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Fusion and transformation properties of the inorganic components in biomass ash

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HIGHLIGHTS

- Comprehensive transformation of inorganic components was studied by multi-means.
- Crystalline structure transformation of different biomass ashes was in-depth explored.
- Systematical analysis using phase diagrams was conducted to get the real fusion property of biomass ash.

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ABSTRACT

In thermochemical utilization of biomass, ash fusion temperature is an important parameter for the efficient and continuous operation of boilers/gasifiers and high value-added utilization of the ash. Fusion characteristics and transformation properties of the inorganic components in biomass ash are investigated using X-ray fluorescence (XRF), thermal gravimetric analyzer (TGA), X-ray diffraction (XRD), ash melting point test system and phase diagrams. XRF and TGA results show the changes of ash content, elemental composition and performance with the variation of temperature. Two main weight loss routes of biomass ash, decomposition and volatilization, are identified. XRD results show the transformation behavior of crystalline structure of different biomass ash. Intense internal reactions that occur in biomass ash at higher temperature generate a large amount of eutectic compounds, which lowered the melting point significantly. The contribution of different ash compositions to fusion can be assessed by binary diagrams while the fusion properties of silica-rich biomass ashes obtained by phase diagrams could be appropriate for industrial running.

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1. Introduction

In the past decades, there has been renewed interest in biomass as an energy source due to the shortcomings of existing fossil fuel energy sources such as greenhouse gas emissions and other harmful effects on the environment [1,2]. Among different bio-energy conversion routes, which are determined by the demand and supply of available types and quantities of biomass, combustion and gasification are the most popular processing technologies [3]. But it is annoying that biomass contains various forms of alkali and alkali earth metals (AAEMs) and considerable amount of silica [4]. As a result, the biomass ash is easy to melt and volatilize [5,6]. So during the combustion or gasification processing, the ash with complex composition and high volatility often leads to slugging, defluidization and erosion/corrosion in thermal convention processing systems [7,8]. In order to improve the operational efficiency of boilers/gasifiers and achieve high value-added utilization of biomass ash, the study of fusion and transformation properties of inorganic elements in biomass ash has been an important issue in the past years.

A number of studies have been carried out so far to investigate the properties of biomass ash through experiment and simulation [4–14]. Niu et al. [9] found that to evaluate biomass ash fusion characteristics the melting characteristics indexes of coal quality for the eutectic compounds formation at high temperature should not be used. Other studies show that the ash-melting temperatures of some cereal grains are lower than 700 °C [11]. But usually, the ash-melting temperature measured by traditional ash melting point testing system cannot faithfully reflect the actual biomass ash fusion characteristics in industrial operations, causing many problems in thermal convention processing systems, especially in biomass-feeding boilers. Thy et al. [12] found that ash with less than 47 wt.% SiO_2 showed significant alkali metal loss. It was also found that ash with higher contents of SiO_2 would retain alkali metal in the melt and crystalline structures, mainly due to the prone reactions between alkali compounds and SiO_2, which stopped the volatilization of alkali chlorides. Direct experimental melting

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studies were carried out to better understand the phase equilibrium and melting behavior of biomass ash [5,13], but so far the research is not comprehensive enough. Although predictive models utilizing equilibrium have been developed [11,15,16], little is known about the high temperature phase relations and the physical and chemical properties of the condensed phases.

Since biomass ash and silicate raw materials are similar in metal oxides composition and high-temperature environment, the phase diagrams from conventional silicate ceramics industry are also used for the analysis of ash fusion characteristics. Huggins et al. [17] used ternary diagrams of SiO_2–Al_2O_3–MO (M represents Fe, Ca, and K_2) to test the coal ash fusibility. But as to biomass ash, there is no systematic analysis by phase diagrams yet. Llorente et al. [18] compared five laboratory methods (fusibility, viscosity and utilization of appropriated phase diagrams, etc.) for predicting the ash sintering during the combustion of biomass to find an accurate and convenient way to evaluate the ash sintering behavior. But the conclusion was drawn only by a single ternary phase diagram of SiO_2–CaO–K_2O, which is not convincing. More diagrams should be employed to better understand the melting mechanism of the complex-composition ash.

Current methods for predicting and preventing fouling and slag deposition are mostly empirical and limited in theoretical analysis. It is necessary to explore the in-depth mechanism for biomass ash fusion characterization. In this study, the fusion characteristics of different biomass ashes are evaluated using XRF, TGA, XRD and ash melting point test system, followed by the systematic utilization of phase diagrams. The comprehensive study of ash transformation behavior was conducted and a new method of ash fusion characteristics evaluation by phase diagrams was proposed. The research findings will be helpful for improving the operational efficiency of biomass-feeding plants in industrial scale.

2. Samples and experimental methods

2.1. Samples

A total of 11 numbered biomass samples are prepared as shown in Table 1. The samples were pulverized and sieved with a 0.45 mm sieve. The results of the proximate and ultimate analysis are listed in Table 1.

