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Measurement of Heating Value of Rice Husk by Using Oxygen Bomb Calorimeter with Benzoic Acid as Combustion Adjuvant

Jianfeng Shen, Shuguang Zhu, Xinzhi Liu, Houlei Zhang, Junjie Tan

School of Energy and Power Engineering
Nanjing University of Science and Technology
Nanjing, China

Abstract

Heating value is a primary parameter availed in the design process of thermochemical conversion apparatus of rice husk. The published data for rice husk are different due to the diversity of testing conditions and rice husk varieties. In this study, the higher heating value of rice husk was measured by using oxygen bomb calorimeter with benzoic acid as combustion adjuvant. The effects of sample mass, oxygen gauge pressure and mass ratio of rice husk and benzoic acid were discussed. The results indicate that the measured higher heating value of rice husk increases at first with the increase of oxygen gauge pressure and the mass ratio of benzoic acid and rice husk, and then decreases. When the rice husk sample mass is 0.6 g, the oxygen gauge pressure is 3.0 MPa, and the mass ratio of rice husk and benzoic acid is 1.2:1, the higher heating value of rice husk reaches maximal, i.e. 15944±55 J/g that corresponds to complete combustion and appropriate testing conditions. The measured heating value in this paper is higher than that based on the testing conditions specified in British and Chinese testing standards respectively. The present study documents new higher heating value of one Chinese rice husk and formulates a useful method for the determination of testing conditions under which the heating value of rice husks is measured.

*Keywords:*rice husk; higher heating value; oxygen bomb calorimeter; benzoic acid; combustion adjuvant;

1. Introduction

Heating value which determines the energy content of biomass material is a primary parameter availed in the design process of thermochemical conversion apparatus of rice husk. Up to now, two main ways, i.e. prediction [1-3] and measurement are used to obtain the higher heating value of rice husk. Though the

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prediction is convenient and cheap, the measurement is considered as a primary and solid method to ensure the accuracy of the higher heating value [4, 5]. But discrepancy among the published experimental data of rice husk is observed. One possible cause comes from the testing conditions specified in different testing standards. In GB 5186-85 (China), the testing conditions are specified as 0.8 g sample mass and 1.5 MPa oxygen gauge pressure [6]. However, in CEN/TS 14918:2005 (Britain) and GB/T 213-2008 (China) the sample mass and oxygen gauge pressure increase to 1.0 g and 3.0 MPa [7, 8], respectively.

It is noteworthy that the testing conditions specified in the above testing standards for biofuels or coal may not be applied to all biomass materials due to the great differences among the materials. For example, for some biomass materials incomplete combustion may occur based on the above testing standards that means the testing conditions are inappropriate. Respect to those fuels with high ash content (e.g. rice husk) or difficult to ignite, benzoic acid is commonly used as combustion adjuvant [9-11]. Mo et al. [9] put a slice of benzoic acid on thick black liquid in order to measure the heating value of the sample. The satisfying results were obtained when the sample mass was 1.0 g, the benzoic acid was 0.2 g, and the oxygen gauge pressure was 2.8 MPa. Wang et al. [10] pressed the ignition wire with the benzoic acid in order to measure the heating value of the heavy oil. Their results indicated that the heavy oil burned completely when the benzoic acid was added to around 0.15-0.20 g. In addition, higher amount of benzoic acid was proposed in elsewhere [11]. However, few studies have been preformed on the measurement of the higher heating value of rice husk by using oxygen bomb calorimeter with benzoic acid as combustion adjuvant.

In this study, the higher heating value of rice husk sampled from Hexian in China was measured by using the oxygen bomb calorimeter with benzoic acid as combustion adjuvant. The effects of sample mass, oxygen gauge pressure and mass ratio of rice husk and benzoic acid were discussed. In addition, the results were compared with those measured according to the British and the Chinese testing standards, respectively.

