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Effects of ash-forming temperature on recycling property of bottom ashes from rice residues

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HIGHLIGHTS

- Ash water solubilities decrease by 80% when temperature increases from 400 to 800 °C.
- K, Na, S, and Cl are major dissolved elements in bottom ashes of rice residues.
- Recycling property of ash from different parts of the same crop vary considerably.

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ABSTRACT

In this paper, effects of ash-forming temperature on recycling property of bottom ashes obtained from combustion of rice straw and rice husk were investigated. Ash solubility and element solubility were chosen for representing recycling property and they were determined based on the measurement of element content using X-ray Fluorescence Spectrometer (XRF). Results show that water solubilities of both bottom ashes decrease with increasing ash-forming temperature and the water solubility of rice straw ash is higher than that of rice husk ash. Investigations also reveal that the easily soluble elements are K, Cl, S, Na in rice straw ash and K, S in rice husk ash. While the solubilities of K and Na decrease with the increasing ash-forming temperature, the solubilities of S and Cl are independent upon this temperature. Difference between the two ashes indicates that the recycling property of ashes from different parts of the same crop varies considerably.

1. Introduction

Sustainable agriculture implies to insure the fertility of soil ecosystem by balancing the input and loss of its nutrients. The high food yield nowadays leads to a fast loss of soil nutrients and these nutrients are transported to crops. Most of them are stored in the agro-residues because ash content in agro-residues (mean 7.8%, estimated [1]) is significantly higher than that in food (e.g. 0.3–1.3% for wheat flour [2]) and the straw-to-grain ratios are normally more than 1.0 [3]. Utilization of agro-residues via thermo-chemical processes, such as combustion [5], gasification [6], pyrolysis [7], is worldwide applied and produces a large amount of biomass ash [4]. Recirculation of nutrients by spreading the biomass ash as fertilizer [8–10] or soil amendment [11,12] is good for sustainable agricultural development, as well as cost reduction of ash deposit [13].

Plant nutrients can be classified into three groups: (a) main macronutrients: nitrogen (N), potassium (K), phosphorus (P); (b) secondary macronutrients: calcium (Ca), sulfur (S), magnesium (Mg); and (c) micronutrients: copper (Cu), iron (Fe), manganese (Mn), chloride (Cl), zinc (Zn), molybdenum (Mo), boron (B), silicon (Si), cobalt (Co), vanadium (V) plus rare mineral catalysts [14]. Most of them are accessible to plants only in the ionic form. One of the fundamental questions in soil application of biomass ash is what amount of accessible nutrients [4]. Thus, solubilities of biomass ash and its elements are the key properties for the recirculation. According to their dissolving characteristics, components in biomass ash can be divided into four groups—water soluble, ammonium acetate soluble, HCl soluble, and solid residue with insoluble—based on a standard leaching operation in water, ammonium acetate, and hydrochloric acid sequentially [4,15]. Because that some of these leaching conditions are not possible in natural soil, to make the problem simple, ash solubility and element solubility in distilled water were chosen for representing recycling property of biomass ash in this paper.

Water solubilities of biomass ash and its elements have been broadly explored. It was found that the water solubility of bio-ash from straw combustion collected from Danish Electrostatic Precipitator can be up to 61.0% [16]. When the distilled water to

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solid ratio is 20:1 and pH is 13, 58% of the total K and 65% of the total Na are leached [17]. 90% of potassium and sodium exists as water soluble salts in biomass ash [12]. The mean contents of the water soluble elements leached from different biomass ashes produced mainly from woody and straw biomass are Cl (68%) > S (58%) > K (44%) > Na (36%) [18]. All elements in biomass ash are grouped into three classes: (a) easily soluble elements (K, S, B, Na); (b) less soluble elements (Ca, Mg, Si, Fe); (c) very insoluble elements (P) [19]. However, elements in different ashes have different solubilities [5]: approximately 30% of K in ashes of straw and cereal from incinerators is water soluble; P in straw and cereal ashes is partially water soluble and that in woodchip and bark ashes is almost insoluble; Cl and S in ashes of straw and cereal are almost completely water soluble but S in ash of wood is only partially water soluble (about 20%).

It is well-known that ash content and property are significantly affected by ash-forming temperature [15,18]. However, the effects of ash-forming temperature on water solubilities of biomass ash and its elements have been scarcely reported.

Rice is the agricultural commodity with the third-highest worldwide production according to the statistics provided by the Food and Agriculture Organization of the United States (FAOSTAT 2012). The total rice production in 2014 is 476 million tons in the world. It is 146 million tons in China and accounts for about 40% of the total Chinese food production. As the byproduct, massive rice residues (rice straw and rice husk) are burned in field, domestic stove and boilers. The recirculation of the ash from rice residues plays a great role in balancing the nutrients in the soil compartment system.

