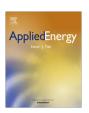
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Upgrading of waste biomass by hydrothermal carbonization (HTC) and low temperature pyrolysis (LTP): A comparative evaluation



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HIGHLIGHTS

- The performance of HTC and LTP was compared to produce solid fuel from waste biomass.
- Fuel qualities of the biochars produced from HTC and LTP were investigated.
- Ash problem related metal contents in two biochars were analyzed.
- Combustion characteristics of two biochars were determined.
- Hydrothermally prepared biochar is suitable for use as a solid fuel.

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ABSTRACT

Hydrothermal carbonization (HTC) and low temperature pyrolysis (LTP) were compared on the basis of fuel qualities of biochars obtained from the upgrading of raw biomass in the present study. The results showed that the hydrothermally prepared biochar had higher energy density while the pyrolytic biochar had higher energy yield due to higher biochar yield. Nearly 100% major ash-forming metals were retained in the pyrolytic biochars while the contents of these metals in hydrothermally prepared biochars were less than 40% relative to those of raw biomass, especially for Na and K (less than 11% retention rate). The reactivities of pyrolytic biochars were higher than their respective raw biomass and the main mass loss occurred at low temperatures. The higher combustion temperature ranges and sharply decreased residue suggested that higher thermal efficiency and lower pollutant emissions could be achieved with the hydrothermally prepared biochars than with pyrolytic biochars. As for the process kinetics, HTC showed lower activation energy in the temperature range of 150–300 °C in spite of deeper decomposition and carbonization of biomass as compared to LTP.

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1. Introduction

Biomass resource used as a solid fuel for power and heat generation is viewed as an efficient option for energy recovery from renewable biomass. However, raw biomass is not suitable for direct combustion as it has several technical constraints which are associated with inherent properties of biomass materials, for example, low energy density and high moisture content [1]. Therefore, it is imperative to pre-treat the biomass to improve its fuel quality prior to combustion. Low temperature pyrolysis (LTP) and hydrothermal carbonization (HTC) are two principal thermal approaches to upgrade biomass feedstocks to accommodate the existing coal-fired boiler or furnace [2–4]. For LTP, biomass feed-

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stock is heated under inert atmosphere with low heating rate and the target fuel in the form of pyrolytic biochar with improved fuel quality is generated. HTC simulates natural coalification in coal petrology, involving the decomposition and carbonization of biomass material in water medium at desired temperature and autogenous pressure [5]. No drying process is needed for HTC, which represents a practical advantage for biomass feedstocks as they are characterized by high moisture content. Both LTP and HTC of biomass feedstocks produce the biochars with improved fuel quality relative to raw biomass such as increased grindability and elevated energy density [3,4]. The increased grindability means the low energy consumption for biomass grinding and the elevated energy density reduces the operating cost for the handing logistics.

Extensive research has been conducted on biomass upgrading by these two approaches, with an aim to investigate the reactions mechanisms involved and optimize operation conditions [4,6–8]. Most of these research has focused on woody biomass, instead of

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abundant agricultural residues [4,9,10]. For example, loblolly pine was treated by HTC and LTP and the resultant biochars showed increased fixed carbon content and elevated energy density [4]. As a solid fuel, one of the key concerns in utilizing biomass feedstocks for energy generation is the occurrence of ash-related problems in boilers [11,12]. Biomass materials, especially agricultural residues, are known to be rich in alkali metals such as Na and K and these alkali metals can cause undesirable slagging and fouling in the high temperature furnaces and boilers due to the formation of low melting- or softening-point alkali silicates [1,13]. Moreover, the ash content and its chemical composition of solid fuel also have an influence on the application of combustion technology and the later ash disposal. Therefore, during pre-treatment the fate of the metals contained in raw biomass, especially those closely related to ash problems, is a key concern as it controls the performance of the subsequent combustion performance of resultant biochars. It has recently been reported that some inorganic components contained in raw biomass can be leached into the water medium during HTC process, leading to decreased ash contents in hydrothermally produced biochar relative to its parent biomass [3]. However, no detailed information is available in the literature on the distribution of metal species, especially those mainly related to ash problems, after HTC and LTP of biomass feedstocks up to date.

