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Fusion characterization of biomass ash

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ABSTRACT

The ash fusion characteristics are important parameters for thermochemical utilization of biomass. In this research, a method for measuring the fusion characteristics of biomass ash by Thermo-mechanical Analyzer, TMA, is described. The typical TMA shrinking ratio curve can be divided into two stages, which are closely related to ash melting behaviors. Several characteristics temperatures based on the TMA curves are used to assess the ash fusion characteristics. A new characteristics temperature, T_m, is proposed to represent the severe melting temperature of biomass ash. The fusion characteristics of six types of biomass ash have been measured by TMA. Compared with standard ash fusibility temperatures (AFT) test, TMA is more suitable for measuring the fusion characteristics of biomass ash. The glassy molten areas of the ash samples are sticky and mainly consist of K-Ca-silicates.

1. Introduction

The energy demand is increasing rapidly in the world. At present, fossil fuel is still the major energy resource. However, for a sustainable development, application of renewable energy is urgently needed. Biomass is one of the most important renewable energy sources which is CO_2-neutral [1]. China has a large amount of biomass production, especially agricultural residues, such as wheat, corn and rice straw. A part of the agricultural residues is burnt in the field in the harvest season, causing severe environmental problems. Therefore, efficient use of biomass conversion techniques is urgently needed, such as combustion and gasification [2]. However, the herbaceous biomass normally has high contents of alkali and silicon [3–5], which results in the formation of sticky molten K-silicates at low temperatures [4–6]. Molten sticky ash may stick to the bed particles, leading to bed agglomeration during combustion and gasification in fluidized bed [7–12].

For making better use of biomass, it's essential to know the fusion characteristics of biomass ash. Some studies have been focused on this issue and several methods have been reported to characterize the ash fusion characteristics.

Standard ash fusibility temperatures(AFT) test is the most common technique to measure the melting temperatures of coal ash [13–15]. Traditional AFT test describes the melting degree of ash using four characteristic temperatures which are related to the geometrical shapes of the sample. The characteristic temperatures obtained from AFT are Deformation, Softening, Hemispherical and Fluid Temperature, which can be represented by DT, ST, HT and FT for short, respectively. But according to GB/T 30726–2014, AFT has poor repeatability (reported ±60 °C for DT, ±80 °C for ST, HT and FT). Furthermore, the initial melting temperature of biomass ash is far lower than DT [16]. Therefore, the characteristics temperatures analyzed by AFT are not suitable to characterize the melting behaviors of biomass ash.

Ash melting behaviors have also been characterized by the changes of electrical conductance or compression strength [17–20]. These characters appear to change with the sintering or initial melting of the sample. But these methods can only measure the onset of melting or sintering, whereas the further melting of ash samples are hard to be evaluated by these methods.

Simultaneous thermal analysis (STA) has been used as an alternative method to analyze the melting properties of chemical substances, but the composition of biomass ash is too complex to be measured by this method [12,16,21]. The shift from exothermic to endothermic conditions on the curve is thought to be indicative

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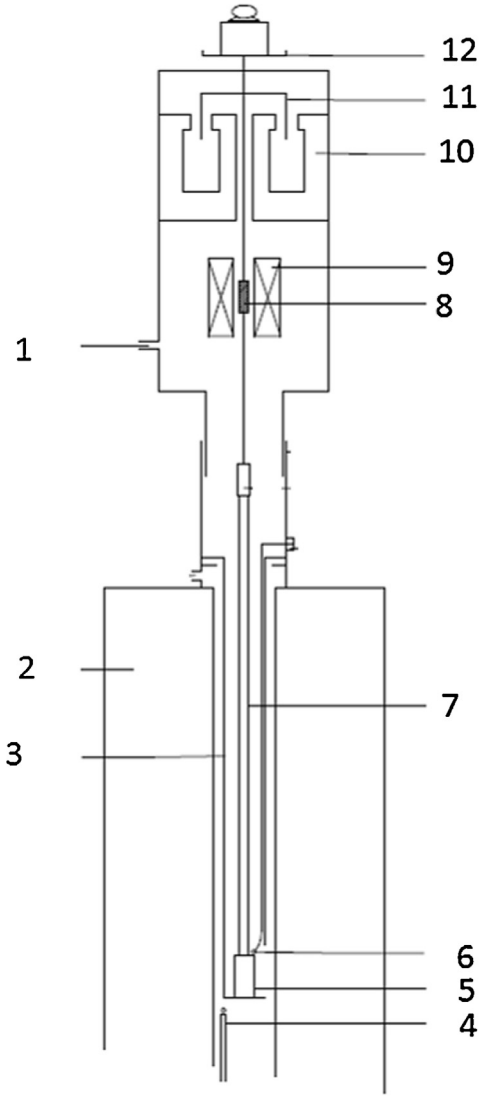

Fig. 1. Schematic diagram of TMA apparatus.

of melting. However, the shift can be also caused by exothermic chemical reaction, which is not related with melting.