2. Materials and Methods

Raw Materials Preparation

Rice husk sampled from Hexian in China was selected as raw material in this study. Prior to the measurement, a sieve with 1.7 mm aperture was used to remove the granular impurities and rice husk powders, which tend to influence the results. The proximate analysis and the ultimate analysis results were presented in TABLE I. The moisture content was measured by heating the rice husk in drying oven at 105 ℃ [12], and the ash content was measured by igniting the rice husk in muffle furnace at 600 ℃ to constant weight [13]. The volatile matter was measured by decomposing the rice husk in muffle furnace at 900 ℃ for a total of exactly 7 minutes. Moreover, the fixed carbon was calculated by difference. The ultimate analysis results were calculated by using prediction correlations proposed by the authors [14].

TABLE I. THE PROXIMATE ANALYSIS AND THE ULTIMATE ANALYSIS RESULTS OF HEXIAN RICE HUSK

Proximate Analysis				Ultimate Analysis		
Moisture (%, air dry basis)	*Volatile matter (%, dry basis)*	*Ash (%, dry basis)*	*Fixed Carbon (%, dry basis)*	*Carbon (%, dry basis)*	*Hydrogen (%, dry basis)*	*Oxygen (%, dry basis)*
9.44	69.80	15.14	15.06	40.23	5.23	37.51

Standard substance, i.e. benzoic acid, with the heating value of 26479 J/g (the expanded uncertainty was 0.1 % when the coverage factor was 0.2), was employed as the combustion adjuvant. The nickel wires, with 0.12 mm diameter, 100 mm length and 1400 J/g heating value were selected in ignition. Moreover, the oxygen with the purity higher than 99.5 % was used to fill the oxygen bomb.

Experimental Apparatus

An isothermal oxygen bomb calorimeter (HR-15, Shanghai Institute of Detecting Technology in China) was used. The inner barrel of the calorimeter was filled with deionized water whose temperature was measured to the accuracy of 10^{-4} K at intervals of 30 s by using SWC-II digital Beckmann thermometer. In addition, the rice husk and the mixture of rice husk and benzoic acid were pressed by using laboratory-scale tablet machine. The samples were weighed by using electronic balance with the minimum sensitivity ±0.1 mg (XS205, Mettle Toledo in Switzerland).

Experimental Procedure

In order to measure the higher heating value of rice husk accurately, the strict experimental procedures should be complied. The main experimental procedures were introduced as follows.

Firstly, the rice husk and the benzoic acid powder with the mass ratio of 2:1, 1.5:1, 1.2:1, 1:1 and 1:1.2 were mixed together, and then pressed to slice by using laboratory-scale tablet machine. Next, the ignition wire was connected to the ignition electrodes. Before the lid of oxygen bomb was screwed on, 10 ml deionized water was poured into the oxygen bomb. Then the lid was screwed on and the oxygen was injected to the oxygen bomb until the gauge pressure rises to the assigned value, i.e. 1.5 MPa, 2.0 MPa, 2.5 MPa, 3.0 MPa and 3.5 MPa. Afterwards, the testing circuit was connected. Finally, about 3 kg deionized water was poured into the inner barrel and the measurement was initiated. The measured data were analyzed according to the method proposed in the literatures [15-17]. It should be mentioned that every measurement was performed five times under each testing condition.

Thermal Capacity Measurement

The thermal capacity of the oxygen bomb calorimeter was measured according to the National Metrological Verification Regulation in China (NMVR). The value of the thermal capacity of oxygen bomb calorimeter is measured as 14013 J/K and the relative standard deviation is 0.17 %, which is less than 0.20 % described in the NMVR. The results indicated that the calorimeter is suitable for heating value measurement [10].

3. Results and Discussion

The Effects of Oxygen Gauge Pressure and Sample Mass

As the first step, the optimum sample mass and oxygen gauge pressure are determined. Because benzoic acid is stored in porous rice husk in the process of pressing the testing sample which does not cause additional splashing, it is acceptable to determine the optimum rice husk sample mass and oxygen gauge pressure without benzoic acid additive.

