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Full Length Article

The condensation and thermodynamic characteristics of alkali compound vapors on wall during wheat straw combustion

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ABSTRACT

Alkali chlorides and sulfates are well-known species induced fouling, slagging and corrosion on the heat transfer surface in biomass combustion/gasification process. This paper aims to study the condensation behavior of alkali compound vapors (ACVs) during wheat straw combustion in laboratory, without the participation of ash particles. The effects of surface temperature of Fe-Cr-Ni alloy probe on condensation morphology, thermodynamic characteristics of mixed salt vapors, and mineralogical variation of straw ashes are also discussed. The K, Cl and S mainly existed as KCl, K_2SO_4 and $K_2Ca(CO_3)_2$ in wheat straw ashes produced at 400 °C. The main released ACVs were potassium chlorides and sulfates. The form of condensation for mixed chloride vapors at surface temperatures of 400/520/600 °C is varied at 815 °C. These mixed salt vapors could condense either separately as cubic crystal particles by homogeneous nucleation, or together as one or two solid solutions by heterogeneous nucleation. The side length of KCl crystal particle condensed homogeneously was less than 2μm. The aggregation and growth among crystal particles at surface temperature of 400 °C were observable. The chlorides are released completely from wheat straw ashes at 815 °C, and carbonates may disappear as either decomposition or sulfation with SO_2/SO_3. When the evaporation temperature was 1100 °C, K_2SO_4 and Na_2SO_4 were released and then condensed as one solid solution with hexagonal crystal structure on the probe surface of 520 °C. Finally, we propose a condensing mechanism for ACVs depending on surface temperature.

1. Introduction

Because of the great advantage on zero carbon dioxide emissions and waste management, biomass is considered as a renewable fuel and has attracted worldwide attention. It has been recognized that using the relatively clean biomass as about 10–20% or 100% of input material in power plants is one of the most promising technologies for reducing CO_2 emission. However, alkali metal elements of high content in biomass are easily released during thermal-chemical conversion [1]. The thermodynamic analysis on K release in combustion and gasification of three types of biomass has been studied by Wei et al. [2]. Released vapors can form a molten or powder layer on the wall, leading to higher sticking propensity of ash particles. Around 10–20% of the recycled wood as input material has resulted in approximately double growth rate of deposits and rapid corrosion rate for a biomass fired CFB boiler [3]. This was mainly attributed to the condensation of alkali vapors. These salt vapors can easily form the eutectics or new mineral phases with lower melting point, which inducing the rapid growth of slagging layer. The ash-related issues in biomass combustion and the mechanism of KCl and K_2SO_4 induced slagging have been reported in detail [4]. In addition, several technologies have also been proposed to reduce the direct condensation of alkali vapors, including leaching [5], utilization of additives (kaolin and zeolite) [6], co-firing [7] and fuel sulfation [8].

Alkali species enriched in the inner deposits on tubes of industrial- or lab-scale furnace have been reported in many studies. The categories of vapor species condensed on tubes are strongly related to fuel properties and boiler types. In straw-fired grate boilers, KCl and K_2SO_4 are the main compositions in the inner layer of deposits [9]. But some eutectics were also formed due to the reaction of K_2SO_4 and $CaSO_4$, which were found in superheater deposits of a 30 MW biomass-fired power plant [10]. For some coal-fired boilers, NaCl and Na_2SO_4 as the main condensing species are found in innermost layer of deposits, with minor amounts of Ca- and Mg-sulfates [11]. High concentrations of NaCl are frequently found in black liquor recovery boilers [12]. In municipal solid waste (MSW) incinerator plants, the first depositing materials are rich in Na, K, Ca chlorides and sulfates, with small amounts of heavy metal (Zn, Pb, etc.) chlorides and sulfates [13]. But it is difficult to understand the condensation behavior of alkali vapors

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by analyzing the real deposits, because of involving in many complicated reactions. Therefore, persistent studies on salt vapors should be conducted to find out their condensation behavior during combustion.

Generally, the condensation of alkali vapors on tubes is temperature-dependent. The depositing surface temperature has an important impact on depositing behavior of salt and ash particles. Zhou et al. [14] proposed the method using a digital camera to study the effect of surface temperature on slagging characteristics of Zhundong coal. It is observed that the deposition thickness decreases with an increase of depositing surface temperature. The low depositing surface temperature can facilitate the formation of sulfates in the initial layer. However, the effect of salt vapors condensation, which could lead to distinct difference in deposits at different surface temperature, is not considered. Lindberg et al. [15] developed a novel laboratory method to study the effect of temperature gradient on chemical and physical behavior of ash deposits. It is found that alkali chlorides evaporate from hotter particles, and condense on colder particles or metal surfaces. In fact, the condensation of alkali vapors on particles is similar to that on tube surfaces. The alkali vapors condense into solid or liquid phase, greatly relying on their physical and chemical behavior as well as local temperature gradient. Broström et al. [16] found that mixed KCl and NaCl vapors probably condense as separate phase at the concentration and temperature below melting points of the salts. The condensation temperature of them may be lower than the dew temperature of any single salt, when chloride and sulfate vapors occur in hot flue gas simultaneously. But the condensation of alkali vapors at hot flue gas involves many processes, such as nucleation, coagulation and surface growth. However, limited experimental investigations with respect to the condensation of alkali vapors are carried out to interpret this common phenomenon.

