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Mechanistic study of the influence of pyrolysis conditions on potassium speciation in biochar "preparation-application" process

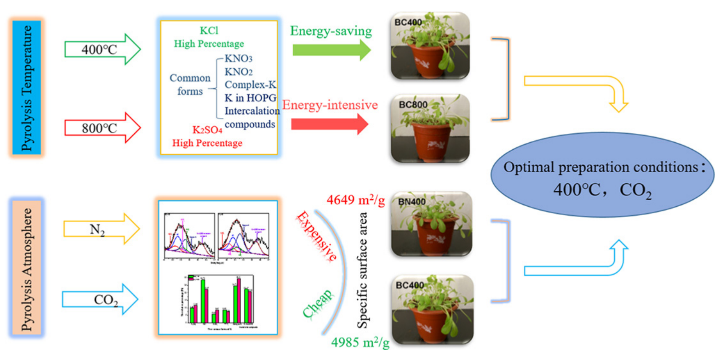
Zhongxin Tan *, Liyun Liu, Limei Zhang, Qiaoyun Huang

College of Resources and Environment, Huazhong Agricultural University, Wuhan, 430070, PR China

HIGHLIGHTS

- N_2 and CO_2 atmospheres were used to produce novel biochar.
- Biochar made under CO_2 atmosphere is better for improving soil fertility.
- Optimal conditions for biochar preparation are about 400 °C and CO_2 atmosphere.
- A transport mode for K species in "straw-biochar-application" system was proposed.

GRAPHICAL ABSTRACT



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ABSTRACT

Biochar samples produced from rice straw by pyrolysis at different temperatures (400 °C and 800 °C) and under different atmospheres (N_2 and CO_2) were applied to lettuce growth in a 'preparation-application' system. The conversion of potassium in the prepared biochar and the effect of the temperature used for pyrolysis on the bioavailability of potassium in the biochar were investigated. Root samples from lettuce plants grown with and without application of biochar were assayed by X-ray photoelectron spectroscopy (XPS). The optimal conditions for preparation of biochar to achieve the maximum bioavailability of potassium (i.e. for returning biochar to soil) were thus determined. Complex-K, a stable speciation of potassium in rice straw, was transformed into potassium sulfate, potassium nitrate, potassium nitrite, and potassium chloride after oxygen-limited pyrolysis. The aforementioned ionic-state potassium species can be directly absorbed and used by plants. Decomposition of the stable speciation of potassium during the pyrolysis process was more effective at higher temperature, whereas the pyrolysis atmosphere (CO_2 and N_2) had little effect on the quality of the biochar. Based on the potassium speciation in the biochar, the preparation cost, and the plant growth and rigor after the application of returning biochar to soil, 400 °C and CO_2 atmosphere were the most appropriate conditions for preparation of biochar.

1. Introduction

Potassium, nitrogen, and phosphorus are the three major nutrient elements considered essential for plant growth. Many plants require a high amount of potassium. The potassium content in plants is only exceeded by the nitrogen content, where potassium accounts for 0.3–5% of the dry weight in the tissues of higher plants.

Monovalent potassium can be absorbed by plants and is readily transported. Monovalent potassium participates in the normal physiological metabolism of crops, but is not a constituent of biological macromolecules. Because of its high reactivity, potassium may affect numerous

* Corresponding author.
E-mail address: tanzx1977@163.com (Z. Tan).

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Table 1
Effects of pyrolysis atmosphere and temperature on K transformation.

Pyrolysis conditions	Changes in K form and content	References
Pyrolysis temperature: 200 °C, 400 °C, 600 °C, 800 °C Under oxygen-limited conditions	TK: increased with increasing temperature	Al-Wabel & Al-Omran (2013)
Pyrolysis temperature: 300 °C, 350 °C, 400 °C, 500 °C, 600 °C Under N_2 atmosphere	TK, Water-K, and HCl-K: all increased as the temperature increased	Zheng et al. (2013)
Pyrolysis temperature: 300 °C, 400 °C, 500 °C, 600 °C, 700 °C, Under N_2 atmosphere	Extractable-K: first increased, then declined Reached a maximum at 400 °C	Wu et al. (2012)
Pyrolysis temperature: 500 °C, 700 °C Under oxygen-limited conditions	TK in biochars derived from different feedstocks: increased with increasing temperature	Wang et al., (2013)
Pyrolysis temperature: 350 °C, 700 °C Under N_2 atmosphere	TK content in biochars derived from different feedstocks: 700 °C > 350 °C	Cantrell et al. (2012)
Pyrolysis temperature: 250 °C, 300 °C, 350 °C, 400 °C, 450 °C	TK content in biochars for different retention times: increased with increasing temperature	Peng et al. (2011)

biochemical and biophysical processes (Zhou, 2010). Potassium can enhance the permeability of tissues to cations, adjust turgor pressure, and control stomatal closure to prevent excessive loss of water from plants in dry and windy conditions, thus improving the drought-resistance of the plants. Moreover, potassium can promote the formation of protein and starch, reduce the amount of soluble sugar available to pathogenic bacteria, and reduce the reproduction and transmission of pathogenic bacteria.