As lower and higher oxygen gauge pressures lead to incomplete combustion of rice husk, they will affect the measured heating value of rice husk. At first, 0.8 g rice husk is used according to the testing method [6]. The effects of oxygen gauge pressure on the measured higher heating value of rice husk are given in Fig. 1. As shown in Fig. 1, the higher heating value of rice husk dramatically increases at first with the increase of oxygen gauge pressure, and then decreases. Actually, when the oxygen gauge pressure is low, the concentration of oxygen is not enough to support the complete combustion of rice husk [10, 11]. Therefore the measured higher heating value is low. As the oxygen gauge pressure increases from low to moderate, the level of burnout of rice husk increases and the measured higher heating value also climbs up. However, over-increased oxygen gauge pressure will lead to the generation of coke [10], which results in lower measured higher heating value of rice husk. It can be found that when the oxygen gauge pressure is 3.0 MPa, the measured higher heating value of rice husk reaches maximal. Because the maximum heating value is the nearest to the complete combustion condition, the correct measurement corresponds to the maximum value search process.

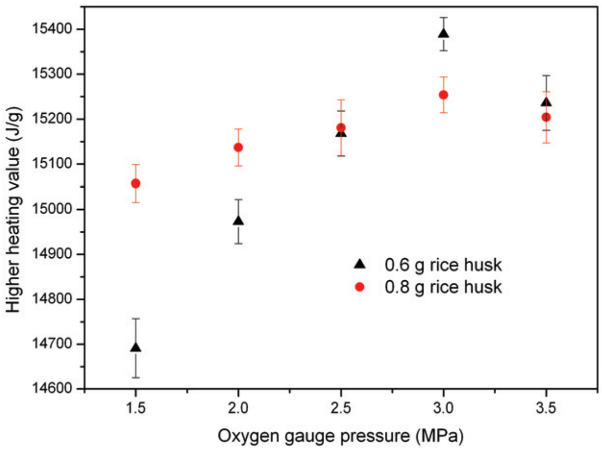

Figure 1. The effects of oxygen gauge pressure and sample mass on the measured higher heating value of rice husk without combustion adjuvant.

Another factor that may affect the combustion completeness is the pressed rice husk sample mass. In the experiments, we have found that the pressed rice husk sample with 0.8 g or larger mass (based on the testing standards introduced in Section I) tends to splash to the deionized water which leads to incomplete combustion of rice husk. So the mass 0.8 g or larger is not appropriate for the measurement of higher heating value of rice husk. When we use the pressed rice husk sample with 0.6 g mass, it can be observed that splash nearly does not occur. Therefore for rice husk 0.6 g mass sample is recommended. In Fig.1, the measured heating value of 0.6 g rice husk displays a similar trend to that of 0.8 g rice husk but with different maximum value. When the oxygen gauge pressure is 3.0 MPa for 0.6 g rice husk, the maximum value, i.e. 15389±37 J/g, is obtained. Because rice husk ash content is high (c.f. TABLE I), the maximum value in Fig. 1 with 0 g benzoic may not equal to the 100% complete combustion condition. Adding combustion adjuvant (e.g. benzoic acid) is an effective way to ensure that.

The Effects of Mass Ratio of Rice Husk and Benzoic Acid

In the above part, we obtained the optimal testing conditions for rice husk samples without any combustion adjuvant. In this part, we further investigate the effects of a commonly used combustion adjuvant (benzoic acid) [9-11]. The values of mass ratio of rice husk and benzoic acid is 2:1, 1.5:1, 1.2:1, 1:1 and 1:1.2 in the case of 0.6 g rice husk and 3.0 MPa oxygen gauge pressure. In the experiments, no splashing was founded.

