Characteristics of Chlorine Emission during Rice Husk Combustion

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Abstract: The erosion of heating surfaces due to chloride release from direct rice husk combustion was investigated. Relationships between chloride release from rice-husk combustion and different influence factors were studied and chloride release models were established. A gas-state chloride absorption testing platform was built according to the characteristics of chloride production from rice husk combustion in real boilers. The chloride release under different designing parameters was absorbed by a NaOH solution, and the chloride release laws during rice husk combustion were investigated. It was found the chloride release was accelerated in a multistage way with the rise of combustion temperature. The chloride release rate increased up to 85% with the prolonging of combustion time. Under the strong oxidative atmosphere, the chloride release rate increased significantly and rose by about 2 times compared with the weak oxidative atmosphere. Increasing the vapor concentration would promote the chloride release from rice husk combustion. A larger size of rice husk further hindered chloride release and decomposition, and took longer time to release the same amount of chloride. Chloride release from rice husk was harder than from wood dust, and chloride release and combustion were synchronous. Chloride release during rice husk combustion was a zero-order reaction.

Introduction

Along with the rapid development of the biomass combustion technology, the harmful gas emissions from biomass combustion have become a research focus [1-3]. Compared with coals, biomass is rich in chlorine and alkaline substances, and during the combustion, easily volatilizes into slagging and ash flouling of the heat exchanger of boiler systems, causing abrasion and erosion to the heating surfaces of heat exchangers [4-5]. Regarding such abrasion and erosion, researchers from Denmark and the US started to study these problems very early and provided much data, but Chinese researchers began very late [6].

The ash flouling, slagging, abrasion and erosion of boilers and heat exchangers during biomass combustion are critically attributed to chlorine [7]. Chlorine plays a transporting role in biomass combustion, favors the volatilization of alkali metals from biomass fuel particles, and chemically reacts with other substances on the surfaces of fuel particles. Compared with volatile alkali metals, the volatile chlorides are very stable and tend to deposit at the downstream of the equipment. Moreover, chlorine also increases the fluidity of inorganic compounds, especially potassium compounds [8-9]. It is indicated chlorine decides the total yield of alkali metal vapor.

The chlorine release should be critically characterized in order to prevent ash flouling, slagging, abrasion and erosion during biomass combustion [10]. In this study targeting at rice husk, the

chloride release rules during rice-husk combustion were tested, so as to determine the relationships between chloride release and different influence factors and to construct chloride release models.

Instruments and Methods

Materials

Rice husk and rawdust were used as the targets which contained medium levels of chlorine. The rice husk and rawdust were collected locally in Kunming, Yunnan. The materials were crushed into particles in sizes of 90 or 250 μm, and then dried at 105 ℃ for 24 h and cooled for 8 h. The industrial analysis and elemental analysis are listed in Tables 1, respectively.

Table 1 Industrial analysis and Elemental analysis of rice husk and sawdust

Sample	Industrial analysis /%				Elemental analysis /%					Cl mg/g
	M_{ad}	V_{ad}	A_{ad}	FC_{ad}	C	H	O	N	S	
Husk	11.6	75.75	9.19	15.06	39.82	5.36	33.54	1.36	0.2	0.9
sawdust	7.2	76.04	6.01	17.95	45.23	5.25	36.51	0.12	0.11	0.6

Instruments and Methods

In real boilers, the chloride formation during rice-husk particle combustion was limited by time, material and labor waste, and low measuring accuracy, which largely complicate relevant research and real measurement [11]. In this study, a gas-state chloride direct absorption analytical method was used, and the experimental setup was showed in Fig. 1. The experimental system consisted of a combustion device, a gas distributing device and an absorption device. The combustion device was a tubular resistance furnace with power at 4 Kw (Hangzhou Lantian Chemical Instruments Co. Ltd.) operated at 0-1000 ℃ with a temperature resolution of 1 ℃ and temperature control precision < 5 ℃, and the workroom sizes were φ40×600 mm². The transparent quartz combustion tubes were sized φ34×1000 mm², and could tolerate up to 1300 ℃. The fuels were put into a small porcelain boat (60×30×15 mm³). The gas was supplied by a compressed air steel cylinder, and the gas flow rate was controlled by a decompression valve and a mass flow meter.

