



Distribution and evolution of organic matter phases during biochar formation and their importance in carbon loss and pore structure



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HIGHLIGHTS

- Distribution and evolution of organic matter phases of biochars were investigated.
- Phases are neutral detergent soluble fraction, hemicellulose, cellulose and lignin.
- Organic phase evolution related to carbon loss in pyrolysis and pore structure.
- Cellulose content in biomass has positive relationship with C retention in biochar.
- Pore structure formation of biochar was attributed to lignin and mineral matrices.

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ABSTRACT

This study investigated the distribution and evolution of organic phases during biochar formation from twelve waste biomass and at the highest heating temperatures between 200 °C and 650 °C. Relation of the organic phase transformation to the carbon loss and pore structure was also analyzed. The organic phases in both feedstock biomass and the derived biochar were sequentially separated into four fractions: neutral detergent soluble fraction, hemicellulose, cellulose, and lignin. Plant-based residues mainly contained cellulose (25.8–64.6%), while municipal solid wastes had a large fraction of neutral detergent soluble fraction (22.9–65.0%). Transformation of cellulose into detergent soluble fraction and hemicellulose initially happened at the charring temperature between 100 °C and 200 °C, and the complete transformation was observed at the higher temperatures from 200 °C to 350 °C. The high lignin amount in biochar may be partly formed from the aromatization of cellulose fraction in addition to the contribution from the existing lignin in feedstock. All biochars had small total pore volumes ranging from 0.009 cm³ g⁻¹ to 0.278 cm³ g⁻¹ and were a type of mesoporous material with the pore sizes between 2 nm and 30 nm. The decrease of detergent soluble fraction, hemicellulose, and cellulose fractions had little effect on pore formation, but it was positively related to the C loss during pyrolysis. Pore volume and surface area seemed to have a positive relationship with lignin percentage and insoluble minerals in feedstock. This study provided insight into the mechanism of biochar formation related to the C loss and pore structure evolution. It will help produce the designated biochar with different environmental functions.

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1. Introduction

Biochar is a carbon-rich substance and encompasses carbon forms with varying degrees of aromatization [1]. There have been numerous studies concerning the physico-chemical properties of biochar and its potential applications [2–4]. Biochar is primarily being actively explored as a tool for long-term soil-carbon sequestration [5]. It has also been proved that addition of biochar into soil

could improve soil quality and increase soil fertility, while simultaneously relieving greenhouse gas emissions [6–8]. Biochar can also be used as a sorbent to remove or immobilize heavy metals and/or organic contaminants from water or in soil [9–11].

Carbon sequestration capacity is one of the most important characteristic of biochar in terms of the atmospheric CO₂ reduction. It involves carbon loss during pyrolysis and the carbon stability of biochar products in soil. Lot of work has been proved that biochar-carbon is relative stable in soil, and it has no obvious influence on greenhouse gases emission [12]. Thus carbon loss during pyrolysis seems important to a carbon sequestration capacity of

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biochar. In previous studies, production yield has been widely used to quantify the mass loss and residue of biomass transformation into biochar. In this study, we attempted to gain insight into the evolution of carbon forms during pyrolysis through the transformation of organic matter phases including hemicellulose, cellulose and lignin. These fractions are not independent, they can be transformed into each other and have differing yields at different biochar formation temperatures. The distribution of these organic matter fractions may determine the carbon forms of biochar.

Pore structure is another one of the important characteristics of biochar, and it has a close relationship with many environmental behaviors of biochar such as adsorption and detoxification of contaminants [13,14]. Many researchers have reported some biochars' specific surface area, which is much smaller than that of active carbons [15]. The general conclusion is that surface area increases with production temperature [16,17]. Yet, further information about the pore volume, average pore size, and pore size distribution of biochar is fairly limited. We assume that the pore structure of biochar may also be affected by the distribution and evolution of organic phases during biochar formation.

The objective of this study is to determine the organic matter phases, carbon loss and pore characteristics of biochar produced from various biomasses, as well as the evolution of these characteristics along a representative charring temperature range. During the pyrolysis process of biomass to biochar, organic fractions such as hemicellulose, cellulose, and lignin undergo a significant change, leading to the formation or alteration of many biochar properties [18]. Thus, an insight into the evolution of organic (C-related) phase during biochar formation would facilitate us to further understand the underlying mechanisms about the carbon loss and pore structure of biochar. The relationship between these chemical phases and carbon loss, as well as pore structure is explored. The potential relationship of these properties with biochar's environmental applications is also discussed.