Fig. 2 shows the mean higher heating value of rice husk and its error bar. The results clearly indicate that the measured higher heating value of rice husk dramatically increases at first with the decrease of the mass ratio of rice husk and benzoic acid, and then decreases. The maximum higher heating value of rice husk, i.e. 15944±55 J/g, is obtained when the mass ratio of rice husk and benzoic acid is 1.2:1. At high mass ratio of rice husk and benzoic acid, e.g. 2:1, due to the weak effect of combustion adjuvant [10], lower measured higher heating value is obtained. At low mass ratio of rice husk and benzoic acid, e.g. 1:1.2, the benzoic acid burns prior to the rice husk and the oxygen partial pressure around the crucible is low. The spunk of rice husk ash may be extinguished before the ash directly contacts enough oxygen. On account of the incomplete combustion of rice husk ash, the measured higher heating value of rice husk is lower than that of mass ratio 1.2:1. The results in Fig.2 show clearly that there exists an optimum mass of benzoic acid additive.

The Comparison of Higher Heating Value Measured According to Different Testing Conditions

As the same sample mass and oxygen gauge pressure are proposed in DD CEN/TS 14918:2005 and GB/T 213-2008, only GB 5186-85 and DD CEN/TS 14918:2005 are used to compare with the testing results in this study. The higher heating values measured according to the testing conditions specified in those two standards are 15012 J/g and 14951 J/g, which are 5.85 % and 6.23 % lower than that measured in this study (15944 J/g), respectively. The value using the proposed 0.6 g rice husk sample mass and 3.0 MPa oxygen gauge pressure but with 0 g benzoic acid is also 3.48% lower than that with 1.2:1 mass ratio of rice husk and benzoic acid.

Figs. 3a-3c show the appearances of rice husk ash obtained after the measurements which follow the different testing standards, i.e. GB 5186-85, DD CEN/TS 14918:2005, and the present, respectively. As shown in Fig. 3a and 3b, there are many black particles entrapped in the rice husk ash which means combustion is incomplete. The sample mass and the oxygen gauge pressure specified in GB 5186-85 are 0.8 g and 1.5 MPa, respectively. As explained above, under such low oxygen gauge pressure, the concentration of oxygen is not enough to realize complete combustion of rice husk sample. However, in DD CEN/TS 14918:2005, the sample mass and the oxygen gauge pressure are increased to 1.0 g and 3.0 MPa, respectively. Under such testing conditions, the rice husk sample tends to splash to the deionized water which leads to incomplete combustion of rice husk, too. Moreover, the potassium and the rice husk powders tend to react on each other and subsequently form the alkali metal rich melts. Once the carbon is entrapped in these melts, it can not be easily oxidized because it is not in direct contact with oxygen [18].

As benzoic acid can be easily ignited and burned prior to the rice husk, some micro- or macro-channels form under the right oxygen gauge pressure and mass ratio of rice husk and benzoic acid. Moreover, the spunk of rice husk ash can support the combustion of rice husk ash until enough oxygen contacts the sample. Actually, very little black particles can be found in Fig. 3c, which means that the combustion is complete and the higher heating value measured under the present testing conditions is reasonable and acceptable.

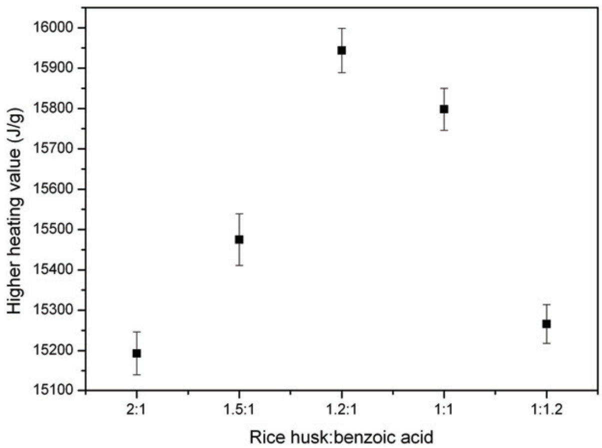

Figure 2. The effects of mass ratio of rice husk and benzoic acid on the measured higher heating value of rice husk.

(a) GB 5186-85 (b) DD CEN/TS 14918:2005 (c) The present study

Figure 3. The comparison of the rice husk ash obtained after higher heating value measurements.

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