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The effects of leaching methods on the combustion characteristics of rice straw

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ABSTRACT

The effects of leaching methods on the removal rate of alkali metals, the combustion characteristics and ash behaviors of rice straw were studied by inductively coupled plasma-atomic emission spectroscopy (ICP-AES), thermogravimetric analysis (TGA) and scanning electron microscope coupled with energy-dispersive spectroscopy (SEM/EDS), respectively. The results show that the removal rate of alkali metals, maximum rate of volatile releasing and ash content all increase with the concentration of HNO_3 used for leaching. De-ionized water leaching reduces the ash content by 10% and has the same effects on straw combustion characteristics as 2.0 kmol m^{-3} HNO_3. 0.5 kmol m^{-3} H_3PO_4 can remove 93% of alkali metals in straw and activate the organic bound alkali metals which retard char combustion dramatically. Experimental results also indicate that the alkali metals in straw may decrease the peak temperature and maximum rate of volatile releasing. The maximum rate of char combustion is subjected to the combined actions of the catalytic effect and melting behavior of alkali species in the straw ash.

1. Introduction

In the past 20 years, biomass as a kind of alternative and CO_2-neutral energy source has been paid a great deal of attention [1]. Biomass fuels contain inherent inorganic elements, including alkali metals, chloride and minor quantities of Si, Ca, Mg, etc. Many of these elements, especially alkali metals, are involved in reactions leading to ash fouling, slagging [2] and bed agglomerate in fluidized bed combustion systems [3,4]. Over 90% of alkali metals in biomass are present in water-soluble and ion exchangeable form and are susceptible to vaporize during heating [5,6]. It has been found that inorganic alkali metals in biomass are easily removed in both tap and distilled water [7]. Acid leaching is considered as a more effective way to remove alkali metals. Davidsson et al. [8] reported that washing with water reduces the alkali emission from wood waste and wheat straw by 5–30%, while acid leaching can reduce the emission by around 70% in the temperature range 200–500 °C. They also reported that washing is ineffective in removing alkali metals bound to the organic structure of biomass. Jenkins et al. [9] reported that reductions in the concentrations of alkali metals by leaching yield remarkable improvement in ash fusion temperature. And alkali metals in biomass have an effect on reaction rates and are thought to be catalytic to pyrolysis. Hesisheng et al. [10] found that the cellulose decomposition peaks of washed rice hull occurs at higher temperatures and the volatile yield increases at the expense of char. Fahmi et al. [11] performed the TGA analysis on de-ionized leached Festuca grass and a strong catalytic effect of alkali metal was observed in biomass pyrolysis and combustion. Jones et al. [12] studied the thermal and catalytic behavior of potassium in the willow coppice combustion. They reported that alkali metals play the most significant role in

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the rate of devolatilization and have a clear catalytic effect on char burnout.

As mentioned above, although it has been proven that leaching can remove most of alkali metals in biomass and alleviate the operational problems of biomass-fired systems, the studies on the effects of different leaching methods on the combustion characteristics of biomass have not been reported up to now. In this study, the effects of leaching with HNO_3, H_3PO_4 and de-ionized water on the removal rate of alkali metals, combustion characteristics and ash behaviors of straw will be studied by ICP-AES, TGA and SEM/EDS, respectively.

2. Rice straw and leaching methods

The rice straw used in this study was harvested from a rice field in Heilongjiang province of China in 2010 and stored in a dry place. Table 1 shows the proximate and ultimate analyses of rice straw as well as the composition of straw ash. The raw straw was first broken into pieces of 1–2 mm in length and oven dried at 105 °C for 1d. Then, the rice straw particles were pulverized to fine grains of 100–150 μm in size for the leaching treatments. Two kinds of leaching methods were used in this study: simple leaching with de-ionized water and acid leaching with HNO_3 and H_3PO_4. De-ionized water leaching was applied to simulate procedures realistic for large-scale leaching applications. HNO_3 is a kind of strong acid. H_3PO_4 is a kind of mild acid and usually used as activation in biomass pyrolysis [13]. In addition, leaching with concentrated acid was not feasible in practice, so 0.5, 2.0 and 5.0 kmol m^{-3} dilute HNO_3 as well as 0.5 kmol m^{-3} dilute H_3PO_4 were used as the acid leaching solutions in this study. All leaching treatments were performed at the room temperature. Per 10 g of straw samples were soaked in 500 ml of each leaching solution for 2 h. After filtration, they were washed with 100 ml of de-ionized water then dried. The summary of leaching methods was shown in Table 2.