The samples can be classified as follows:

Herbaceous biomass: cotton stalk, corn stalk, rape straw, wheat straw, rice straw, tobacco stem. The annual herbaceous biomasses also can be divided into two sub categories. One is soft straw with high ash content (~10%), e.g., wheat straw and rice straw. The other is gray straw with relatively lower ash content and property analogous to woody biomass, e.g., cotton stalk.

Woody biomass: pine, poplar, bamboo. The main feature of woody biomass is its low ash content, about 1%.

Chaff biomass: rice husk, peanut shell. The two chaff biomasses differ remarkably. The rice husk has the ash content as high as 16.8% while the peanut shell only 1.5%.

Table 1
Ultimate and proximate analysis of the samples.

No.	Samples	Ultimate analysis (wt.%)					Proximate analysis (wt.%)			
		N	C	S	O[a]	H	M_{ad}	V_{ad}	A_{ad}	FC_{ad}
1	Cotton stalk	1.2	45.2	0.3	46.9	6.3	5.1	73.0	3.1	16.7
2	Corn stalk	1.2	42.7	0.3	49.6	6.2	5.0	70.2	8.3	16.6
3	Rape straw	0.8	44.9	0.2	47.5	6.6	5.5	74.3	6.3	13.9
4	Wheat straw	0.6	40.4	0.3	52.9	6.0	4.4	68.5	12.9	14.2
5	Rice straw	0.9	37.5	0.1	42.8	5.9	5.0	82.1	7.7	5.1
6	Tobacco stem	2.6	36.1	0.8	55.6	4.9	3.6	68.5	21.7	6.1
7	Pine	0.1	51.0	0.0	42.9	6.0	15.3	70.4	0.2	14.2
8	Poplar	0.3	41.4	0.3	39.1	5.3	6.8	79.7	1.3	12.2
9	Bamboo	0.3	48.4	0.1	45.2	6.1	4.6	72.8	0.7	21.7
10	Rice husk	0.5	48.6	0.1	55.4	5.5	6.3	60.4	16.8	16.6
11	Peanut shell	1.9	60.5	0.4	30.1	7.1	9.1	56.6	1.5	31.9

[a] By difference. ad: the analysis was based on air dried basis.

2.2. Experimental methods

Ashing temperatures were set at 450 °C, 600 °C (ASTM E 1755–01, Standard test method for ash in biomass), 815 °C (GB/T212–2008, Proximate analysis method for coal, China) and 1000 °C for the experiments. In particular, experiments were conducted at 450 °C and 1000 °C to investigate comparatively the transforming properties of inorganic elements in biomass ash.

Ashing process: 1 g of biomass sample in a corundum crucible is placed into a muffle furnace below 100 °C and then heated up to the final temperature at 10 °C/min. Finally, a constant temperature is maintained for a specified period to ensure complete ashing: 5 h for 450 °C, 4 h for 600 °C, 2.5 h for 815 °C, and 1.5 h for 1000 °C. The ash content was obtained from the average value of several ashing trials.

The experimental methods are described as follows:

(a) The composition of biomass ash obtained by XRF (EAGLE III, EDAX Inc., USA) was used for elemental determination. Each ash sample was scanned three times and the average value was used to minimize the error.
(b) A thermal gravimetric analyzer (Perkin Elmer-Diamond TG, USA) was used to study weight loss properties of ash. The sample of approximately 5 mg is heated from room temperature to 1400 °C at a constant heating rate of 10 °C/min with the carrier gas of air. Reproducibility of the apparatus was tested before the experiment.
(c) Ash content and elemental composition analysis can only reflect the apparent changes of elemental content in biomass ash. Further work is required to analyze the interactive reaction of inorganic elements and the change of crystal structure using XRD [19,20]. The crystalline compounds in ash were identified using XRD (X'Pert PRO, PANalytical B.V., Netherlands). Peak identification was performed using High Score Plus software package.
(d) Fusion temperature test of biomass ash was conducted using a sintering instrument (Cabolite, UK). The heating process is observed and photographed using a high definition video camera in the atmosphere of air. The test is based on the changes in shape detected during the heating of the ash cone from 700 °C to 1500 °C under the heating rate of 10 °C/min and the storage interval is 2 °C. The four feature temperatures are recorded by computer, including deformation temperature (DT), softening temperature (ST), hemisphere temperature (HT) and flow temperature (FT). The experiment was conducted after verifying the reproducibility of the apparatus.

3. Results and discussion

3.1. Inorganic elements loss of ash

The results of XRF analysis are listed in Table 2. The main ash compositions are K, Na, Mg, Al, Ca, P, etc. in forms of oxides, silicates or chlorides [21], but the contents of the individual elements in different ashes differ significantly, which lead to great variance in performance.

It can be seen that with the increase of ashing temperature, the ash content drops straightly, especially at higher temperature (e.g., 1000 °C). Furthermore, the relative contents of K, Na and Cl also de-

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