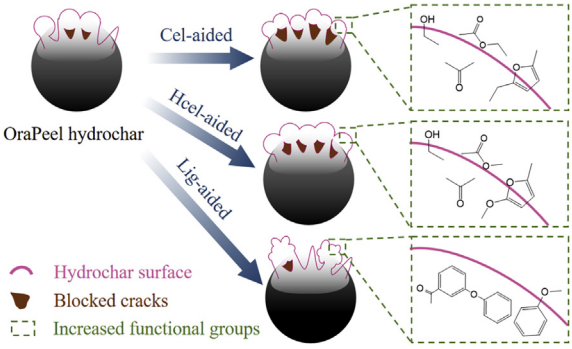
GRAPHICAL ABSTRACT



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ABSTRACT

For efficient hydrothermal treatment of biomass, this study aims to figure out the correlations between complex chemical constitution of orange peel (OraPeel) as typical bio-waste and the physicochemical structure of its derived hydrochar, which could be utilized to adjust hydrochar properties for specific applications (e.g., adsorbent, fuel) by regulating respective proportions of each component in bio-waste. Cellulose, hemicellulose and lignin were used as the control variables of feedstocks composition in this work. After hydrothermal process, lignin added feedstock produced more hydrochar, which contained rougher surface with nearly doubled BET areas and more benzene rings. Hemicellulose-aided hydrochar possessed higher density of carbonaceous microspheres and richer hydroxyl. This char was simultaneously covered by more esters or lactones with more aromatic oxygen-containing groups inside. Similar to hemicellulose, cellulose improved the formation of diverse oxygenous groups but reduced the size of microspheres on hydrochar.

1. Introduction

Orange peel is a typical bio-waste in food industry, which derived from the huge global orange production estimated over 50 million tons for 2013/14 (Fernandez et al., 2015). High moisture content and complex organic matter are also the major challenges for the disposal of this kind of biomass, due to the massive cost for reducing water and homogenizing different constitution (Cheng et al., 2012; De and Debnath, 2016; Liang et al., 2008; Lu et al., 2011).

Recently, hydrothermal carbonization (HTC) has attracted tremendous attention as a bio-waste treatment technique with the skip of pre-drying procedure and the increasing potential in energy application

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(Berge et al., 2011; Parshetti et al., 2014; Sun et al., 2014). HTC is a thermo-chemical process under relatively mild temperatures (180–250 °C) and autogenous pressures in watery environment (Huang and Yuan, 2016; Mäkelä et al., 2016; Reza et al., 2013). During HTC, valuable carbonaceous residue, referred to as hydrochar, is the solid product formed through a series of hydrolysis, dehydration, decarboxylation, condensation, polymerization and aromatization reactions in subcritical water (Basso et al., 2016; Li et al., 2013; Libra et al., 2011). Hydrochar receives growing focus of researchers owing to its abundant oxygenated functional groups (OFG) which make it an effective precursor for pollutants adsorbent and soil amendment (Ronix et al., 2017; Sun et al., 2014; Wu et al., 2017a,b), as well as its high-energy density for the feedstock of carbon fuel cells (Cao et al., 2007; Trohalaki, 2009).

There is no doubt that hydrochar performances largely depend on chemical constitution of feedstocks. Many researchers have investigated the typical features of hydrochar prepared from single component. Sevilla and Fuertes (2009a) reported that agglomerates of carbonaceous microspheres (size 2–5 μm) were formed through a dehydration process from cellulose, during HTC in the 220–250 °C range. Hu et al. (2014) found that hydrochar derived from lignin had the largest surface area (2.6 m^2/g) and the largest pore volume (0.019 cm^3/g) after hydrothermal treatment at 330 °C. Obviously, hydrochar derived from different single component possesses individual characteristics, which make these components play different roles during a complex hydrothermal carbonization process. As for orange peel, cellulose, hemicellulose and lignin, accounting for around 50% of total dry basis (Wang et al., 2015), will have significant influences on char properties. However, hardly researches have touched upon this issue (Funke and Ziegler, 2010; Fernandez et al., 2015).

In view of the above, the present work is conducted to find out how hydrochar with specific physico-chemical structure can be obtained by controlling the composition of feedstocks. Cellulose, hemicellulose and lignin were employed as control variables for orange peel HTC experiments. After carbonization, mechanism of the feedstocks constitution influence on the char performance will be inferred by analyzing morphologies and chemical structure of different hydrochar. In the following, preliminary predictions according to these relations could be applied to adjust characteristics of hydrochar for functional applications by regulating respective proportions of cellulose, hemicellulose and lignin components.

