



Pore characteristics and fractal properties of biochar obtained from the pyrolysis of coarse wood in a fluidized-bed reactor

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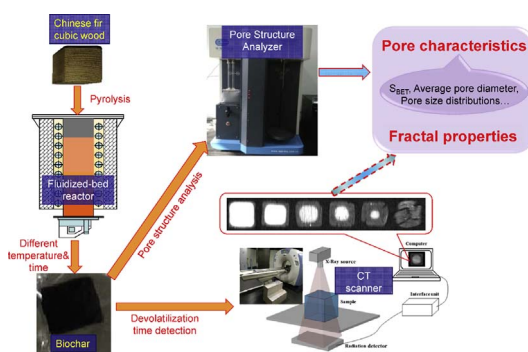
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HIGHLIGHTS

- Biochar formation of coarse wood are studied aided by a computed-tomography detector.
- Pore characteristics and fractal properties of biochar were also investigated.
- Fluidized-bed coarse wood pyrolysis reduced time much compared with other methods.
- Coarse samples with complete devolatilization have well-developed pore structure.
- Fractal analysis yielded additional information on the pore characteristics.

GRAPHICAL ABSTRACT



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ABSTRACT

Conversion of coarse wood into biochar is being considered as one of several waste disposal and energy recycling options. In this study, biochar was produced by coarse wood of Chinese fir from furniture factory in a fluidized-bed reactor under pyrolysis condition. Aided by a computed-tomography detection system, the pyrolysis process of the coarse wood was visible without destroying the solid sample. The resultant samples were characterized for pore structure property related to its potential use in adsorption. The results show that coarse samples with complete devolatilization have the well-developed pore structure. The maximum surface areas of the solid samples are 33.87 and 214.60 m²/g for coarse wood pyrolyzed at 500, and 700 °C, respectively. Most of the pores in the solid samples are mesopores with diameters between 2 and 10 nm. Fluidized-bed coarse wood pyrolysis significantly reduced the pyrolysis time compared with other sawdust pyrolysis methods. Fractal analysis yielded additional information on the roughness of the pore surfaces and the pore structures. The results indicated that the coarse wood has potential application in a fluidized-bed reactor to convert into high-quality biochar with higher efficiency.

1. Introduction

Global trade in furniture has grown rapidly in the past decades. Some developing countries, such as China, Malaysia, Indonesia, and Mexico, account for a large per cent of the wooden furniture production

in the world [1]. The increasing amount of leftover materials produced has been one of the primary waste disposal and energy recycling issues in these countries. These recovered woods were used in various options including papermaking, animal bedding, chopsticks manufacturing, and recycling into particleboard. However, the products with lower

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value-added from these applications limited their markets. Therefore, enhancing availability and utilization of these recovered woods from timber processing manufacturers has recently become the subject of increasing attention [2].

Solid biochar, also known as “black gold,” has drawn considerable international attention in recent years. It is the raw material for activated carbon and has many applications, such as in gas purification, sewage treatment, and heavy metal adsorption [3]. Biochar mainly produced using the methods of biomass pyrolysis [4,5], and hydrothermal carbonization [6]. In general, the biomass most used within the published literatures are sawdust [7], rice husk [8], straw [9], bagasse [10], etc. These biomasses have the similar properties including the smaller particle size, lower weight, and lower bulk density, resulting in high cost of procuring, harvesting, storing, and transporting biomass to a processing facility. This also significantly limited the widespread adoption of biochar. Compared with these biomasses, the recovered wood from timber processing manufacturers can be processed into coarse wood with higher bulk density. Using this feedstock can provide a solution to the shortcomings associated with small particle biomass utilization [11]. Therefore, it is very attractive to explore efficient ways to obtain the high-quality biochar using the coarse wood.

Fluidized-bed (FB) biomass pyrolysis is considered as one of the most promising thermochemical biomass–energy conversion technologies because of its excellent fuel flexibility, uniform temperature distribution, excellent solid–fluid mixing, and high heat transfer rate [12–15]. Several published literatures reported that the high-quality biochar was produced with higher efficiency using this method. Kang et al. found that the biochar obtained from the sawdust pyrolysis in a bench-scale FB had a high heat value of around 26 MJ/kg [16]. Wang et al. studied the fast pyrolysis of *Chlorella vulgaris* remnants using a FB reactor, and they found that the biochar yield was 31 wt%, which is higher than those data obtained from the fast pyrolysis of other biomass [17]. Therefore, these results also offer a promising conversion process to produce high-quality biochar using coarse wood in existing FB reactor. However, until now, there have been few reports focusing on the FB pyrolysis of coarse wood.