In this paper, the effects of temperature on water solubilities of ashes from rice straw powder and rice husk powder were investigated experimentally. The objectives are to assess and to compare the recycling property of ashes from different parts of rice residue.

2. Experiments and data processing

2.1. Materials

The rice husk and rice straw samples were collected from rural northern China in 2014. The materials were milled to a particle size of less than 1 mm. To facilitate the milling process, the air-dried rice straw was first oven dried at 105 °C for 12 h to decrease its moisture. The proximate and ultimate analysis of the samples were performed and the results are summarized in Table 1. It can be seen that, in addition to the obvious difference in moisture content of the two materials, the ash content of rice husk is almost 1.5 times that of rice straw.

2.2. Ash preparation

Ashes were prepared in a muffle furnace (MF) at different ash-forming temperatures by a modification of standard procedure (GB/T 38731 2012). About 4–5 g of biomass powder was put into a crucible, heated from the ambient temperature to ash-forming temperature in MF at the heating rate of 10 °C/min. Then they were kept in MF at the ash-forming temperature for 4 h. After the temperature of the MF drops to less than 200 °C, the ash left in the crucibles was taken out and placed in a desiccator, cooled to the ambient temperature, weighted and then sealed in a sample bag for further analysis. It should be noted that the ash we analyzed here is often referred as bottom ash [10].

In this paper, the temperature range of 400–800 °C with the interval of 50 °C was chosen for investigation. Because when ash-forming temperature was above 800 °C, most of ashes adhered to crucible and the water solubilities of the ashes were very low.

Table 1
Properties of experimental materials.

Materials	Proximate analysis (%)				Element analysis (%)		
	Moisture	Volatile	Ash	Fixed carbon	C	H	O
Rice husk	7.48	59.77	18.24	14.5	49.3	6.1	43.6
Rice straw	3.58	68.93	13.17	14.32	42.4	6.9	48.8

2.3. Measurement of ash solubility

Ash solubility was measured in accordance with the Chinese standard GB/T 8307-2002. The operation procedure is as follows: total ash (m_o) of about 0.2–0.3 g was put in a beaker of 50 ml, and about 25 ml of distilled water was added into it. Then the mixture was heated and boiled for 2 min. The solution was filtered through a quantitative filter paper. The insoluble ash was washed using another 25 ml of distilled water and the wash was repeated for 5 times. After that, the filter paper and the insoluble ash were collected and dried in an oven at 105 °C for 0.5 h. Then they were put into the MF and burned at 550 °C for 2 h. After cooling, the insoluble ash (m_r) was weighed. The ash solubility (S_A) was calculated using Eq. (1).

$$S_A = 1 - m_r/m_o \tag{1}$$

The water insoluble ash was then sealed in a sample bag for further analysis.

2.4. Measurement of element content in ash

The element content of the original and the water insoluble ash was measured using X-ray Fluorescence Spectrometer (XRF). The sample ash was pressed into a slice with the diameter of 20 mm and the thickness of 3–5 mm. Then it was fully scanned in vacuum by a ZSX100e XRF Analyzer. The obtained data was processed using semi-quantitative nonstandard analysis program (SQX) and the element contents were determined.

2.5. Calculation of element solubility

According to mass conservation law, the water insoluble fraction of the element i (WIF_i) is the ratio of residue mass of this element in the insoluble ash (m_r) to the total mass of this element in the original ash (m_o). It was calculated using Eq. (2).

$$\mathrm{WIF}_i = (m_r \times Y_{r,i})/(m_o \times Y_{o,i}) = (1 - S_A) \times (Y_{r,i}/Y_{o,i}) \tag{2}$$

where $Y_{r,i}$ and $Y_{o,i}$ are the contents of the element i in the insoluble ashes and in the original ashes, respectively. Thus, the water solubility of element i (WSF_i) can be calculated using Eq. (3).

$$\mathrm{WSF}_i = 1 - \mathrm{WIF}_i \tag{3}$$

Since the XRF measurement is a semi-quantitative method, to assess the reliability of our calculation, silicon (Si) tracer method (in which all silicon is assumed to be insoluble) is also used to calculate element solubility as shown in Eq. (4).

$$\mathrm{WSF}_i = 1 - (Y_{r,i}/Y_{o,i})/(Y_{r,\mathrm{Si}}/Y_{o,\mathrm{Si}}) \tag{4}$$

where $Y_{r,\mathrm{Si}}$ and $Y_{o,\mathrm{Si}}$ are the contents of Si in the insoluble ashes and in the original ashes, respectively.

2.6. Calculation of fertilizer content of ash and recycling content of raw biomass

Potassium (K) is one of the main macronutrients of fertilizer. The water soluble fraction of K in ash ($\mathrm{WSF}_{K,A}$) is very important