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Effect of water-washing of wheat straw and hydrothermal temperature on its hydrochar evolution and combustion properties

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ABSTRACT

In order to upgrade wheat straw, hydrothermal treatment at 160–240 °C was investigated. Meanwhile, the influence of temperature and leaching on the fuel's physicochemical and combustion properties were explored. A temperature of 180–220 °C was found to benefit the generation of hydrochar, with solid and energy yields of at least 57.3% and 69.9%, respectively. When temperature increased to 160 °C, hemicellulose was hydrolyzed and this led to the formation of carbon microspheres. The diameter of the carbon microspheres reached 0.05–0.7 μm. Hydrochars obtained at 160, 180, and 200 °C exhibited better combustion performance with higher comprehensive combustibility index value. While leaching heavily impacted the hydrochar derived at 160 °C and increased its activation energy (178 kJ/mol) above those obtained for treatment at 180 °C (164 kJ/mol) and 200 °C (169 kJ/mol). Overall, the recommended hydrothermal temperature for production of fuel from wheat straw is 180–200 °C.

1. Introduction

Wheat straw is a major agricultural biomass resource. Its enormous production and ready availability make it widely used as a fuel in China (Khan et al., 2009). According to the 2017 National Bureau of Statistics report, the wheat yield was 129.77 million tons, which resulted in the production of 177.26 million tons of wheat straw (Zhou et al., 2011). Because of increasing restrictions on carbon emissions, renewable and carbon-neutral agricultural biomass resources have received extensive attention and their use is developing gradually (Dodson et al., 2011). However, variance in composition between biomass and coal leads to enormous differences in combustion characteristics and ash composition. Therefore, the substitution of coal with biomass in existing coal-fired systems could result in operational challenges and slagging problems. From the perspective of an engineer looking to improve a boiler's thermal efficiency, decrease slagging problems and the recycle the produced fly ash, it is essential to carry out efficient and environmentally friendly pretreatment of biomass fuels to processes to improve its quality and homogeneity.

Hydrothermal carbonization (HTC), also referred to as wet torrefaction (Yan et al., 2017), is a biomass pretreatment method in which the biomass is submerged in hot pressurized water at temperatures between 180 and 260 °C, but below water's critical point (Bach et al., 2013). The advantages of employing HTC as a pretreatment stage for biomass use are compelling. Solid hydrochars that result from HTC have condensed carbon structures with higher energy densities than the raw materials (Funke and Ziegler, 2010; Nizamuddin et al., 2017). This makes them suitable for co-firing with coal and even for direct combustion as the sole energy source. Indeed, HTC have the advantage of generating a higher calorific value fuel with lower reaction temperature and less time than dry pyrolysis (Bach and Skreiberg, 2016; Bach et al., 2013).

Currently, work has reported using HTC to treat sewage sludge (He et al., 2013), moso bamboo (Yan et al., 2017), municipal solid waste (Lin et al., 2017), woody biomass (Bach et al., 2015) and lignocellulosic biomass (Reza et al., 2013) to transform waste biomass into a clean fuel. The HTC temperature plays a crucial role in the carbonization of the sample (Wiedner et al., 2013), which, in turn, affects its fuel and combustion characteristics. In investigation of HTC of moso bamboo, Yan et al. (2017) revealed that the mass and energy yields of hydrochars decreased as the treatment temperature increased, but that the hydrochars' calorific value continued to increase with treatment temperature. Accordingly, 260 °C was found to be most suitable for producing bamboo hydrochar. He et al. (2013) treated high-moisture sewage sludge with HTC to produce a solid hydrochar that was easier to burn with a more stable combustion. Work by Yang et al. (2016) showed that the combustion kinetics of HTC-generated hydrochar were different to those of the raw material.

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In a study of HTC process, Parshetti et al. (2013) and Berge et al. (2011) found that dehydration and decarboxylation reactions caused highly aromatic structures in the hydrochars. Elsewhere, Kang et al. (2012) investigated HTC of cellulose, lignin and D-xylose and proposed carbonization mechanism for each material. Another study used cellulose to produce a lignite-like fuel using HTC at 200 °C (Düdder et al., 2016). Sevilla and Fuertes (2009) indicated that the final hydrothermal conversion products of glucose, sucrose and starch sugars are carbon microspheres with highly aromatic cores. Recently, Volpe et al. (2018) found evidence of secondary carbon generation at high temperatures and biomass-to-solid ratio from *Opuntia ficus-indica* cladodes using microscopic observation. The variety of research makes it clear that HTC can be applied to a wide range of raw materials. Much work has focused on the characterization of the hydrothermal carbon's basic characteristics and combustion behavior under different temperature conditions. However, the reaction process for hydrothermal pretreatment has not been fully resolved (Peterson et al., 2008), especially regarding how the reaction pathway varies with temperature. This detail affects the optimization of temperature conditions for different samples as well as the maintenance of HTC equipment.

The water medium plays an important role during HTC process (Funke and Ziegler, 2010). As well as acting as the solvent, water also functions as a reactant and catalyst, especially promoting the hydrolysis reaction (Siskin and Katritzky, 2001). Rasmussen et al. (2014) indicated that some reaction site, such as protonation site, depend on the structure of the water solvent used. In addition to water's direct chemical effect, leaching can impact the process (Bach et al., 2013) and competition between parallel reactions may affect the composition of any carbonized product, thereby impacting its combustion properties. It remains unclear to what extent leaching impacts the hydrochars' production.

