Journal of Analytical and Applied Pyrolysis 116 (2015) 1–9

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

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

Characteristic evolution of hydrochar from hydrothermal carbonization of corn stalk

Shuqing Guo*, Xiangyuan Dong*, Tingting Wu, Fengjuan Shi, Caixia Zhu

Department of Energy & Environment Engineering, Zhongyuan University of Technology, Zhengzhou 450007, People's Republic of China

ARTICLE INFO

Article history:
Received 23 June 2015
Received in revised form 26 October 2015
Accepted 31 October 2015
Available online 3 November 2015

Keywords:
Hydrothermal carbonization
Reaction severity
Hydrochar
Characteristics
Corn stalk

ABSTRACT

Reaction severity is a comprehensive parameter which combines temperature and time to describe the severity of a process. In this work, hydrothermal carbonization (HTC) of corn stalk was carried out at reaction severity levels of 5.05–8.29. The effect of reaction severity on the solid yield, the chemical, energetic, and structural properties of hydrochar products were studied in detail. The hydrochar yield varied from 71 to 36%. The higher heating value increased from 20.8 MJ/kg at reaction severity of 5.05 to the maximum value of 29.79 MJ/kg at severity of 8.29. When the reaction severity was greater than 7.11, the hydrochar exhibited coal-like oxygen/carbon and hydrogen/carbon atomic ratios. The evolution of microcrystalline structure for hydrochar was examined by XRD and the results showed that the component degradation led to develop hydrochar structure. The functional group results revealed that the high aromatization performance and carbonization extent of the hydrochar could be achieved with reaction severity increasing. The correlations between solid yield, carbon content, oxygen content, HHV, relative peak intensity ratios of the functional groups for hydrochar and reaction severity were fit with the experimental data. The results indicated that the dose-response models fit these characteristics data well, which would be favorable to understand and design the hydrothermal carbonization process for corn stalk.

1. Introduction

Biomass is an important renewable resource which can be potentially utilized to cope with the rising problem of energy shortage and environmental pollution. In past decades, various techniques such as combustion, pyrolysis and gasification have been successively applied in biomass treatment and conversion [1–3]. Hydrothermal carbonization (HTC) is currently one of the most interesting processes for biomass thermochemical conversion. HTC has some key benefits compared to other techniques, such as its simplicity to perform, mild reaction condition, wide availability of raw materials and less greenhouse gas emission. During HTC process, the biomass should be submerged in saturated water to ensure the hydrothermal reaction. The final solid residue of the HTC process, often called hydrochar, is potentially suitable for wide scale applications such as for carbon sequestration, adsorbents, container nurseries, fuels and even as soil additive [4,5].

In the recently reported studies, various types of feedstock ranging from simple model compounds (D-xylose, cellulose, lignin, etc.) to complex biomass materials (maize silage, wheat, sunflower stem, etc.) [6–18] have been treated by HTC for hydrochar production. These HTC studies have illuminated that after different reactions including hydrolysis, dehydration, decarboxylation, polymerization, aromatization, and solid–solid reactions [4,5] most of the carbon content of feedstock remains in the solid hydrochar and the higher heating value (HHV) of hydrochar can be significantly increased. In addition, the chemical and energetic characteristics of hydrochar are dependent on reaction conditions, that is reaction temperature, residence time and solid load (ratio of feedstock and water) [9–12,16–23]. However, the effect of solid load seems to be less strong as those of temperature and time [9,10,23]. During hydrothermal carbonization process, the feedstock is usually heated from about environmental temperature to a given reaction temperature, and held at this temperature for a certain residence time, then cooled down to room temperature. In recent years, staged temperatures in the same HTC process have been also proposed [14,19]. During these heating, cooling and other temperature variation periods, the components of biomass may undergo significant conversion and carbonization, which may thus augment the difficulty in comparing and analyzing the experimental results. To exactly describe the correlation between hydrochar formation and reaction conditions for a whole HTC process including heating, holding, cooling and other temperature variation stages, it is

* Corresponding authors. Fax: +86 371 62506050.
E-mail addresses: shuqing.guo@163.com (S. Guo), dongxiangyuan@163.com (X. Dong).

http://dx.doi.org/10.1016/j.jaap.2015.10.015
0165-2370/

necessary to employ a comprehensive reaction parameter. Reaction severity, which combines both temperature and reaction time, can be used to examine the combined effect of reaction conditions and is favorable to understand the influence of reaction conditions on formation and evolution of hydrochar. This parameter has been successfully applied in studying xylan, hemicellulose, lignin removal, and solubilization of lignocellulose materials [25]. Correlations between residual of feedstock and reaction severity have been also established and interpreted. However, little information has been provided to describe the dependence of the chemical, energetic, and structural characteristics for hydrochar on the whole process reaction severity with temperature variation. Understanding such relationships is critical in process control and parameter selection.

