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Review

The structure evolution of biochar from biomass pyrolysis and its correlation with gas pollutant adsorption performance

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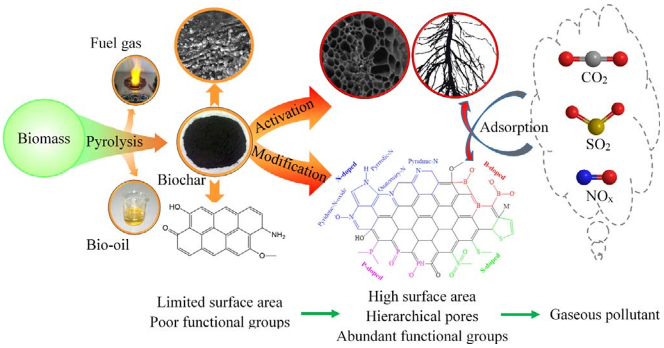
GRAPHICAL ABSTRACT



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ABSTRACT

Biochar is carbon-rich, porous and with a great potential in gas pollutant controlling. The physical-chemical structure of biochar is important for the application. This paper firstly reviewed the evolution behavior of physical-chemical structure for biochar during pyrolysis. At lower temperature (< 500 °C), biomass firstly transformed to "3D network of benzene rings" with abundant functional groups. With temperature increasing (500–700 °C), it converted to "2D structure of fused rings" with abundant porosity. As temperature increasing further (> 700 °C), it may transit into a "graphite microcrystalline structure", the porosity and functional groups were diminished correspondingly. The modification of biochar and its application as sorbent for gas pollutant were also reviewed. Activation and doping can significantly increase the porosity and special functional groups in biochar, which is favorable for gas pollutant adsorption. With a higher porosity, the adsorption capacity of gas pollutant is bigger, however, the functional groups determined the sorption stability of gas pollutant.

1. Introduction

As one of the most important renewable energy sources, biomass and its conversion have attracted widely attention. It is significantly important that biomass is the only renewable carbon source which can replace not only fossil fuels in the production of energy carriers (bio-fuel) but also many important chemicals (bio-chemicals) (Ptasinski, 2016). Pyrolysis is an important conversion technology of biomass to produce biofuel and bio-chemicals, meanwhile, biochar is also the major products during biomass pyrolysis (Kan et al., 2016). Currently, how to utilize biochar has received increasing attention.

After retrospective study and literature review, firstly biochar is defined as the charcoal for soil amendment. Numerous researchers have proved that the potential biochar applications on soil amendment

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include carbon sequestration, soil fertility improvement, pollution remediation, and agricultural by-product/waste recycling (Ahmad et al., 2014; Brassard et al., 2016; Gul & Whalen, 2016; Nguyen et al., 2017; Si et al., 2016). Currently, since the carbon-rich and porous property, biochar has attracted many researchers to investigate the non-soil amendment application. Liu et al. (2015) reviewed the biochar-based functional materials and these application including catalytic utilization, energy storage and environmental protection, and they pointed out that biochar can be used as sustainable platform carbon material for the high-value application. Qian et al. (2015) also provided an overview in other several biochar utilizations including its use as catalyst, fuel cell and gas storage. The potential of utilization as adsorbent for biochar is especially attracted a widely investigation. Ahmad et al. (2014) and Tan et al. (2015)reviewed the application of biochar as sorbent for the removal of pollutants in water. Tan et al. (2015) suggested the interaction between biocharsand water pollutants includes electrostatic attraction, ion-exchange, physical adsorption, and chemical bonding (complexation and/or precipitation). To effectively increase the sorption capacity of the organic contaminants, biochar should have high surface area, good microposity and hydrophobicity; while, to remove inorganic/polar organic contaminants, biochar needs more oxygen-containing functional groups, electrostatic attraction, and precipitation (Ahmad et al., 2014). Not only as sorbent for the removal of pollutants in water, biochar also has a great application potential as sorbent for the removal of pollutants in flue gas, such as SO_2, NO_X and Hg, however, the review of biochar as sorbent for the removal of pollutants in flue gas is limited.

The application prospect of biochar has a strong correlation with the pyrolysis parameter. Several researchers reviewed the influence of pyrolysis process parameter on biochar property (Brassard et al., 2016; Kan et al., 2016; Tripathi et al., 2016). Pyrolysis process parameters such as temperature, heating rate, residence time influence biochar yield and its physical-chemical structure. Indeed, the physical-chemical structure of biochar determine the sorption capacity of biochar (Liu et al., 2015). The deeply understanding of evolution on physical-chemical structure of biochar during pyrolysis may provide the guideline how to choice a biochar product with a best sorption capacity. On the other hand, if the biochar is undergone the modification treatment like activation, its sorption capacity may increase dramatically. Tan et al. (2017) reviewed the production of activated carbon using biochar as potential sustainable precursors, and point out that these activated biochar appears to be a new potential cost-effective and environmentally-friendly carbon materials with great application prospect in water pollution treatment.