The work, thus, focuses on the following three tasks: (1) characterize the fuel composition of hydrochars and water-washed samples; (2) explore the structure composition of hydrochar and the generation process of secondary coke with temperature; and (3) analyze differences of combustion characteristics and kinetics of the various derived fuels.

2. Materials and methods

2.1. Materials

Wheat straw was collected directly after harvesting and removed root and ear from the Shangzhuang Experimental Station of China Agricultural University in Beijing in July 2017. The sample was naturally air-dried for 2 weeks and then crushed and passed through a 20-mesh sieve and stored in a sealed bag. The initial moisture content was 3.1%.

2.2. HTC experiments

Samples were carbonized in a 1 L stainless steel Parr 4532 reactor (Parr Instrument Company, Moline, IL, USA) with auto stirring. A total of 30 g of crushed wheat straw (WS) sample and 300 mL of deionized water were added into the HTC reactor to obtain a solid-to-liquid ratio (S/L) of 1:10. Nitrogen was used to purge air from the sealed reactor and was injected across three 10-minute periods to ensure an inert gas environment. Reactions were carried out at 160, 180, 200, 220 and 240 °C. All reactions included a 1-hour hold time once the desired temperature had been reached. Reflecting the temperature used, experiments were denoted HTC160, HTC180, HTC200, HTC220 and HTC240. After holding for 1 h at the prescribed temperature, water was introduced to quickly cool the reactor to 25 °C. The solid product was then recovered by vacuum-filtration and dried in an oven at 105 °C for 24 h.

Water-washing treatment was carried out for comparison with hydrothermal carbonization in order to explore the leaching effect during pretreatment process. An absolute solid mass of 12 g wheat straw was soaked in 600 mL deionized water for 3 h for water-washed (WW) sample preparation. After the 3 h washing, the solid–liquid mixture was then separated by suction-filtration, and residual ions on the straw surface were fully rinsed off by deionized water. The remaining solid was dried in an oven at 105 °C for 24 h before being analyzed.

2.3. Hydrochar characterization

2.3.1. Physicochemical properties

Proximate analysis was performed according to ASTM E1131-08 standard using SDT Q600 Thermogravimetric Analyzer (TA Instruments, New Castle, Pennsylvania, USA). Ultimate analysis was determined using Vario Macro Elemental Analyzer (Elementar Analysensyteme GambH, Langenselbold, Deutschland) according to BS EN 15104:2011. The higher heating value (HHV) of each sample was obtained using a Parr 6300 Calorimeter (Parr Instrument Company, Moline, IL, USA) combined with the element content as per Chinese National Standard GB/T 30727-2014.

The solid and energy yield of solid hydrochars and WW sample were calculated using following equations:

$$\text{Solid Yield (\%)} = \frac{Filtrated\ solid\ weight}{Dry\ WS\ weight} \times 100\% \quad (1)$$

$$\text{Energy Yield (\%)} = \frac{HHV\ of\ pretreated\ sample}{HHV\ of\ WS} \times solid\ yield \times 100\% \quad (2)$$

2.3.2. Structural and morphological characterization

Cellulose, hemicellulose and lignin dominate the composition of straw (Vassilev et al., 2012). The characterization of the straw's composition is an important part of the investigation of the carbonization process. Cellulose is a glucose polymer and hemicellulose is mainly composed of xylose and arabinose. Lignin is a phenolic polymer, most of which are insoluble in inorganic acids, i.e., acid-insoluble lignin, and the other part is acid-soluble lignin. The NREL/TP-510-42618 method (Sluiter et al., 2012) was used to determine the cellulose, hemicellulose and lignin content. Each dried sample was hydrolyzed into monosaccharides using a two-step hydrolysis involving 72 wt% followed by 4 wt% H_2SO_4. Glucose, xylose and arabinose can be quantitatively analyzed by HITACHI High-Performance Liquid Chromatography (Hitachi, Ltd, Tokyo, Japan). The corresponding cellulose and hemicellulose content was then deduced from the monosaccharides. Acid-soluble lignin was measured using a UV-2550 Ultraviolet spectrophotometer (SHIMADZU Ltd., Tokyo, Japan). The acid-insoluble lignin content was then calculated by mass difference.

A Spectrum 400 Fourier infrared spectrometer (PerkinElmer, Waltham, MA, USA) was used to analyze the functional groups in the raw material and the pretreated solids. 200 g of KBr and 2–3 mg of sample were thoroughly mixed and ground using a mortar. A sample of the mixture was formed into a tablet and then analyzed. Infrared spectra in the range 4000–400 cm^{-1} at a resolution of 4 cm^{-1} were used for the analysis. Dried samples was taped to the carrier platform with conductive tape directly. The samples' image were captured with Merlin compact cold field emission scanning electron microscope (ZEISS, Oberkochen, Germany) at 1 kV.

2.4. Combustion characterization

2.4.1. Thermogravimetric experiments

Thermogravimetric analysis (TGA) was used to evaluate the influence of HTC on wheat straw's combustion behavior. All tests were carried out by a SDTQ600 Thermogravimetric Analyzer (TA