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Engineered biochar from microwave-assisted catalytic pyrolysis of switchgrass for increasing water-holding capacity and fertility of sandy soil

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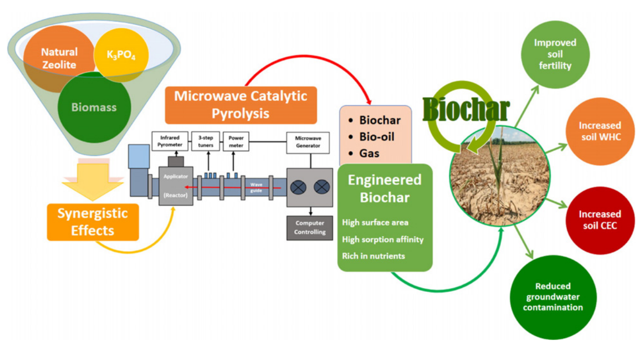
HIGHLIGHTS

- High quality biochar was made by catalytic pyrolysis in a microwave reactor.
- High heating rate and good biochar quality were achieved using K_3PO_4 and clinoptilolite mixture.
- Biochars showed significant increase in soil WHC and CEC.
- Microwave catalytic pyrolysis can produce efficient biochar at low temperature (300 °C).

GRAPHICAL ABSTRACT



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ABSTRACT

Engineered biochars produced from microwave-assisted catalytic pyrolysis of switchgrass have been evaluated in terms of their ability on improving water holding capacity (WHC), cation exchange capacity (CEC) and fertility of loamy sand soil. The addition of K_3PO_4, clinoptilolite and/or bentonite as catalysts during the pyrolysis process increased biochar surface area and plant nutrient contents. Adding biochar produced with 10 wt.% K_3PO_4 + 10 wt.% clinoptilolite as catalysts to the soil at 2 wt% load increased soil WHC by 98% and 57% compared to the treatments without biochar (control) and with 10 wt.% clinoptilolite, respectively. Synergistic effects on increased soil WHC were manifested for biochars produced from combinations of two additives compared to single additive, which may be the result of increased biochar microporosity due to increased microwave heating rate. Biochar produced from microwave catalytic pyrolysis was more efficient in increasing the soil WHC due to its high porosity in comparison with the biochar produced from conventional pyrolysis at the same conditions. The increases in soil CEC varied widely compared to the control soil, ranging from 17 to 220% for the treatments with biochars produced with 10 wt% clinoptilolite at 400 °C, and 30 wt% K_3PO_4 at 300 °C, respectively. Strong positive correlations also exist among soil WHC with CEC and biochar micropore area. Biochar from microwave-assisted catalytic pyrolysis appears to be a novel approach for producing biochar with high sorption affinity and high CEC. These catalysts remaining in the biochar product would provide essential nutrients for the growth of bioenergy and food crops.

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1. Introduction

The global demand for bioenergy crops is rapidly increasing as a result of increasing population and the quest for renewable sources of energy posing greater stress on the water and land resources (Basso et al., 2013; Zhang and You, 2013). In addition, many soils are becoming less suitable for food crops and bioenergy plants cultivation because of water deficiency and low soil fertility (Basso et al., 2013; Zhang and You, 2013; Koide et al., 2014). Increase in drought conditions also poses severe negative impacts on sandy soils through water loss by evaporation and facilitates the degradation of organic matter. Furthermore, water drains rapidly through sandy soils, leaching soluble nutrients and contaminating groundwater (Cai et al., 2011; Zhang and You, 2013; Koide et al., 2014). To reduce the competition between crop productions for bioenergy and food, bioenergy crops should be cultivated in low productivity areas or marginal lands. Soil limitations (salinization, desertification and water shortage) need to be alleviated to ensure food security and increase biofuel crops production. One of the major reasons for improving soil fertility is to address the issue of food security, particularly in South Asia and sub-Saharan Africa, with malnutrition in 22 and 32% of the total population, respectively (FAO, 2006). Increasing the ability of soil to retain water and nutrients is a crucial need for achieving higher growth of bioenergy raw materials in desert land, arid and semi-arid areas and to provide enough food for the soaring population (Cai et al., 2011; Basso et al., 2013; Zhang and You, 2013; Koide et al., 2014; Agegnehu et al., 2016). Biochar application to soil may mitigate some of the portended deficiency in water as a consequence of climate change effects in order to retain the future productivity of bioenergy crops (Mulcahy et al., 2013; Koide et al., 2014; Agegnehu et al., 2016). Biochar, a co-product of thermochemical conversion of biomass into valuable biofuel, can be applied to soil as an amendment to improve the sustainability of biomass and crop production, enrich fertility and quality of agricultural soils (Laird et al., 2010; Novak et al., 2012; Zhang and You, 2013; Koide et al., 2014). Nevertheless, the information on distinguishing feedstocks and proper pyrolysis conditions to maximize the capability of soils is sparse (Novak et al., 2012). Thus, more research is needed to develop suitable approaches to improve biochar characteristics with respect to soil applications and increase biofuel crops yield and food production.