Samples (250 μm, 0.2 g) were put into the porcelain boat, and sent by a putter into the high-temperature zone of the resistance stove. Under standard working conditions, the oxygen flow was 500 ml/min, and the generated gas was absorbed by two absorption bottles in series filled with 50 ml of 0.1 mol/L NaOH. The HCl gas was collected every 20 min. After the collection, the absorption liquid was diluted to 100 ml, and the chlorine concentrations were detected via an Asca potassium thiocyanate method. It was found this absorption method fully met the experimental requirements and could absorb up to 94% of gas chloride [11].
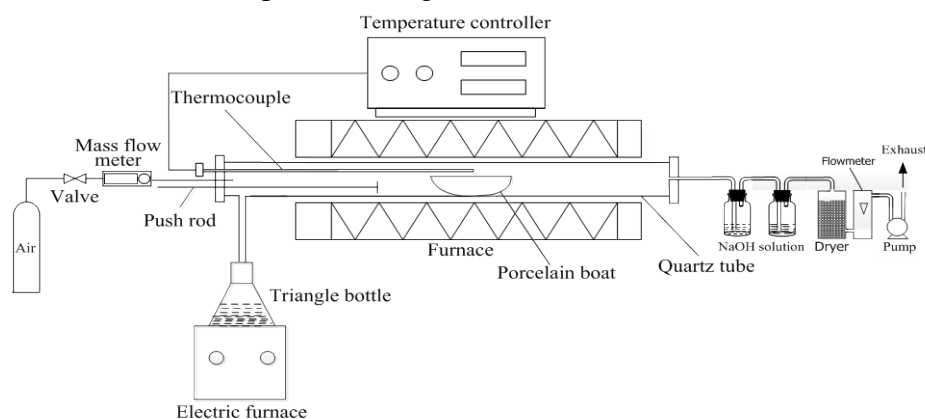

Fig. 1 The absorption experiment system of gas phase chloride

Results and Analysis

Effects of Combustion Atmosphere on Chloride Release

The rice-husk combustion would experience the alternation between reductive and oxidative atmosphere [14], which would affect the chlorine release. To analyze such effect, we set the experimental conditions at rice-husk specimen dosage = 0.2 g, temperature at 900 ℃, retention time = 30 min, and oxygen ventilation amount = 50-800 ml/min (Fig. 2).

Clearly, as the oxygen ventilated amount increased, the chloride release rate first rose and then decreased, and stabilized around 75% within 400-500 ml/min (Fig. 2). As the O_2 ventilated amount decreased at the range below 400 ml/min (namely the oxidative atmosphere in the furnace was weakened), the chloride release rate decreased significantly from 75% to about 22%. When the O_2 ventilated amount was over 500 ml/min, the intratubular gas flow rate rose and led to the entrance of abundant cold gas, thereby reducing the combustion temperature and thereby the chlorine release. These results suggest the optimal O_2 ventilated amount was 400-500 ml/min.
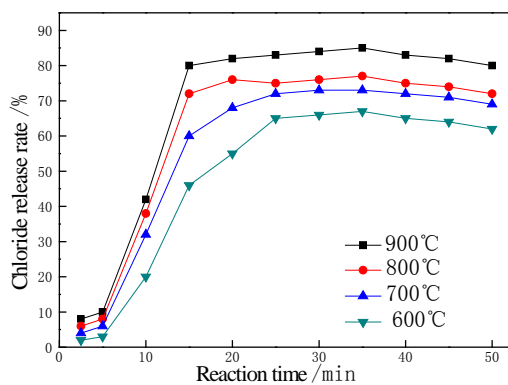