In view of the limitations of these traditional methods, it's essential to develop a new technique to analyze the biomass ash fusibility properties. The shrinkage would accompany with the melting of ash. Thermo-mechanical analyzer (TMA) can measure the shrinking ratio of samples, which is directly related to the melting degree of ash. TMA has been used to predict the melting temperatures of coal ash [22–27] and proven to measure slight presence of melting phase with higher accuracy than AFT test [14]. TMA is applied in analyzing the deposition tendency of biomass ash [6,28]. However, application of TMA to determination of melting temperatures of biomass ash is not found in open literature.

In this study, we use TMA to measure the melting temperatures of different biomass ash and try to explain the variation of ash characteristics during ash melting.

2. Materials and methods

2.1. Facility

Experiments are carried out in a Thermo-mechanical analyzer (TMA, Setsys evolution). A schematic diagram of the apparatus is shown in Fig. 1. TMA mainly consists of two parts, the furnace and the electromagnetic location measuring assembly. The furnace is located in the lower part of the setup (2 in Fig. 1). In the furnace, two thermocouples (4,6 in Fig. 1) are used to measure and control the furnace temperature. The sample is loaded in the sample holder (3 in Fig. 1), in contact with a flat-bottom probe (7 in Fig. 1) that is placed on the top. Above the furnace is an electromagnetic location measuring assembly, including the core of a transformer, a differential transformer, a magnet and a movable coil (8,9,10,11 in Fig. 1). The probe is connected with the core of the transformer. The movement of the core produces a current in the differential transformer. The current signal can be recorded and transformed to a location signal of the probe.

Approximately 50 mg of ash sample is pelleted into a cylinder compacted with 0.3 MPa pressure. The height of the cylindrical sample is around 2 mm. The ash column is placed in a cylindrical corundum crucible contacting with the flat-bottom probe on the top with a constant force of 200N. During test, the sample is heated in the furnace from ambient conditions to 550 °C at the rate of 20 °C/min, after that, the heating rate is decreased to 5 °C/min. Slow heating rate is needed to guarantee the good heat transfer after 550 °C. But the effect of heating rate on TMA result can be neglected when heating rate is decreased below 5 °C/min. Therefore, 5 °C/min is chosen to save time. Argon is chosen as the carrier gas.

As the sample is heated, the location of the probe changes with the shrinkage or expansion of the samples. These changes, corresponding to sintering or melting, are continuously recorded by the sensor. The results of the TMA test present the shrinking percentage as a function of temperature.

2.2. Materials

The known pure substances, including KCl, K_2CO_3 and K_2SO_4, are first used to test the reliability of TMA.

Table 1
Proximate analysis of biomass (wt%).

Biomass	V_{ar}	FC_{ar}	A_{ar}	M_{ar}
Rice straw	74.97	6.05	11.28	7.7
Wheat straw	74.18	7.58	10.45	7.79
Corn straw	73.88	8.85	9.49	7.78
Peanut shell	76.24	11.21	3.98	8.57
Rice husk	57.11	14.84	20.26	7.80
Sawdust	72.56	15.41	3.64	8.40

Table 2
Chemical composition of investigated ashes as oxides (wt%).

Biomass ash	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	Fe_2O_3	ZnO	Cl
CS	0	4.93	2.17	25.32	4.36	5.35	33.76	9.61	1.48	2.58	10.44
RS	1.36	5.51	1.12	38.66	1.49	6.88	25.95	8.09	0.69	0	10.23
WS	0.3	1.86	0.85	41.14	0.7	11.61	24.72	6.87	0.39	0	11.55
PS	1.26	7.91	6.05	22.17	4.77	9.53	23.64	21.38	2.93	0	0.37
RH	0.25	4.59	0.92	63.54	14.55	2.61	10.68	2.04	0.51	0	0.32
SD	2.06	2.02	9.01	33.23	0.45	5.23	4.58	37.47	5.72	0	0.22