This paper firstly provides the overview of recent advances on evolution of physical-chemical structure in biochar, and the mechanism of biochar modification, such as activation and doping, is also discussed, with expect to find out how to fabricate a desired structure in biochar. Finally, an overview of biochar application as sorbent for the removal of pollutants in flue gas is provided.

2. Evolution of physical structure of bio-char during pyrolysis

2.1. Surface area of solid char

The physical structure of bio-char underwent great changes during biomass pyrolysis. Fig. 1 shows the evolution of the surface area of solid char resulted from biomass pyrolysis at variant temperatures (Chen et al., 2012; Fu et al., 2009a; Fu et al., 2009b; Fu et al., 2012a; Fu et al., 2012b; Jimenez-Cordero et al., 2013; Newalkar et al., 2014; Pottmaier et al., 2013; Yang et al., 2016; Zhang et al., 2015; Zou et al., 2016). The surface area of feedstock is from 0.1 to 3.2 m^2/g, which is mainly contributed by the nature channel pores for the mass transmission during the growth process as a plant (Chen et al., 2012).

Below 400 °C, no obvious change showed for biomass pyrolytic chars, especially the porosity of chars decreased, which may be affected by the incomplete removal of volatile matter from biomass (Jimenez-Cordero et al., 2013). A dramatically increase of surface area of biomass chars is observed begin at 400–500 °C, and the increase trend may remain until 900 °C. The value of surface area increases from $\sim$10 m^2/g to 100–500 m^2/g, affected by feedstock and pyrolysis condition. The increase of surface area at this temperature range was attributed to the significantly releasing of volatiles which favors the development of some new porosities (Cetin et al., 2005; Wafiq et al., 2016). The measured surface area remain at a constant or begin decreasing from the maximum when above 900 °C. The amount of pores may be decreased by the structural ordering, pore widening, and/or the coalescence of neighboring pores, and meanwhile, some pores may be blocked from the softening, melting and fusing of ash (Fu et al., 2009b). Furthermore, the collapse microporous structure and the occlusion of the micropores by the secondary reaction between chars and volatiles were also contributed to the surface area decrease (Burhenne et al., 2013). The conversion of the amorphous carbon structure to graphite microcrystalline structure also might lead to the decrease of surface area (Chen et al., 2012).

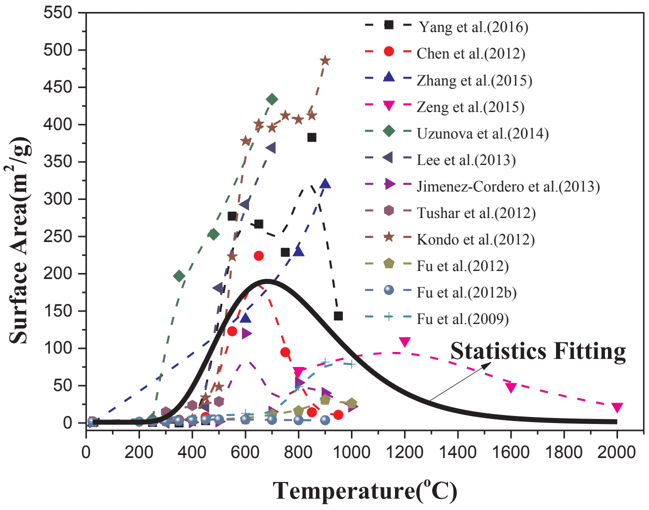

Fig. 1. The evolution of surface area at variant temperature during biomass pyrolysis.

Zeng et al. (2015) investigated the surface area of beech wood chars pyrolyzed at higher temperature (> 600–2000 °C), and found that the surface area increased from 70.2 m^2/g to 110.2 m^2/g with temperature increased from 800 °C to 1200 °C then it decreased dramatically to 22.2 m^2/g at 2000 °C. The process “intensifying volatile release” and the process “thermal deactivation over 900 °C” effected the surface area of biochar.

2.2. The morphology

With pore structure evolution, the surface morphologyalso showed great change with pyrolysis undergoing. Firstly, the pyrolytic chars remained most of features of parental fuels despite treatment temperatures and heating rates (Pottmaier et al., 2013). The porous structure in corncob (Bourke et al., 2007), “honeycomb-like” pore structures in sugarcane (Kondo et al., 2012), the anatomical structure in wood (Burhenne et al., 2013) and the origin surface morphology structure in rice husk and sawdust (Zhang et al., 2015) were all preserved after pyrolysisat 400–900 °C.

Secondly, devolatilization during pyrolysis created many new pores and etched surface of char particle irregularly and rough (Halim & Swithenbank, 2016; Uzunova et al., 2014), which was the dominant observation on the chars obtained at variant temperature. It was found that the control shrank of chars became thinner and twisted; meanwhile, the mechanical intensity exerted by pyrolysis influenced the biochar structure and the effect was accelerated as pyrolysis