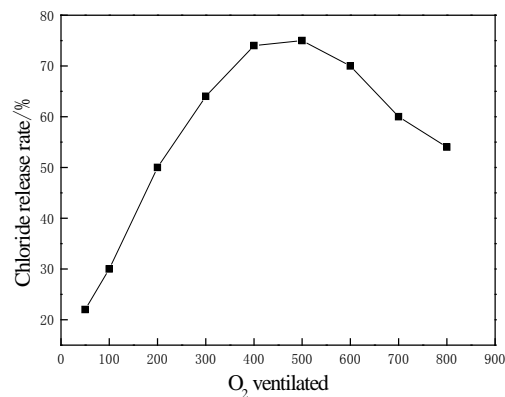**Fig. 2** Effects of oxygen on chlorine release   **Fig. 3** Effects of burning time on chlorine release

Effects of Burning Time on Chloride Release

The chloride release during rice-husk combustion was also related to the residence time of rice-husk in the furnace, in addition to combustion temperature and combustion atmosphere. The effects of combustion temperature from 600 to 900 ℃ were tested at rice-husk specimen dosage of 0.2 g and O_2 ventilated amount = 500 ml/min (Fig. 3).

At the combustion temperature 900 ℃, the chloride release rate was the largest (about 80%) from 0 to 15 min, in which the released chlorine was mostly active organic chlorine. After 15 min, the chloride release rate was significantly slowed down to about 85%, from which it was thought the HCl release from the rice-husk was basically stable and chloride was released in the form of ions. Beyond the reaction time of 35 min, the chloride release rate decreased, which was mainly because too long residence time increased the amount of the absorption liquid and affected the accuracy of chlorine concentration measurement.

Effects of Vapor on Chloride Release

During the high-temperature combustion of rice-husk, evaporation also significantly affected rice-husk combustion. The effects of evaporation were tested at combustion temperature = 900 or 700 ℃, rice-husk dosage of 0.2 g and O_2 ventilated amount = 500 ml/min (Fig. 4).
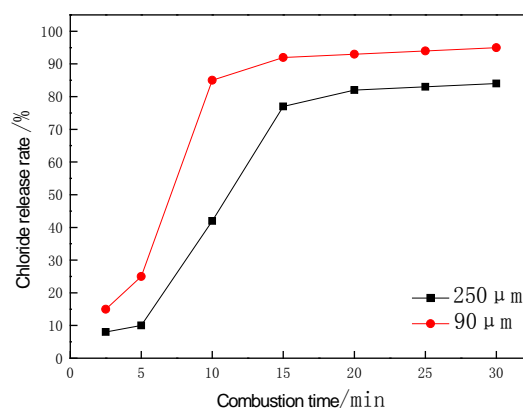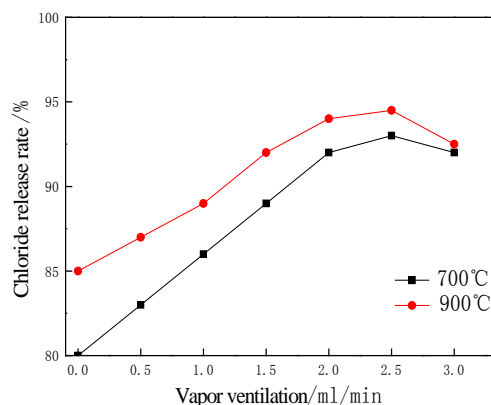
Fig. 4 Effects of water vapor on chlorine release   **Fig. 5** Effects of particle size on chlorine release

At 700 ºC, the chloride release rate without vapor ventilation was about 80%, and then it significantly rose with the increasing vapor ventilation. The chloride release rate rose linearly as the vapor ventilation increased from 0 to 2 ml/min, but rose slowly when the vapor ventilation exceeded 2 ml/min, when the promoting effect of vapor on chloride release was weakened. At higher combustion temperature of 900 ºC, with the rise of vapor ventilation, the increasing rate of chloride release was slowed down, and the chloride release rate without vapor ventilation (84.9%) was larger than that at 700 ºC. The above results suggest vapor promotes the chloride release and significantly accelerates the chloride release from rice-husk. The chloride hydrolysis reactions showed since the participation of vapor in the combustion led to abundant chloride release, and the chloride release rate was faster at middle and low temperatures, and the appropriate vapor ventilation was 2 ml/min.