Table 2 – Summary of straw samples used in this study.

1	Untreated, 100–150 μm
2	Leached in 0.5 kmol m^{-3} HNO_3 acid for 2 h, 100–150 μm
3	Leached in 2.0 kmol m^{-3} HNO_3 acid for 2 h, 100–150 μm
4	Leached in 5.0 kmol m^{-3} HNO_3 acid for 2 h, 100–150 μm
5	Leached in de-ionized water for 2 h, 100–150 μm
6	Leached in 0.5 kmol m^{-3} H_3PO_4 acid for 2 h, 100–150 μm

3. Results and discussion

3.1. Removal rate of alkali metals for different leaching methods

In order to study the effectiveness of different leaching methods in removing alkali metals from the rice straw, ICP-AES is performed on every sample. Each sample is digested in perchloric acid plus hydrofluoric acid followed by nitric acid for 12 h, and then heated with vibration for 6 h. Above treatment can break down and digest entire sample. The acid solution is then diluted to bring the concentration of elements of interest into the range of linear response of instrument. ICP-AES results are listed in Table 3. For comparison, the removal rates of K and Na for different leaching methods are shown in Fig. 1. Here, the removal rate is defined as the percentage reduction of element concentration. From Fig. 1, it can be seen that the removal rates of K and Na are almost equal for the same leaching method. This indicates that the existence forms and chemical characteristics of K and Na in straw are almost same. In the following, the removal rate of alkali metals will refer to the averaged removal rate of K and Na. For HNO_3 leaching, the removal rate of alkali metals increases from 66% to 81% with HNO_3 concentration increasing from 0.5 to 5.0 kmol m^{-3}. For de-ionized water leaching, the removal rate of alkali metal is around 73% and very close to 2.0 kmol m^{-3} HNO_3 leaching. It is noticeable that for 0.5 kmol m^{-3} H_3PO_4 leaching, the removal rate of alkali metals reaches upto 93% and is much higher than other leaching methods. It has been reported that over 90% of alkali metals in rice straw are water soluble and ion exchangeable [5]. The residual organic bounded alkali metals can hardly be removed by acid and water leaching [8]. According to present results, if de-ionized water leaching removes all water soluble alkali metals in straw, 0.5 kmol m^{-3} H_3PO_4 leaching should already remove all water soluble and ion exchangeable alkali metals. While, 0.5 kmol m^{-3} HNO_3 leaching cannot even remove all water soluble alkali metals. In addition, from Table 3, it can be seen that although H_3PO_4 leaching can remove K and Na effectively, it is not good at removing other inorganic metals such as Ca and Mg. For HNO_3 leaching, the removal rates of K, Na, Ca and Mg are almost equal. De-ionized water can remove most of Mg and more than half of Ca.

3.2. Effects of leaching methods on the behaviors of straw ash

The TGA analyses are performed on all samples in order to study the effects of leaching methods on the combustion characteristics of them. Per 20 mg of each sample is heated

Table 1 – Proximate analysis of straw and ultimate analysis of straw ash.

Proximate analysis of rice straw (as received) (g kg^{-1})								
Moisture		Ash		Volatile	Fixed carbon		Heat value	
49.9		138.7		650.5	160.9		13,860 kJ/kg	
Ultimate analysis of rice straw (dry basis) (g kg^{-1})								
Carbon		Hydrogen		Nitrogen	Sulfur		Oxygen	
419.3		56.4		10.9	0.8		366.6	
Ultimate analysis of rice straw ash (g kg^{-1})								
Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	Fe_2O_3
19.8	24.7	19.4	562.3	19.3	49.5	194.0	101.2	9.8

Table 3 – Element content of straw samples (g kg^{-1}).

	Untreated	HNO_3 (kmol m^{-3})			H_3PO_4 (kmol m^{-3})	De-ionized water
		0.5	2.0	5.0	0.5	
Na	1.418	0.479	0.398	0.27	0.094	0.346
K	8.20	2.732	2.134	1.558	0.523	2. 094
Ca	2.128	0.679	0.56	0.426	1.648	0.962
Mg	2.072	0.675	0.575	0.437	1.187	0.193