Loss of potassium from soil is mainly due to absorption by crops and leaching, whereas the main supply of potassium is from fertilizers and precipitation. However, at present, most fertilizers applied to soil contain nitrogen and phosphorus as the major constituents; thus, the potassium content in soil is generally inadequate, which has a serious impact on the growth and yield of crops. Nevertheless, excessive application of potassium is undesirable. Therefore, it is necessary to find a method of reducing potassium leaching from soil and to achieve timely supply of potassium to plants to aid nutrition. Biochar contains a large amount of "activated" potassium, which can be used as a soil-conditioner to provide a large amount of K (Zhang, 2012). Moreover, biochar has high adsorption capacity (Zhang et al., 2009; Rondon et al., 2005) and can retain the nutritive potassium in soil to provide 'a steady stream of potassium' for the growth of crops.

Potassium is an alkali metal that is present in plant biomass in high concentrations. In plant biomass, potassium occurs partially in the speciation of water-soluble salts and the rest is bound to carboxyl groups or other functional groups. Because about 90% of K in biomass is present in the speciation of water-soluble salts or can be exchanged with other ions, K has high mobility. Potassium plays an important role in the chemical utilization of biomass and becomes volatile during pyrolysis (Salo & Moitahedi, 1998).

In the process of thermochemical conversion, metallic species in biomass are transformed (including partial conversion of potassium into gaseous products) or dissolve out. The process can be divided into two stages. (1) Due to its low thermo-stability, organic potassium is released from the biomass and converted into the gaseous phase at lower temperature (500 °C); (2) under high-temperature conditions, the inorganic potassium in biomass enters the gaseous phase due to an increase in the vapour pressure in the biomass. The alkali metal elements in rice straw biomass are in the water-soluble state, and under high-temperature conditions, the Moore curve is very similar to that for chlorine. Therefore, the alkali metal elements may exist mainly in the speciation of chloride under high-temperature conditions (Tang, 2004).

Most of the studies about potassium as a nutrient in biochar have focused on the change in the total potassium (TK) content and have concentrated on the variation in the speciation of potassium with temperature (see Table 1).

In the prior studies (Table 1) and as indicated in the aforementioned discussion, there has been very limited discussion about the effect of the pyrolysis conditions on the speciation of potassium and the resulting bioavailability of potassium in the biochar (i.e. the feedback-effect for K transport to plants). Therefore, to investigate the speciation of potassium in biochar, we herein employ X-ray photoelectron spectroscopy (XPS) to analyse biochar prepared under different temperature and

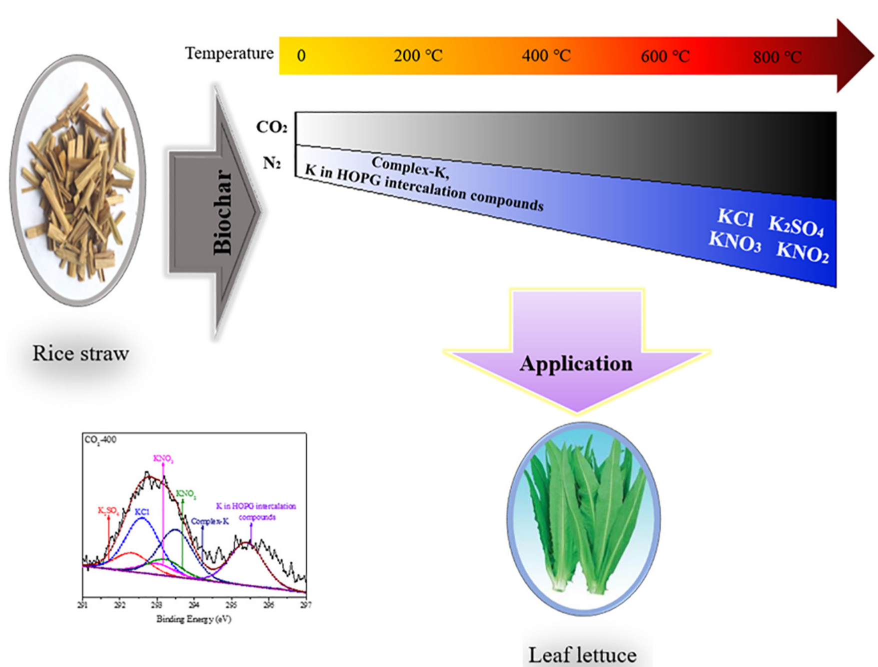

Fig. 1. Experimental flow chart.