Effects of Particle Size on Chloride Release

As reported, with the decrease of particle size, the chlorine content in coals declines, which is mainly because the moisture evaporation during sample grinding brought away a part of chlorine [15]. Rice- husk particle size affects the chlorine contents in a similar way. This is because rice-husk crushing was accompanied with mechanical chemistry actions and thereby exothermic reaction, which led to partial moisture evaporation from the rice-husk, and induced the temperature rise in the small-size rice-husk particles, leading to the reduction of chlorine concentrations in the small-size rice-husk particles.

The effects of particle size (90, 250 μm) were tested at combustion temperature 900 ºC, oxygen ventilated amount of 500 ml/min and specimen dosage of 0.2 g. The temporal changes of chloride release with particle size are showed in Fig. 5.

Clearly, with the rise of particle size, the chloride release was gradually slowed down, and its curve moved backwards with the prolonging of burning time, indicating larger particle size was less favorable for chlorine release. At the initial residence in the furnace (2.5-5 s), the smaller-size chloride was released faster. After residence in the furnace for more than 15 s, the chloride release rates of the two particle sizes both basically stabilized, and the effect of particle size on the chloride release at later stages was gentle. On this basis, the effect of particle size on chlorine release was dominated by chemical thermodynamics and kinetics.

Chloride Release of Different Biomasses

Rice-husk with 0.09% chlorine and sawdust with 0.06% chlorine were tested. The tests with specimens (each 0.2 g), oxygen ventilated amount of 500 ml/min, residence time of 20 min, and temperature from 200 to 970 ºC were conducted. During the rice-husk combustion, chlorine was mainly released in the form of HCl. Clearly, the HCl release rate significantly rose with the rise of combustion temperature. During the rice-husk combustion, HCl release started at 200 ºC, exceeded 80% at 600 ºC and rose to about 96% at 970 ºC, indicating the majority of chlorine was released from the rice-husk at 600 ºC. On this basis, the chloride release process was divided into three stages: 200-300, 300-600, and >600 ºC. About 50% of chloride was released from the rice-husk at the second stage; organic chlorine was released below 600 ºC, and inorganic chlorine was released

at above 600 ℃ [15].

The chloride release rates from rice-husk and sawdust both increased in a multi-stage way with the rise of combustion temperature, and the uptrends were very similar. The chloride release rates were very low within 200-300 ℃, and the majority of chlorine was released at 300-600 ℃, in which the chloride release rate significantly increased with the rise of combustion temperature and exceeded 80%. The chloride release rate increased slowly and basically became consistent beyond 600 ℃.
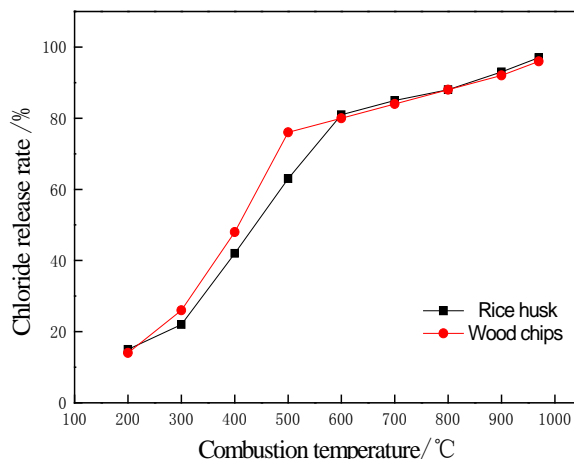

