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Influence of reaction conditions and feedstock on hydrochar properties

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ABSTRACT

Hydrothermal carbonization (HTC) is a biomass conversion process to produce a renewable solid fuel (hydrochar). The reaction conditions, such as temperature, time, and water/biomass ratio have key effects on hydrochar characteristics. However, it has not been fully investigated to establish and compare models of hydrochar properties (solid yield, carbon content and HHV) for different biomass HTC at different reaction conditions. These models and the corresponding analytical methods are favorable to optimize operating parameters and process design of HTC. In this work, HTC experiments from corn stalk, longan Shell and NaOH-pretreated longan Shell were carried out at 210 °C, 250 °C and 290 °C for 30 min, 240 min and 480 min with different water to biomass ratios. New models of the hydrochar properties of corn stalk, longan Shell and NaOH-pretreated longan Shell were established based on severity parameter (combined time and temperature) and dose-response function. Also, data of wood, olive stone and grape marc hydrochars (collected from literatures) were used for comparison. The first and second derivative methods were also employed to analyze and compare the variation of these hydrochar properties. The results showed that the hydrchar yield, carbon content, and HHV curves decrease monotonically and can be divided into three significant stages with increasing reaction severity. The water to biomass ratio has a significant effect on the hydrochar yield. With increasing the water to biomass ratio, both the maximum decrease rates and the variation regions of hydrochar yields for corn stalk and longan shell shift to lower severities. The chemical composition of the feedstock has also a significant effect on the hydrochar properties. However, the maximum decrease rates and the variation regions of hydrochar properties (determined by the first and the second derivative methods) show similar profiles for different feedstock. The maximum variation rate of the hydrochar properties for six biomass samples can be found at severity of 5.8–6.4.

1. Introduction

Biomass is being regarded as one of the most important sustainable, renewable, and clean energy sources which may be utilized to reduce reliance on fossil fuels and protect against energy shortages, greenhouse effect, environmental pollution, as well as climate change. Over the last several decades, research in biomass thermochemical conversion has been very active, and different techniques have been applied for producing biofuels, such as pyrolysis, gasification, liquefaction and hydrothermal carbonization (HTC) [1–3]. Among these techniques, HTC is becoming an increasingly attractive topic in biomass conversion due to its advantage of simplicity to perform, less greenhouse gas emission, and less mass transfer limitations. It is a technique of using hot, saturated water to convert biomass into a solid product at mild reaction conditions. The solid product, known as hydrochar, is nontoxic, low-sulfur, hydrophobic, and value-added that can be potentially used as activated carbon, soil amendment, adsorbent, carbon black, solid fuel, co-fired fuel with coal, feedstock or co-feedstock of pyrolysis [3,4].

In recent years, different types of complex biomass feedstock [5], including woody biomass [6–10], herbaceous biomass [11–15] and fruit biomass [16–19], have been used for hydrothermal carbonization. These studies help to understand the HTC process and the hydrochar properties. It has shown that the hydrochar properties highly depend on reaction temperature, residence time and feedstock type [3,20]. At the same time, there is a certain effect of water to biomass ratio on the hydrochar yield, which was discussed in some references only [10,11,16]. These studies also have revealed that different lignocellulose materials are mainly composed of hemicellulose, cellulose, lignin and some extractives, which may experience similar reactions, including hydrolysis, dehydration, decarboxylation, polymerization, aromatization, and solid-solid reaction [3,4,13]. This indicates that there may be similarity in the characteristic evolution of hydrochar from different feedstock. Therefore, to establish models of hydrochar properties of different biomass and explore their similarity is critical for energy system

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analysis and optimization of HTC. Unfortunately, previous studies have been carried out at various temperatures and times. It is difficult to build models of hydrochar properties and compare them based on these different reaction conditions. Reaction severity is a factor which combines time and temperature [21]. It has been widely used to study the hydrothermal treatment of biomass materials [22], which in essence facilitates description of HTC process. In addition, the literature about the effect of reaction conditions and feedstock type on the evolution rate of the hydrochar properties is still scare. Knowledge about these characteristics is necessary to optimize and control of the HTC process for energy saving.

The specific aims of this work are to: (1) investigate how reaction conditions and feedstock type influence yield, carbon content and HHV of hydrochar, and explore whether these influences have inherent similarity; (2) try to understand the evolution rate of hydrochar under various operating conditions and with different feedstocks, and provide valuable information for HTC process optimization and control. Different types of biomass, such as Wood (woody biomass), corn stalk (herbaceous biomass), longan shell, olive stone and grape marc (fruit biomass) were used as HTC materials. The evolution models of the hydrochar properties were established. The different reaction stages and the maximum variation rates for yield, C content, and HHV were analyzed by using the first and second derivative methods.

