

Effects of La-involvement on biomass pyrolysis behaviors and properties of produced biochar

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Abstract: In order to evaluate the effects of La-involvement on biomass pyrolysis behaviors and properties of produced biochar, oak sawdust (OS) and corn straw (CS) were employed for thermogravimetric-differential thermogravimetric (TG-DTG) analysis and producing biochar with/without La-involvement. Results indicated the initial and final temperatures were shifted toward lower temperature as LaCl₃ was involved in pyrolysis. Mass loss and average mass loss rate during pyrolysis decreased with La-involvement. The kinetics indicated that the first-order reaction kinetic model well matched the pyrolysis process. As La-involved OS and CS were employed, their apparent activation energies (E_a) were reduced, and their pyrolysis characteristic index (I) were higher comparing with the OS and CS without La-involvement. Based on the produced biochar, the yield and ash content were increased by La-involvement, and the O/C ratio and iodine sorption value (ISV) were also enhanced. Obviously, the loaded LaCl₃ could facilitate pyrolysis process, and the produced biochar exhibited a great adsorption potential in aqueous solution. According to the results from FT-IR (Fourier transform infrared spectroscopy) analysis, La in pyrolysis functioned as accelerating lignin decomposition via condensing -OH, breaking aliphatic C-H and aromatic rings on lignin, cutting the links of C-O-C among the monomers in lignocellulose. LaCl₃ was finally converted to La₂O₃ in biochar after pyrolysis.

Keywords: lanthanum; pyrolysis kinetics; biochar; properties; rare earths

Biomass pyrolysis, is a thermo-chemical decomposition process, in which biomass was heated in the absence of oxygen and can be converted into different products including bio-oil and pyrolytic gas that can be used as fuels and chemicals^[1]. As an important by-product, biochar, a solid carbon-rich organic matter, also can be obtained from biomass pyrolysis. The specific properties of biochar generally are characterized by high aromaticity, large surface area, highly porous structure, enriched surface functional groups and mineral components^[2,3]. Due to its stability and unique physicochemical properties, biochar has raised great concerns throughout the world for the potential applications in carbon sequestration^[4], soil amendment^[5,6] and polluted environment remediation^[7-9].

Currently, biochar has been widely accepted in soil application, because it can provide multiple environmental benefits, for instance, improving soil quality, reducing greenhouse gas emissions, increasing long-term sequestration of carbon and controlling nutrients sorption and release^[10]. Consequently, some positive effects on

plant growth can be observed after biochar application in soil^[11]. Biochar also plays a crucial role in heavy metals immobilization, pesticides removal in pedosphere^[5,12]. Besides, special absorption capacity in removal of organic and inorganic contaminants from aqueous solution also can be achieved by biochar application^[8]. It is well known that the functional applications of biochar are closely related to its inherent physicochemical properties, such as surface area, polarity, organic functional groups and mineral contents^[5], which are greatly controlled by the feedstock types^[13,14], pyrolysis conditions^[15,16] and pre-treatment or post-treatment methods^[1,17]. For example, biochar derived from oak and corn straw exhibited obvious difference on sorption capacities to NH₄⁺ due to their distinguishable cation exchange and pH, which was mainly attributed to the discrepancy of feedstocks^[18]. Several studies indicated increasing pyrolytic temperature increased ash content, specific surface area, pore volume, basic functional groups and pH of biochar, which greatly affected the ions removal and soil properties^[6,19]. Moreover, the biochar stability can be promoted

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greatly at higher pyrolytic temperatures which may benefit the carbon sequestration^[16]. In addition, Wang et al.^[17] prepared an engineered biochar by pyrolyzing hickory wood pretreated with KMnO_4 . The pretreatment not only introduced ultrafine MnO_x particles on the carbon surface within the biochar matrix, but also increased the amount of surface oxygen-containing functional groups and surface area. As a result, the engineered biochar displayed much better sorption ability to heavy metal ions than the pristine biochar. Thus, it is essential to investigate the physicochemical properties so that the potential mechanisms of some special functions in biochar application can be elucidated in depth.