The ability of biochar to improve soil WHC is associated with many factors: surface functional groups, total pore volume, porosity structure and specific surface area (Ismadji et al., 2005; Zhang and You, 2013). It has been found that the presence of polar oxygen-containing groups raises hydrophilicity of carbon materials, aiding the formation of hydrogen bonds (Pastor-Villegas et al., 2010). Another important factor is biochar porosity structure, where the adsorption process occurs mostly in micropores. Macro and meso-pores play important roles in the adsorption process where they act as conduits for adsorbate to reach the micropores (Pastor-Villegas et al., 2006; Zhang and You, 2013). The specific surface area of biochar is generally higher than sand and comparable to clay. Blending biochar with soil would raise the total soil specific surface area (Chan et al., 2007; Novak et al., 2012).

Specific surface area and cation exchange capacity (CEC) are considered indirect measures of the ability of soils to hold water and retain nutrients (e.g., ammonium, nitrate, P, Mg and Ca), which will improve soil fertility, and bind different contaminants (Major et al., 2009; Laird et al., 2010; Crombie et al., 2014). Improving N-fertilizer use efficiency would lead to reduced fertilizer application rates, and reduced GHG emissions from the whole process, starting from the production of fertilizer to the application to soil (Major et al., 2009; Crombie et al., 2014; Wang et al., 2015). Therefore, there is an increasing need for new methods to create oxygenated biochar possessing high CEC to increase soil CEC. Such biochar could retain soil nutrients, reduce fertilizer leaching, sequester carbon and improve soil hydrological properties (Major et al., 2009; Lee et al., 2011; Agegnehu et al., 2016). Most biochars created from virgin biomass without additives possess fewer nutrients compared to conventional fertilizers. In addition, most of biochar studies focused on biochars produced from slow conventional heating methods which are not suitable for industrial production (Zimmerman, 2010; Novak et al., 2012; Kinney et al., 2012; Crombie et al., 2014). Producing biochar capable of releasing nutrients for plants is thus in great need and interest (Novak et al., 2012; Spokas et al., 2012; Crombie et al., 2014).

Clinoptilolite is a natural zeolite which can retain water up to 60% of their weight due to the high porosity of its crystalline structure, high CEC, relatively high absorption rate and dehydration capacities. It can also reduce the amount of water required for irrigation, improve water use efficiency in semiarid and arid areas and can serve as a carrier of agricultural pesticides due to their high absorption capacity which in turn will reduce groundwater contamination and increase plant growth by ameliorating the value of fertilizer. Thus, clinoptilolite will diminish the costs of water and fertilizer significantly by holding useful plant nutrients (Polat et al., 2004; Milosevic and Milosevic, 2009; Ozbahce et al., 2014). Clinoptilolite also possesses a great potential for heavy metal immobilization in contaminated soils (Reháková et al., 2004). Bentonite improves soil fertility, increases soil water and nutrient retention, and improves the agrochemical and physical properties of soil, resulting in significantly increased sorghum grain yield compared to soil without bentonite (Agafonov and Khovanskii, 2014). Furthermore, bentonite increased the surface charge and CEC of different types of soils, increased the availability of nutrients in low fertility soils and improves fertilizer use efficiency (Croker et al., 2004; Satje and Nelson, 2009). Bentonite also plays an important role in detoxifying heavy metals, chlorinated hydrocarbons, and oxyanions from contaminated sites (Vandenhove et al., 2003; Gates et al., 2009). K_3PO_4 is used as a soil fertilizer for providing plants with two essential nutrients (potassium and phosphorus). Phosphorus is considered as a major nutrient for plants and also a good immobilizer for heavy metals such as As, Pb, Cd, Co and Ni which are extremely harmful for plants (Bolan et al., 2014). As a consequence, mixing these additives/catalysts (K_3PO_4, clinoptilolite and bentonite) to biomass would greatly improve the physical and chemical properties of the produced biochars, and increase their sorption affinity for water, nutrients, and heavy metals.

Microwave-assisted pyrolysis has been proven to be more efficient than conventional heating and produces biochars with higher surface area than conventional heating at low temperatures (Mohamed et al., 2016). Despite the fact that microwave heating is a unique heating method, most of biomass materials are poor in absorbing microwave (Luque et al., 2012). A microwave absorbing additive can be mixed with biomass to speed up microwave heating. Based on their potential effectiveness for microwave absorption and catalytic performance, those potential additives (K_3PO_4, clinoptilolite and bentonite) have been selected and mixed with switchgrass to improve biochar quality for soil applications.

The overall goal of this research is to use the multi-functional catalysts for biomass pyrolysis: (1) as a good microwave absorber for speeding up the heating rate; (2) as a catalyst to improve the quality of bio-oil and biochar; and (3) as a nutrients/soil conditioner imbedded in biochar to increase its performance as a fertilizer or soil remediate. The current study focuses on evaluating the performance of the produced biochars in terms of their ability to improve soil water holding capacity, cation exchange capacity and fertility of loamy sand soil, investigating the synergistic effects of the combinations of two different catalysts on biochar properties in contrast with the addition of one catalyst, and examining the effect of the incubation period on WHC and CEC of the incorporated soil with the biochar.

2. Materials and methods

2.1. Biochar preparation

Biochars used in this study were produced from microwave-assisted catalytic pyrolysis of switchgrass at 400 °C in a 750 W 2.45 GHz single