2. Materials and methods

2.1. Biomass sampling and biochar production

Twelve biomass residues were collected from a farm located in the suburban of Shanghai City, China and divided into two main categories on the basis of their sources: one was the plant-based waste biomass including sawdust, grass, wheat straw, peanut shell, chlorella, and waterweeds. The other one was the municipal waste including cow manure, pig manure, shrimp hull, bone dregs, wastewater sludge, and waste paper. Each biomass sample was air-dried at 60 °C to a moisture content of lower than 5% and then ground to less than 1 cm for biochar production. Details on the production of biochar were described previously [19]. To evaluate organic phases distribution during conversion from biomass to biochar, all feedstocks were heated to the designated temperature of 500 °C under N₂ gas with a heating rate of 18 °C·min⁻¹ and held at the highest temperature for 4 h. To examine the evolution of organic phases during biochar formation over charring temperatures, one municipal waste-based feedstock (pig manure) and one plant-based feedstock (wheat straw) were chosen and pyrolyzed at four different temperatures of 200 °C, 350 °C, 500 °C, and 650 °C, with the same holding time of 4 h. The two samples are typical bio-wastes and are produced with a great amount per year. Also, these two materials have very different properties in organic fractions concentration and minerals concentration and they can represent plant-like wastes and municipal solid wastes, respectively. Note that low holding temperatures (<500 °C) and short heating times (<2 h) are generally used for biochar production [20], a longer time (4 h) and higher temperature (650 °C) were

applied to minimize the effects of pyrolysis kinetics that could result in incomplete biochar formation [9].

2.2. Sequential extractions of organic fractions

The original biomass and their derived biochars were sequentially fractionated into four organic fractions: neutral detergent soluble fraction (NDF), hemicellulose (HEM), cellulose (CEL), lignin (LIG) using a modified method proposed by Van Soest [21–24]. The solvents used in the fractionation were chosen according to their gradual dissolving capacity. First, the sample was extracted with a neutral detergent solution at 100 °C for 60 min. The weight loss (%) from this step represents the most soluble sample fraction (NDF). The residual solid was sequentially extracted by acid detergent solution (HEM) and 72% H₂SO₄ (CEL). The remaining residue consisted of lignin, cell, cutin and suberin, representing the lignin-like fraction (LIG) and ash (ASH). ASH can be measured by heating at 650 °C for 5 h.

The neutral detergent solution consisted of 30 g L⁻¹ sodium lauryl sulfate, 18.61 g L⁻¹ disodium ethylenediamine tetraacetate, 6.81 g L⁻¹ Na₂B₄O₇·10H₂O, 4.56 g L⁻¹ Na₂HPO₄, and 1% triethylene glycol. The acid detergent solution consisted of 20 g L⁻¹ hexadecyltrimethylammonium bromide and 1.0 mol L⁻¹ H₂SO₄. Acid detergent fiber is an AOAC-approved method of analysis [25]. A common variation of the acid detergent fiber method is to use neutral detergent solution as a pretreatment [26].

2.3. Pore structure and total carbon analysis of biochar

The biochar samples were pretreated in vacuum for 2-h under temperature of 50 °C lower than the biochar production temperature. The pore structure characteristics were determined using a BET-N₂ specific surface area (SSA) analyzer (BK122T-B, JWGB, China) according to the standard of the International Union of Pure and Applied Chemistry (IUPAC). Specific surface area is obtained based on multi-point BET (Brunauer–Emmett–Teller) adsorption isotherm. The analysis of mesopore and macropore was based on BJH (Barrett–Joyner–Halenda) method [27]. Micropore calculation was based on HK (Horváth–Kawazoe) method [28]. Total carbon analysis of biochar was conducted on an elemental analyzer (Vario EL III, Elementar, Germany). Point of zero net charge (PZNC) was determined by potentiometric titration [29].

3. Results and discussion

3.1. Basic physical and chemical properties of biochars

The basic physicochemical properties of biochars obtained from all selected twelve feedstocks including total carbon, fixed carbon, yield, pH, cation exchange capacity (CEC) and ash content have been reported in detail in our previous publication [19]. In this study, we presented the elements content (C, H, N, and O) of biomasses and biochars, as well as the point of zero net charge (PZNC) of biochars (Tables 1 and 2). Overall, plant-based biomass and biochar contained more C and O than municipal waste biomass and biochar except plant-like waterweed and municipal-based wastewater in which the contrary case was observed (Table 1). Though waterweed is plant-like, it is rich in minerals [19]; so it contained low contents of C and O. For waste paper, although it is municipal-source based, it is made of wood; so it contained high contents of C and O. Both plant-based biochar and municipal waste biochar have similar PZNC of between 9 and 11 (Table 1). Increasing heating temperature increased C and PZNC in both wheat straw and pig manure biochars, while H and O contents decreased with increasing heating temperature (Table 2). That is to say, elevating

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