Fig. 6 Effects of biomass on chlorine release

The above analyses indicate at 200-300 ℃, mainly volatiles were released from either rice-husk or sawdust, but the released amount was very small, about 10% of chloride release from rice-husk or sawdust. These results suggest the less chlorine was released with the volatiles, and mainly occurred at the carbon combustion stage. As reported, the chloride release rate within 300-600 ℃ was significantly higher than at other temperatures, and the majority of chloride released was inorganic chlorine [16-17]. At below 300 ℃, organic or water-soluble chlorine in the form of Cl-Cl, and a small amount of inorganic chloride were released, and the majority of inorganic chlorine was stable. At above 600 ℃, the chlorine release was very slow and seemed extremely difficult. As reported, the residual chlorine at below 600 ℃ was more stable than the released chlorine, and would be only released at higher temperature [18].

Chloride Release Model from Rice-Husk Combustion

Garcia-Labiano[19] thought when the differences in the chlorine hosted forms of biomass and the intermediates from chloride release reactions were ignored, the solid-phase chlorine in biomass could be directly converted to HCl:

$$Cl(solid) + H^+ \rightarrow HCl. \tag{1}$$

If the reactions at different temperatures were all isothermal, volume-constant irreversible zero-order reactions, then the HCl formation rate and its integral form were [20]:

$$-\frac{dM}{d\tau} = k. \tag{2}$$

$$k\tau = M_0 - M. \tag{3}$$

where M_0 and M were the initial and final Cl concentrations o HCl at a certain temperature (μg·g^{-1}); k was the reaction rate constant; τ was the reaction time.

The reaction rate constant k obeys the Arrhenius equation:

$$k = Ae^{-E/RT}. \tag{4}$$

where A was a frequency factor, min^{-1}; E was the activation energy, kJ/mol; R was a gas constant, kJ/mol·K; T was reaction temperature, K. As showed in Fig. 3, the reaction rates k at different combustion temperatures could be calculated (Table 2).

Table 2 The reaction rate of HCl the rice husk combustion under different combustion temperatures

Temperature t/ °C	Reaction rate k/mg·s^{-1}
600	0.00648
700	0.00952
800	0.01188
900	0.01296

The two sides were logarithm-treated, then:

$$\ln k = \ln A - \frac{E}{R} \cdot \frac{1}{T}. \tag{5}$$

The frequency factor A and activation energy E were computed (Table 3). Arrhenius equation can be written as:

$$k = 1.2913e^{-\frac{11.37}{RT}}. \tag{6}$$

Table 3 The kinetic parameters of chloride precipitation by rice husk

Sample	Frequency factor A/min	Reaction kinetics /kJ·min^{-1}	Correlation coefficient
Rice husk	1.2913	11.3719	0.9869

Conclusions

In the self-made fixed-tube resistance furnace, the chloride release from biomass combustion was characterized via the gas-phase chloride absorption method.

(1) The chlorine release from rice-husk combustion was mainly in the form of gas-phase chlorine (HCl), and was affected by combustion temperature, residence time, combustion atmosphere, and particle size.

(2) The chloride release rate was accelerated in a multistage way with the rise of combustion temperature. The chloride release rate increased up to 85% with the prolonging of combustion time. Under the strong oxidative atmosphere, the chloride release rate increased significantly and rose by about 2 times compared with the weak oxidative atmosphere. Increasing the vapor concentration would promote the chloride release from rice husk combustion. A larger size of rice husk further hindered chloride release and decomposition, and consumed longer time for the same amount of chloride release. Chloride release from rice husk was harder than from wood dust, and chloride release and combustion were synchronous.

(3) During rice-husk combustion, the chloride release was a zero-order reaction: $k = 1.2913e^{-\frac{11.37}{RT}}$.

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