2. Materials and methods

2.1. Materials characteristics

Oranges peels (OraPeel), from a local market in Wuhan, China, were dried at 105 °C for 24 h in oven. Then they were crushed into powder and screen-sieved (< 200 μm). Cellulose (α-Cellulose, Aladdin Reagent Co. Ltd., Shanghai, China), hemicellulose (Anca-Couce, 2016; Shen et al., 2017), Dibo Reagent Co. Ltd., Shanghai, China) and lignin (TCI Co. Ltd., Shanghai, China) were used as three composition variables of OraPeel material.

2.2. Hydrothermal experiments

HTC experiments were performed using a 250 mL reactor composed of a stainless steel autoclave body, heater, temperature controller and water-cooled tube under autogenous pressure and Ar atmosphere. 10 g of OraPeel, cellulose (named as Cel in following text), hemicellulose (xylan, named as Hcel) and lignin (named as Lig) were separately added into reactor as 4 blank groups. Afterwards, 5 g of Cel, Hcel and Lig, separately mixed with 10 g of OraPeel powder were subjected to hydrothermal process. The feedstocks of experimental groups were named as OraPeel-Cel, OraPeel-Hcel and OraPeel-Lig respectively. Deionized (DI) water was subsequently added to meet the solid-liquid mass ratio of 1:8. The HTC temperature was 240 °C and the residence time was set at 120 min with an agitation speed of 200 rpm. In the above hydrothermal environment, the reactor pressure is 4.0 MPa in both blank and experimental groups. HTC products were taken out of reactor when the temperature returned to 20 °C. The process liquid and solid products were separated by vacuum filtration with medium speed qualitative filter papers. The gas was collected in 2 L foil gas sampling bags. All solid char was washed abundantly with DI water and dried at 80 °C. Then solid, liquid and gas products were weighed respectively. Each group was conducted twice.

2.3. Analytical procedures of hydrochar

Elemental analysis for carbon, oxygen, hydrogen, nitrogen, and sulfur was carried out with an elementary analyzer (Elementar, Vario Micro cube). Surface physical characteristics were studied by field emission scanning electron microscopy (FE-SEM, MIRA3 TESCAN, 15 kV) and specific surface area analyzer (MICROMERITICS, ASAP 2020M). Element distribution in hydrochar surface was conducted by X-ray photoelectron spectroscopy (XPS, Kratos, AXIS-ULTRA DLD-600W). The spectrum decomposition from XPS was performed using the XPS PEAK 41 program with Lorentzian-Gaussian function after subtraction of a Shirley background. Functional groups were tested by fourier transform infrared spectroscopy (FTIR, Bruker, VERTEX 70). The infrared spectrum was recorded by using the KBr disk method, with 1:200 to the sample-to-KBr mass ratio. Carbon structures were analyzed by solid-state ^{13}C CP-MAS NMR spectra (Bruker, AVWB III-600), with spinning rate of 10 kHz, a resonance frequency of 600 MHz, a contact time of 3 ms, and a recycle delay time of 2 s. ^{13}C chemical shifts were referenced relative to tetramethylsilane. Quantitative data for all blank groups were calculated linearly by corresponding feedstock mass as weight to obtain the linear superposition data of OraPeel groups adding other three blank groups separately. This method can also be described by the following equation.

$$D_P = D_O K_O + D_X K_X \quad (1)$$

where D_P is the predicted data from linear superposition calculation, D_O and D_X are the quantifiable data from OraPeel and another blank group respectively, K_O and K_X are the mass proportion of OraPeel and a pure material (Cel, Hcel or Lig) in the corresponding OraPeel-X experimental group separately. Obviously, $K_O + K_X = 1$, and D_P belongs to the linear range between the data from OraPeel group ($K_O = 1$) and another blank group ($K_X = 1$).

Some analytical results (XPS and NMR for blank groups, SEM images and FTIR spectra for OraPeel and experimental groups) were placed in the Supplemental file.

3. Results and discussion

3.1. Field distribution of three-phase hydrothermal products

As shown in Fig. 1, the total recovery of three-phase products was 84.9–90.6%, which was in a reasonable range. These lost parts resulted from a small fraction of volatile in liquid and residue in the reactor. The yield of HTC products indicated that the relative increase in the cellulose and hemicellulose contents had no significant effects on the yield of solid products. On the contrary, the char yield from OraPeel-Lig was higher than that from OraPeel-Lig*. This difference suggested the thermal stability of OraPeel was improved with lignin content increasing. Some researchers found that lignin was more resistant to degradation than cellulose and hemicellulose during HTC (Kim et al., 2016). More information is needed to determine other probable pathways of increased solid mass when lignin added.

3.2. Physical characteristics of hydrochar

SEM images revealed the morphological information of hydrochar