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Effects of hydrothermal treatment on the pyrolysis behavior of Chinese fan palm

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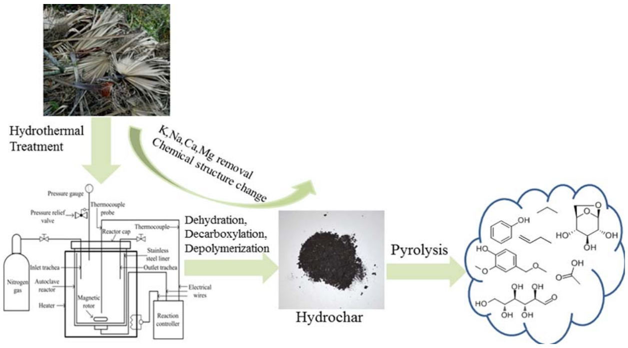
GRAPHICAL ABSTRACT



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ABSTRACT

The effect of hydrothermal treatment (HTT) on Chinese fan palm pyrolysis was investigated. It indicated that HTT could effectively remove a large portion of alkali/alkaline earth metals and disrupt the chemical structure to a certain extent. HTT delayed the initial decomposition temperature but accelerated the pyrolysis process completely. HTT also increased the relative contents of both sugars and hydrocarbons in pyrolysis. At 210 °C, HTT had the most significant promotion effect on the sugars formation with the relative content of 30.58%. While, The relative content of phenols, acids, furans, aldehydes, esters and CO_2 decreased more or less after HTT. With increasing pyrolysis temperature, the relative content of most groups of chemicals except hydrocarbons decreased. Response contours were analyzed to find the optimal reaction conditions for generating acids, phenols, sugars and hydrocarbons, respectively. The results indicated both pyrolysis temperature and HTT temperature had distinct influence on relative contents of products.

1. Introduction

Due to the carbon neutrality, biomass is a clean and renewable energy source. If we can make full use of biomass, we can reduce the dependence on fossil fuels such as coal and petroleum, and reduce emissions of sulfur dioxide (SO_2) and nitrogen oxides (NOx) (Yao et al., 2017a). It can be converted into high-grade energy via thermo-chemical and biochemical processes. Among the thermochemical conversion processes, although the burning process has many advantages, including high degree of decomposition, the decrease of land use and the potential of energy recovery, high fly ashes and emissions of harmful gas also caused serious environmental problems. Pyrolysis is regarded as a promising method to convert biomass to high-value added gaseous, liquid and solid products in an efficient and clean way(Yao et al.,

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2017b). A thorough investigation should be conducted on biomass pyrolysis technology in order to study the optimal reaction severity for the desired products. Cellulose, hemicellulose and lignin are three major components of biomass, each of which has its unique kinetic characteristics and thermal behaviors during pyrolysis (Wang et al., 2017). Therefore, the compositions of biomass could significantly influence the characteristics of pyrolysis. In addition, there is a small amount of inorganic ash, which is mainly composed of mineral elements. The pyrolysis characteristics of biomass are mainly affected by these three major components, and the mineral elements also affect biomass pyrolysis process to some extent (Chen et al., 2017; Zhang et al., 2016). Generally, the main elemental constituents of biomass inorganics are Ca, K, Na and Mg with smaller amounts of Fe, Al, Mn and Zn (Dong et al., 2015). It has been demonstrated that even minor certain inorganics could alter both the thermal degradation rate and chemical pathways during biomass pyrolysis. Therefore, extensive studies have been conducted to investigate the effect of inorganics on biomass pyrolysis by removing the inherent inorganics or adding alkali metals (Dalluge et al., 2017).

The previous literature reported (Huang and Yuan, 2016; Wang et al., 2016) that hydrothermal treatment (HTT) was effective to remove a large proportion of the inherent inorganics in the feedstocks. Compared with other biomass pretreatment, HTT has great advantages of mild reaction condition and low energy input (Kambo and Dutta, 2015). During the HTT process, subcritical water acts a reaction medium as well as catalyst, because it shows a high ionic strength, leading to diffusion coefficient and dynamic viscosity of water increase, thus the feedstock was allowed to get hydrothermal conversion in a homogeneous reaction system (Yao et al., 2016). This reaction condition enhanced dissolution of the feedstock and condensation into the solid phase. The output of this process is a high-carbon-energy density hydrochar, and it possesses a low moisture content and easier handling, transport, and storage, providing a more suitable solid fuel for further thermochemical conversion (Hu et al., 2016). So HTT is a good scheme to convert biomass feedstock into carbon rich products (hydrochar) for premium fuel or other upgraded solid products with lower alkali/alkaline earth metal content and sulfur element(Liu et al., 2013). Some complex reaction process occur during HTT, including hydrolysis, dehydration, decarboxylation, depolymerization, condensation, and aromatization (Lu et al., 2011; Zhao et al., 2014). In addition, some literature revealed that the chemical composition and structure of biomass changed to a certain extent after HTT (Dai et al., 2017; Patel et al., 2016). The degradation of hemicellulose and cellulose starts at the beginning of HTT, where most of the lignin still remains stable until near or above critical point of water. Due to the best thermal stability of lignin among the three major components, leading to the hydrochar with high lignin content (Kambo and Dutta, 2015). Therefore, the pyrolysis behavior was remarkable different between the raw and hydrochar samples. A plenty of researches were focused on the combustion performance of hydrochar with excellent fuel properties (Lin et al., 2015; Yao et al., 2017a). Only a small number of studies were carried out to evaluate the gaseous and/or liquid products from hydrochar pyrolysis with considering the influence of the changes in inorganic compounds, chemical composition and structure of biomass caused by HTT. Hence, the effects of HTT on the pyrolysis behavior of biomass should be studied.