This work aims to present a novel method to study the condensation behavior of ACVs released from wheat straw, by using an air-cooled probe of Fe-Cr-Ni alloy. The way of condensation and morphologies were studied at different surface temperatures as well as the thermodynamic characteristics of ACVs. The morphology and chemical composition of condensates on probe surface were analyzed by a scanning electron microscope (SEM) equipped with energy dispersive X-ray spectrometry (EDS). The thermodynamic characteristics of ACVs were determined by the corresponding phase diagrams. The collected residual ashes were analyzed by X-ray diffraction (XRD), to provide complementary information about mineralogical variation of wheat straw ashes. Finally, a condensation mechanism of ACVs was proposed, depending on surface temperature during wheat straw combustion.

2. Experimental section

2.1. Biomass properties

The wheat straw used in this research is from Baoji city of Shaanxi Province. Table 1 presents the proximate, ultimate and ash composition analysis of wheat straw. The content of ash-forming elements was obtained by X-ray Fluorescence. The Cl in ash was converted into KCl and other elements were converted into the corresponding oxide, as given in Table 1. The samples were crushed and ground to a particle size below 300 μm before use.

2.2. Experimental system

Experiments were performed to study the evaporation and condensation behavior of ACVs from wheat straw. Fig. 1 shows the schematic diagram of experimental apparatus [17]. It consisted of a tubular furnace, a quartz tube, a condensing probe and some associated temperature or flow measuring instruments. The tubular furnace can be electrically heated to 1300 °C, with a rate of less than 25 $°C\cdot min^{-1}$. The tubular furnace was 50 mm in inner diameter and about 400 mm in length. The dimension of quartz tube was 1100 mm in length and 48 mm in diameter. A crucible filled with wheat straw particles was heated, acting as the releasing source of ACVs. In addition, there was a thermocouple used to monitor the evaporation temperature in which the crucible placed.

The condensing probe was made from 310 stainless steel rod (Fe-25Cr-20Ni; 28 mm in diameter) and a 12 mm o.d steel tube. This probe consisted of a sampling surface, an outflow plate, a hollow cylinder and an inlet tube (see Fig. 2). The sampling surface could slip into the bottom of hollow cylinder easily. The specific sizes of condensing probe are given in Fig. 2. The sampling surface was like a hat, and its hollow interior surface was cooled by using air jet. The surface that used to capture the vapor species was less than 1 mm in thickness. A thermocouple was welded on the center of its back to monitor its surface temperature. The condensing probe was located at a calibration position in the quartz tube. The distance was about 100 mm from the sampling surface to the upper surface of evaporating crucible. The total air flow was supplied with an air pump. It was divided into two branches, i.e., cooling airflow and dilute airflow. The cooling airflow was used for controlling the surface temperature of sampling probe, which could be changed from 8.3 to 41.7 L/min. The dilute one kept at 2.1 L/min was used to carry the ACVs released from wheat straw. After finishing a test, the sampling surface could be removed from probe easily, which made it convenient to do the SEM/EDS analysis.

2.3. Design of the surface temperature of sampling probe

The probe surface temperatures selected are corresponded to the wall temperatures of heat transfer tubes in a 30 MW biomass-fired vibration grate furnace. This furnace is a typical M type arrangement with four stage superheaters. Its furnace temperature was around 1200 °C. The flue gas passed through the third (SH3), fourth (SH4), secondary (SH2) and primary (SH1) superheaters successively. The wall temperatures (WT) of water wall (WW), SH1, SH2, SH3 and SH4 are given in Table 2. Moreover, the flue gas temperature (FGT) is also presented in Table 2. More details about this grate furnace and the mature deposits formed

Table 1
Properties of wheat straw.

Sample	Proximate analysis (wt%, air dry basis)					Ultimate analysis (wt%, air dry basis)					LHV (MJ/kg)
	Moisture	Ash	Volatile matter	Fixed carbon	C	H	O	N	S_{total}	Cl	
Wheat straw	3.88	6.01	72.01	18.01	43.92	4.47	40.98	0.44	0.30	0.49	14.77

Ash compositions (%)								
SiO_2	Al_2O_3	CaO	MgO	P_2O_5	K_2O	KCl	Na_2O	SO_3
32.67	4.96	20.49	12.19	6.55	14.41	1.64	0.74	6.38