In the FB biomass pyrolysis, devolatilization time is a key parameter in optimizing the processing setting and designing the FB reactor. Compared to biomass with small particle size, coarse wood particles tend to be larger, and the large particle size affects the pyrolysis process significantly [12,18]; that is, during pyrolysis, the rate of the heat transfer into the inner part of the feed decreases with increasing particle size. Moreover, the internal heat and mass transfer in coarse wood are complicated and non-uniform, resulting in the significantly delayed devolatilization time [12]. This delay is significant considering the short residence time of commercial FB reactor. Meanwhile, the bed temperature exhibits a considerable influence on the devolatilization time for all the shapes and size of wood particles studied [12]. Therefore, determination of the devolatilization time at different bed temperatures is the key and difficult step for the FB coarse wood pyrolysis operation. Several techniques have been reported to measure the devolatilization time in a FB reactor. Stubington and Sumaryono [19] reported a continuous gas analysis technique that does not consider the time lag arising from the diffusion of volatiles from the center of the particles to their surfaces. Ross et al. [20] discussed the determination of particle-center temperature history. The time taken for the center temperature to become equal to the bed temperature of FB was used as the devolatilization time. However, this method lacks accuracy because the devolatilization temperature is usually lower than the bed temperature. There have also been reports of a flame-extinction-time method that is based on the determination of flaming [21], which is the period between the particle contacting the bed and the extinction of any visible flame at the surface of the bed. This method also excludes the time lag for the transport of volatiles from the center of the particle to their surfaces. Meanwhile, the flame may not be visible instantaneously at the surface of the bed under the turbulent fluidization. This method

was also analyzed by Dhanarathinam et al. [22]. They proposed a new method using X-ray detection to detect the devolatilization time. This method successfully solves the measurement problems concerning the devolatilization time in two directions; however, coarse wood is the material with anisotropic property. The devolatilization velocities in different directions are different. Therefore, to obtain the development of the inner boundary in different directions, the sample should be treated with X-ray method at least twice. In the current work, a new method, a combination of non-destructive detection methods using computed-tomography (CT) detectors, was proposed for the determination of the devolatilization time. Using this method, the problems discussed above can be solved successfully once and for all.

It is well documented that the pore property of biochar is a highly important factor for its adsorption application [23,24]. However, due to the larger particle size of coarse wood, its porous structure formation is much different with that of biomass with smaller particle size. Coarse sample at any instance before complete pyrolysis in FB reactor has three different regions, namely (i) completely pyrolyzed region (particle surface and close to surface) (ii) partially pyrolyzed region and (iii) inner core virgin wood. Typically, the pores of the raw material were not well developed [25]. Effect of the quantity of inner core virgin wood during the pyrolysis process on the pore characteristics of the product is significantly. Therefore, to explore the pore development of coarse wood sample, the low-pressure nitrogen gas adsorption (LP-N₂GA) analysis aided by the results of devolatilization time were applied in this study. Furthermore, the traditional Euclidean model has been proposed to describe species diffusion and adsorption in the interior of a porous material. However, this model is limited and cannot accurately describe the complex surface morphology and pore structure of complicated samples [26]. Consequently, fractal geometry is being widely used in many fields and has been proven to be a powerful and reasonable method for the quantitative description of irregular or disordered self-similar fractals that occur in nature [27,28]. In fractal systems, most physical and chemical properties are closely related to their fractal characteristics, such as chemical reactions in fractal pore structures, reactivity distributions, and the mass transfer of gas in the pores. In the published literatures, fractal analysis was used to study the pore characteristics of biomass pyrolysis [29–31]. However, for the products with more complex surface morphology and pore structure in this study, more investigation is still needed to determine the corresponding relationship between the pore characteristics and the fractal data both obtained from the nitrogen gas adsorption analysis.

In the present study, we converted coarse wood into biochar in a FB reactor at two temperatures (500 °C and 700 °C) and under nitrogen atmosphere for its prospective use as an absorbent. Coarse particles of Chinese fir from the furniture factory were used as the input material. The pyrolysis process of coarse wood in a FB reactor was investigated aided by a CT detection system. Effects of the pyrolysis temperature and time on the pore characteristics and fractal properties of biochar were also studied. At last, these data obtained in this study and those in published literatures were compared.

2. Methods

2.1. Experimental setup

The wood pyrolysis experiments were carried out in a laboratory-scale turbulent fluidized-bed reactor system. Fig. 1 displays the schematic diagram of the FB reactor and CT scanner systems. Fig. 1A shows the schematic diagram of the experimental setup, which is mainly composed of the fluidized-bed reactor, gas supply system, and data acquisition system. The gas supply system consists of a group of nitrogen cylinders and a mass flow meter. The reactor, a cylinder-shaped chamber, was fabricated from 316-grade stainless steel. The reactor was 750 mm in height with a 108-mm inner diameter and 4-mm thick walls. An air distributor was fitted at the bottom of the chamber to ensure that

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