In our previous work, the biochar obtained from La-involved biomass pyrolysis displayed great capacities on removing ammonium, nitrate and phosphate from aqueous solution. The maximum sorption capacities of NH_4^+ , NO_3^- and PO_4^{3-} significantly were to 10.1, 100.0 and 142.7 mg/g, which were 1.9-, 11.2- and 4.5-folds higher comparing with the biochar without La-involvement^[20]. The results demonstrated that La-loaded biochar could be potentially applied to control the typical pollutants in eutrophication. However, the effects of La-involvement on biomass pyrolysis behaviors and the physicochemical properties have not been given a full understanding until now.

In order to fully understand the occurring pyrolysis process with La-involvement, and make it possible to tune the morphology and functionality of the resulting biochar, two representative feedstocks of oak sawdust (OS) and corn straw (CS) were employed for pyrolysis with/without La-involvement. Their pyrolysis behaviors and kinetics were investigated via thermogravimetric-differential thermogravimetric analysis (TG-DTG). Some basic physicochemical properties of produced biochar were differentiated and compared to elucidate the possible mechanisms on the special function of removing N and P.

1 Materials and methods

1.1 Feedstocks

2 kinds of biomass, including oak sawdust (OS) and corn straw (CS) were employed, which were collected from the local furniture plant and farmland, respectively. The collected feedstocks were air-dried and milled through a 40-mesh screen (~0.45 mm). The milled feedstocks were dried at 105 °C for 6.0 h prior to use. The dried OS and CS (40.00 g) were immersed in 1000 mL of 0.1 mol/L LaCl_3 solution with magnetically stirring for 6.0 h. The impregnated biomass afterwards was vacuum-filtered and oven-dried at 105 °C lasting for 6.0 h before pyrolysis. Similarly, these 2 biomasses were also immersed in deionized (DI) water (without LaCl_3) for

preparing biochar as a comparison (CK).

1.2 Biochar preparation

30.00 g prepared OS and CS were pyrolyzed in a tube furnace (OTL 1200, Nanjing NanDa Instrument Co., Ltd., China) at 400 °C for 30 min with a heating rate of 10 °C/min. N_2 (purity of 99.999%) was employed as protective gas to form an oxygen-free atmosphere with a flow rate of 0.1 m³/h. After pyrolysis, the tube furnace was rapidly cooled down to room temperature, and the biochar was collected for the further analysis. 2 biochars obtained with La-involvement were labeled as La-OSBC, La-CSBC, respectively, and 2 corresponding CKs were named as CK-OSBC and CK-CSBC. The yield of biochar was defined as the weight ratio (dry basis) of the produced biochar and the employed biomass for pyrolysis.

1.3 Characterization of feedstocks and biochars

The proximate analysis, including ash, volatile matter (VM) and fixed carbon (FC), was carried out according to the standard method in ASTM D 1762-84^[21]. The component analysis for OS and CS was performed according to the method of National Renewable Energy Laboratory (NREL)^[22]. Biochar pH was measured by a pH meter (PHS-3C, LeiCi Instruments Co., Ltd., China) with a biochar-to-water ratio of 1:20 (m/v)^[20]. Elemental content of biochar (C, H, N, S) was analyzed using an elemental analyzer (EA112, Thermo Finnigan, USA) and the oxygen (O) content was calculated by the difference^[3]. Surface morphology of biochar was determined by using a scanning electron microscopy (SEM) equipped with an energy-dispersive X-ray spectroscopy (EDS) (SU1510, Hitachi, Japan) for analyzing surface mineral compounds. Fourier transform infrared spectrometer (FT-IR) was recorded in the range of 4000–400 cm^{-1} with a resolution of 4 cm^{-1} and 64 scans per sample (Nicolet 6700, Thermo Fisher Scientific, USA). The method of Brunauer-Emmett-Teller (BET) was employed to determine the surface area (SA) of biochar via N_2 sorption isotherms. The iodine sorption value (ISV) of biochar was employed to evaluate the adsorption capacity, which was measured according to Hessler's method^[6].

1.4 TG-DTG analysis

In order to investigate the pyrolysis behaviors with/without La-involvement, La-impregnated OS (La-OS), CS (La-CS), and their corresponding blanks (CK-OS and CK-CS) were conducted on a thermogravimetric-differential thermal analyzer (TG-DTG) (SDT Q600, TA instrument, USA). The experiment was performed at the heating rate of 10 °C/min from ambient temperature to 700 °C under a N_2 atmosphere.

Several pyrolysis characteristic parameters can be obtained by TG-DTG curves^[23], including (1) the initial decomposition temperature (T_i , °C), (2) the terminal de-

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