For the present work, corn stalk was chosen as the precursor for hydrothermal conversation. This precursor was a major agricultural waste and was abundantly available in China and its annual production was over 200 million tons in 2009–2013 [24]. In addition, as a lignocellulosic biomass which contained 35–39.6% cellulose, 16.8–35% hemicelluloses, and 7–18.4% lignin, it was a promising low-cost material for production of biofuels [25]. There were limited reports on hydrothermal carbonization of corn stalk in the past few years [26,27]. Fuertes et al. [26] addressed the physical and chemical properties of hydrochar from corn stover at a reaction temperature of 250 °C and a 4 h reaction time, and found that the characteristics of hydrochar approached those of the low-grade coal. Xiao et al. [27] also discuss the physical and chemical properties of hydrochar from corn stalk obtained at 250 °C for 4 h, they revealed that hydrochar was lignite-like and contained a large amount of oxygen-containing groups. These studies helped to understand the physical and chemical properties of hydrochar at the given reaction condition. However, the specific aims of this work are to: (1) understand how reaction severity influences the yield, carbon content, HHV, functional groups characteristic of corn stalk hydrochar; (2) try to explore the correlations between reaction severity and characteristics of corn stalk hydrochar and provide valuable information for process scale-up.

2. Materials and methods

2.1. Preparation of hydrochar

The raw material corn stalk was collected from Zhengzhou Suburb, China. It was broken into less than 5 mm and air dried. The dried samples were sealed in a plastic container for further use. HTC experiments were performed in a 2 L stainless pressure reactor. The experimental temperature was controlled by a single-display PID controller. 30 g of corn stalk and 300 g of water were loaded into the reactor and heated to the desired temperature. During the whole reaction process the mixture of water and feedstock was stirred continuously to ensure even heating by a magnetic stirrer. More descriptions about the experimental system can be found in Ref. [28]. The residence time was set as eight hours for all experiments. To deeper investigate the influence of temperature on corn stalk carbonization process, the reaction temperature varied from 180 °C to 290 °C in the single-stage HTC. This temperature range can cause biomass components to become more reactive: hemicellulose is degraded at about 200 °C, cellulose starts to react above 230 °C, and lignin can be decomposed partially above 260 °C [5,16]. Two-stage HTC experiments were also carried out. In the first stage, the reaction temperature was the same as that of the single-stage HTC, while the second stage temperature was from 180 to 230 °C, which could avoid excessive decomposition of the intermediate products [14]. The detailed experimental conditions are shown in Table 1. Hydrochar samples were named as THC and SHC, and T and S denotes the two-stage and the single-stage in the later part of the paper respectively. The heating and cooling rates for both single and two-stage HTC were set at about 3 °C min^{-1} and 4 °C min^{-1} respectively. After cooled to room temperature for each experiment, the solid products were collected and separated by filtration and then dried at 105 °C until a constant weight was achieved for further analysis. All experiments were repeated three times.

2.2. Analysis

In this study the hydrochar yield was determined by the ratio of the dry hydrochar mass to the dry feedstock mass (Eq. (1)). Chemical elemental analysis (CHNS) was carried out in an organic elemental analyzer (Vario Micro, Elementa, Germany). The O content was determined by sub-traction of the CHNS and the ash content from 100%. The microcrystal structure analysis was performed in an X-ray diffraction (XRD D8 ADVANCE, Bruker, Germany). XRD spectra were obtained with Cu target using kα radiation (λ = 0.1542 nm) generated from 40 kV voltage and 40 mA current. Intensities range was from 5° to 50° with 1.8°/min continuous scan speed. FTIR(Nicolet iS10, Thermo Fisher Scientific, USA) spectra were recorded by varying wave number over the range of 500–4000 cm^{-1} with a resolution of 0.4 cm^{-1}, using pure KBr as the background. The surface morphologies of the samples were characterized by scanning electron microscopy (SEM, JSM 6701- F, JEOL Ltd., Tokyo).

The solid yield was defined as,

$$\text{Solid mass yield (\%)} = \frac{\text{mass of dried hydrochar}}{\text{mass of dried feedstock}} \times 100\% \quad (1)$$

As mentioned above, the present work involved different heating periods and staged HTC. Thus, the reaction severity which combines temperature and time [29] could be calculated as follows:

$$R_0 = \sum_{i=1}^{n} \int_{t_{i-1}}^{t_i} \exp\left[\frac{T_i(t) - 100}{14.75}\right] dt \quad (2)$$

where i denotes the ith period, and n denotes the numbers of the periods including heating, holding, and cooling periods. t_{i-1} (min) and t_i is the initial and end time for the ith period, respectively. $T_i(t)$ (°C) stands for the temperature profile of the ith period. $LogR_0$ (reaction severity) is used to present the results in this paper.

The higher heating value (HHV) was calculated by Kang et al. [8],

$$\begin{aligned}\text{HHV(MJ/kg)} &= 0.3491\text{C}+1.1783\text{H} + 0.1005\text{S} \\ &-0.1034\text{O} - 0.0015\text{N} - 0.0211\text{A}\end{aligned} \quad (3)$$

3. Results and discussion

3.1. Hydrochar yield

Solid mass yield is one of the key characteristics for hydrochar. Fig. 1 shows the hydrochar yields for both single- and two-stage tests and their dependence on the reaction severity. From Fig. 1 we can see that although the temperature is changed during two-stage HTC, the yield variation with reaction severity presents similar tendency to that for single-stage HTC. The solid yield shows a significant decrease from 71% to 36% as the reaction severity increases from 5.05 to 8.29. A possible two-step trend can be found. As the reaction severity is less than 7.11 and greater than 5.05, the solid yield decreases remarkably. However, when the reaction severity exceeds 7.11, only slow changes in solid yield can be observed. The decline in hydrochar yield may be mainly due to the decomposition of the feedstock. Within the reaction severity ranging from 5.05 to 7.11, the least stable hemicellulose and relative stable cellulose