The Chinese fan palm (CFP) is very abundant in southern China. In southern china, the CFP is the most widely spread plant. The huge dead leaves which are the main component of biomass wastes are difficult to deal with. The utilization of CFP has attracted extensive interest in the field of biomass pyrolysis because of its great potentiality as a bio-energy resource. In this study, the dead leaves of CFP as a typical biomass were selected as the feedstock for HTT at 180, 210 and 240 °C, respectively. The quantitative analysis on the inorganics contents in raw CFP and hydrochars was conducted via an inductively coupled plasma optical emission spectrometer (ICP-OES). Fourier transform infrared (FT-IR) spectrometer was used to identify the difference in the chemical structures for the raw CFP and hydrochars. Thermogravimetric Analysis (TGA) was conducted to analyze the thermal behavior of the CFP and the hydrochars. On the basis of these results, the pyrolysis characteristics and the pyrolysis volatiles from these samples were analyzed via Py-GC/MS. Furthermore, four pyrolysis temperatures (400, 500, 600 and 700 °C) were selected to investigate the effect of pyrolysis temperature on products distributions. In order to analyze the optimum reaction conditions, the response contours in terms of the RPA of chemical groups according pyrolysis temperature and HTT temperature were plotted. The obtained results can be helpful for understanding the effects of HTT on biomass pyrolysis and for the further utilization of biomass wastes.

2. Materials and methods

2.1. Materials

In this study, the dead leaves of CFP purchased from the urban district of Guangzhou, Guangdong province, was adopted as parent feedstock. Dirt and impurities on the leaves of were washed off. The washed CFP samples were ground using a small grinder and screened small size less than 178 μm for HTT. The screened particles were dried in an oven at 105 °C for 24 h.

2.2. Hydrothermal treatment

The HTT experiments of CFP were carried out by using an autoclave 250 ml reactor which has reported in our previous paper (Yao et al., 2016; Yao et al., 2017a). The reactor was filled with 8 g of completely mixed CFP and 150 ml of deionized water. Before each experiment, a large amount of nitrogen gas was injected into the reactor to isolate the air. The reactor then was heated up to the desired temperature (180, 210 and 240 °C) and maintained for 60 min. The stirring rate was set to 500 rpm throughout the reaction process. After reaction, the reactor was rapidly cooled to ambient temperature with air and water. Then the hydrochar samples were dried in a drying oven at 105 °C for 24 h and crushed into the particle size of less than 178 μm before analysis. The hydrochars were marked as ‘C-XXX’ in accordance with HTT temperature (°C). All the experiments were carried out three times to ensure reproducibility and consistency.

2.3. Analytical methods

The ultimate analysis was conducted using an Elementar (Vario EL cube). Proximate analysis of solid products was performed using an Industrial analyzer (Henan Hengke). The proximate analysis and ultimate analysis were tested according to National Standard in China GB/T 28731-2012 and General rules for elemental analyzer JY/T 017-1996, respectively. Fourier transform infrared (FTIR) spectrometry (Nicole, Model iS10) was employed to analyze various functional groups contained in the samples. The FTIR spectra were collected using a mixture of sample and KBr in a sample/KBr ratio of 1:100. Inductively coupled plasma–optical emission spectrometry (ICP-OES, Agilent) was employed to determine the metal elements present in samples. FTIR spectra were recorded from 4000 to 500 cm^{-1} by the software OMNIC. The thermogravimetric analysis was carried out by the NETZSCH simultaneous thermal analyzer (STA 409PC). The flow rate of the nitrogen gas was 80 ml/min. The experiment temperature increased from 50 to 900 °C at a heating rate of 20 °C/min.

2.4. Py-GC/MS

The fast pyrolysis analyzer (CDS 5200) was coupled with gas chromatography/mass spectrometry (Agilent 7890BGC, 5977AMS) systems to research the distribution of volatiles from samples fast