2. Materials and methods

2.1. HTC experiments

Corn stalk and longan shell were chosen as the raw materials. Corn stalk was gathered from Zhengzhou, China, while longan shell was purchased from supermarket in Zhengzhou. They were dried outdoor by natural air and then further broken into particles less than 5 mm.

The HTC experiments were carried out in a stainless steel reactor. More detailed descriptions could be found in references [23,24]. During each experiment, 30 g of feedstock and water were loaded into the reactor and sealed at water to biomass ratios of 5:1, 10:1, 20:1 for corn stalk and 5:1, 10:1 for longan shell, respectively. The mixture was heated from ambient temperature to a given temperature (210 °C, 250 °C, or 290 °C), at the same time, the mixture was continually stirred at a speed of 200 r/min by a magnetic stirrer for even heating. After being maintained for 30 min, 240 min, and 480 min at the desired temperature, the reactor was cooled to room temperature by cooling water. All experiments were repeated at least three times to obtain the average values. The solid products were collected and separated by filtration. Then they were dried at 105 °C for at least 4 h and sealed in plastic bags for further use.

NaOH pretreatment was also applied to longan shell. The pretreatment conditions were determined according to previous reported results [25,26]. First, broken and dried longan shell was soaked with 3% (w/w) NaOH solution at a liquid to biomass ratio of 20:1. After it was stirred for 2 min, the mixture was sealed and maintained at room temperature for 18 h. Then the mixture was filtered and washed until the eluent became neutral. At last the solid residue was dried and used for later HTC. The HTC reaction temperature and residence time were the same as described above, and the water to biomass ratio was set as 10:1during HTC.

2.2. Analytical method

The hydrochar yield was calculated as,

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

The ash content was measured in a muffle furnace at 550 °C ± 10 °C for at least 2 h. The elemental analysis was carried out in an elemental analyzer (Vario Micro, Elementa, Germany) to measure the C, H, N, and S content. The O content was obtained by subtracting the measured C, H, N, S, and ash content from 100%. Cellulose, hemicelluloses, and lignin contents were measured according to Laboratory Analytical Procedures (LAP) established by National Renewable Energy Laboratory (NREL) [27].

The higher heating value (HHV) was calculated according to the following equation [28],

$$\begin{aligned} \mathrm{HHV(MJ/kg)} = {} & 0.3491\mathrm{C} + 1.1783\mathrm{H} + 0.1005S - 0.1034\mathrm{O} \\ & - 0.0015N - 0.0211A \end{aligned} \tag{2}$$

2.3. Raw material data

Apart from corn stalk (herbaceous biomass), longan shell (fruit biomass) and NaOH-pretreated longan shell mentioned in Section 2.1, other three types of biomass resources: wood (woody biomass), olive stone and grape marc (fruit biomass) were also used in this work. Both the raw material and hydrochar properties of wood, olive stone and grape marc were gathered from literatures [6,16,22,29–32]. Table 1 presents the ash contents, HHVs, ultimate and composition analysis results of these raw materials. It can be seen that wood, longan shell and grape marc have higher carbon content than corn stalk and olive stone. The lignocellulosic composition shows that the cellulose content follows this trend: wood > corn stalk, longan shell and NaOH-pretreated longan shell > olive stone > grape marc, while that the lignin content follows: grape marc > olive stone > wood and longan shell > corn stalk and NaOH-pretreated longan shell. It can also be seen that there are less hemicellulose, lignin, carbon content and higher ash content for NaOH-pretreated longan shell than those of longan shell.

2.4. Reaction severity model

Severity factor could be expressed as the following equation [21]:

$$R_0 = t \exp\left[\frac{T - 100}{14.75}\right] \tag{3}$$

where t (min) is the residence time. T (°C) stands for the temperature.

The dose-response function could be used to correlate hydrochar properties (yield, C content, and HHV) with reaction severity and expressed by,

$$Y = f(\log R_0) = A + \frac{B - A}{1 + 10^{(\log x_0 - \log R_0)\times C}} \tag{4}$$

where A, B, C and $\log x_0$ are constants.

In order to further analyze the hydrochar properties, the first and second derivatives of the dose-response function were derived and shown as Eqs. (5) and (6), respectively,

$$Y_1 = f'(\log R_0) = \frac{(B - A)C \times 10^{(\log x_0 - \log R_0)\times C} \times \ln(10)}{\left[1 + 10^{(\log x_0 - \log R_0)\times C}\right]^2} \tag{5}$$

$$\begin{aligned} Y_2 = f''(\log R_0) = {} & \frac{2(B - A)\left(C \times 10^{(\log x_0 - \log R_0)\times C} \times \ln(10)\right)^2}{\left[1 + 10^{(\log x_0 - \log R_0)\times C}\right]^3} \\ & - \frac{(B - A)(C \times \ln(10))^2 \times 10^{(\log x_0 - \log R_0)\times C}}{\left[1 + 10^{(\log x_0 - \log R_0)\times C}\right]^2} \end{aligned} \tag{6}$$