In addition, the knowledge of reaction kinetics is vital to design and operate the waste biomass-to-energy conversion reactors efficiently. Different decomposition reactions occur for biomass feedstocks during the course of HTC and LTP. Therefore, kinetic analysis should be performed to gain a better understanding of the relative performance of both HTC and LTP. Although the kinetics of biomass pyrolysis has been widely studied, that of HTC is scarcely reported in the literature [14–18].

The objective of this preliminary study is to make a comparative evaluation of the performance of HTC and LTP for conversion of biomass feedstocks to biochars by (1) investigating the contents of metals prior to and after HTC and LTP of biomass feedstocks and energy analysis of resultant biochars; (2) evaluating fuel qualities of the two biochars based on combustion analysis and (3) determining the kinetic parameters to better understand the upgrading of biomass by HTC and LTP processes. The ultimate goal of this work is to develop a viable pre-treatment process to produce solid fuels with improved fuel quality from biomass feedstocks while maintaining relatively high energy recovery rate and less energy consumption.

2. Experimental

2.1. Biochars preparation

Coconut fibers (CF) and eucalyptus leaves (EL) were selected as model raw biomass feedstocks for biochar production and their ultimate analysis is shown in Table 1. Based on the earlier findings reported in the literature [3,8,16], the biochars produced at 250 °C

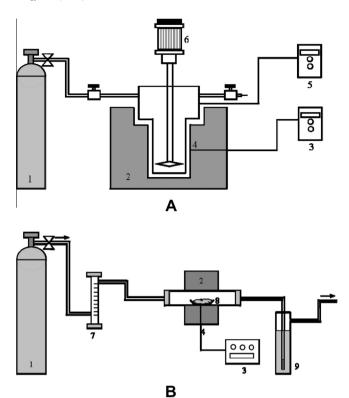


Fig. 1. Schematic diagrams of (a) HTC reactor and (b) LTP reactor for biomass upgrading (1: N₂ cylinder, 2: Heater, 3: Temperature controller, 4: Thermocouple, 5: Pressure meter, 6: Stirrer, 7: Gas meter, 8: Alumina boat, and 9: Gas trap).

were used for various investigations in the present study. Fig. 1 shows the schematic diagrams of HTC and LTP reactors for biomass upgrading. A laboratory scale semi-batch 500-ml Parr autoclave reactor (USA) was used for the production of hydrothermal biochar and the detailed description of HTC can be found elsewhere [3]. The LTP of the biomass was conducted in a horizontal fixed-bed quartz reactor (60 mm i.d., 800 mm length). The biomass sample was loaded into an alumina boat which was then placed in a quartz tube and argon gas was introduced to maintain an inert atmosphere in the experimental system. The furnace was heated to the 250 °C at a heating rate of 20 °C/min and kept at this final temperature for 20 min, before cooling it down to room temperature. The biochars produced from HTC and LTP were designated as HC and PY, respectively. For example, CF-HC and CF-PY refer to the biochar produced from HTC and LTP of CF, respectively. All the raw biomass and biochars were dried at 105 °C for 24 h for subsequent analysis. The biochar yield and energy yield are defined as follows:

Biochar yield =
$$\frac{\text{Mass of the biochar}}{\text{Mass of the raw biomass}} \times 100\%$$
 (1)

Table 1Ultimate analysis and energy analysis of hydrothermal and pyrolytic biochars produced from CF and EL.

| | Ultimate analysis (%) | | | | | Energy analysis | | |
|-------|-----------------------|------|------|------|----------------|-------------------|-------------|------------------|
| | С | Н | S | N | O ^a | Biochar yield (%) | HHV (MJ/kg) | Energy yield (%) |
| CF | 47.75 | 5.61 | 0.23 | 0.90 | 45.51 | = | 19.2 | = |
| CF-HC | 67.10 | 5.20 | 0.29 | 0.98 | 26.43 | 45.3 | 28.4 | 67.0 |
| CF-PY | 53.77 | 4.76 | 0.28 | 1.13 | 40.06 | 69.2 | 21.5 | 77.5 |
| EL | 46.96 | 6.22 | 0.77 | 1.23 | 44.82 | _ | 18.9 | _ |
| EL-HC | 62.30 | 5.47 | 0.44 | 1.44 | 30.35 | 46.4 | 25.8 | 63.3 |
| EL-PY | 49.83 | 5.77 | 0.90 | 1.28 | 42.22 | 72.2 | 20.3 | 77.6 |

^a By difference.

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