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Experimental study of potassium release during biomass-pellet combustion and its interaction with inhibitive additives

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ABSTRACT

In the present study, two types of biomass were investigated as typical agricultural and woody biomass fuel, i.e., corn straw and poplar. Firstly, laser induced breakdown spectroscopy (LIBS) was employed to investigate the release characteristics of potassium (K) from a burning biomass pellet. In order to further investigate the correlation between K release and the combustion process, combustion parameters including pellet surface temperature and pellet diameter were simultaneously measured with LIBS. A dual-peak trend is observed in the K release history of poplar, but only a single peak is found in that of corn straw. Both biomass samples show the strongest K release during the devolatilization stage in comparison with the subsequent char burnout and ash cooking stages. Similar tendencies are observed between K release and pellet temperature, which suggests that K release is closely related to the combustion process. The K release mechanism can be attributed to temperature rise and therefore breakdown of chemical bonds during combustion. Then the release of different chemical forms of K was investigated by chemical fractionation treatment of the biomass samples. The released amount of H_2O-soluble, NH_4Ac-soluble and HCl-soluble potassium compounds were obtained. The H_2O-soluble potassium is found to be the major released potassium compound. Finally, four kinds of additives (two pure additives, i.e., silica and alumina, and two typical natural mineral additives, i.e., kaolin and mica) were added to the biomass samples to investigate their inhibition effects on K release. The natural sorbent additives show better inhibition effects than the pure ones.

1. Introduction

Biomass, as a renewable energy source, has been utilized to support 10–15% of the worldwide energy consumption [1], especially with soaring applications in thermal power production. However, advanced thermo-utilization of biomass is largely limited by severe ash deposition issues caused by alkali metal emissions [2]. Since potassium (K) is an important element for plants, it is usually rich in biomass. The potassium vapor released during the thermo-utilization of biomass tends to condense on cooler heat exchange surfaces and develop a sticky potassium layer. The sticky layer could capture fly ash and then result in ash deposition [3,4]. Moreover, potassium could also react with sulfur and chlorine species, leading to severe fouling and corrosion [5,6]. It is therefore important to understand potassium-release mechanisms during biomass combustion in order to develop potassium control technologies and achieve better utilization of biomass resources [7–10].

In the past few decades, experimental study on potassium release characteristics during biomass combustion has evolved from offline sampling approaches to online in-situ measurements using optical techniques [11–13]. These non-intrusive optical techniques can directly capture dynamic potassium-release characteristics during biomass combustion. For instance, flame emission spectroscopy method has been employed to investigate potassium release characteristics [11] and the effects of different combustion atmosphere on potassium release [14] during biomass combustion. Weng et al. [15] measured the release of atomic potassium from burning coal, wood, and straw pellets using tunable diode laser absorption spectroscopy (TDLAS). Qu et al. [16] used the same technique to simultaneously measure the flame temperature, water vapor and atomic potassium distribution during entrained-flow biomass combustion and they observed that potassium species rapidly undergo primary ash transformation reactions even if the fuel particles reside in an oxygen-deficient environment. Other laser optical diagnostics techniques have also been used, including collinear

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Table 1
Chemical analyses of biomass samples.

	Proximate analysis (wt.%)				Ultimate analysis (wt.%)				
	M_{ad}	A_{ad}	V_{ad}	FC_{ad}	C_{daf}	H_{daf}	N_{daf}	S_{daf}	O_{daf}
Corn Straw	11.6 ± 0.22	7.9 ± 0.12	64.2 ± 1.27	16.3 ± 0.42	43.9 ± 0.94	4.5 ± 0.09	1.8 ± 0.06	0.4 ± 0.09	49.3 ± 1.03
Poplar	11.6 ± 0.19	2.3 ± 0.05	66.3 ± 1.69	19.8 ± 0.39	45.9 ± 0.87	4.1 ± 0.06	0.7 ± 0.05	0.1 ± 0.03	49.2 ± 1.28

	Ash analysis (wt.%)								Cl_{ad}	K_{ad}	P_{ad}
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O		mg/g	mg/g	mg/g
Corn Straw	47.52 ± 1.10	5.64 ± 0.29	1.04 ± 0.17	4.51 ± 0.38	12.6 ± 0.72	7.87 ± 0.77	1.97 ± 0.14	Corn Straw	1.34 ± 0.12	13.1 ± 0.79	2.1 ± 0.24
Poplar	30.97 ± 0.89	5.09 ± 0.37	2.6 ± 0.21	29.32 ± 0.92	5.96 ± 0.42	6.94 ± 0.85	2.9 ± 0.17	Poplar	1.04 ± 0.11	7.09 ± 0.61	0.24 ± 0.08

photo-fragmentation atomic absorption spectroscopy (CPFAAS) [17], laser induced fragmentation fluorescence (ELIF) [18], laser-induced breakdown spectroscopy (LIBS) [19] and planar laser-induced fluorescence (PLIF) [20]. In order to obtain the potassium proportion in solid residues, inductively coupled plasma-optical emission spectrometry (ICP-OES) is usually employed [21] to measure the remaining elemental potassium. Very recently, Liu et al. [22] used ICP-OES to investigate the effects of atmosphere and chlorine on potassium release during biomass combustion in a fluidized bed and the results show that the release proportion of potassium in air atmosphere was bigger than oxy-fuel environment and the overall activation energy for potassium release under air atmosphere is less than that under oxy-fuel atmosphere.

From previous studies [2,23], we know that potassium compounds in biomass can be classified into four groups: (1) H_2O-soluble potassium, which exists as potassium salts, e.g., potassium chloride; (2) CH_3COONH_4 (NH_4Ac)-soluble potassium, which is bounded to carboxyl groups; (3) HCl-soluble potassium, which is organically bounded to functional groups containing oxygen or nitrogen; (4) insoluble potassium, which is attached to minerals. NH_4Ac- and HCl-soluble potassium compounds together are also referred to as organically-bound potassium. The release characteristics of individual forms of potassium compounds have been investigated mainly via offline inductively coupled plasma (ICP) measurements. For instance, Deng et al. [24] studied the transformation of different forms of potassium compounds during rapid pyrolysis of wheat straw, corn stalk and rice hull under different temperatures. On the other hand, numerical methods have also been utilized to investigate the release of different forms of potassium [25], e.g., the first order Arrhenius expression model [26], the two-step kinetics model [20] and even the two-step kinetics release model combined with the gas phase potassium transformation kinetics [27], although some key information such as the time-resolved release history of different forms of potassium are still lack for a complete model validation. To the authors' best knowledge, the online dynamic release characteristics of different forms of potassium compounds during biomass combustion have not been revealed yet.

To reduce harmful potassium emissions, inhibition technologies can be used and classified into the following two categories: (1) pretreatment by water washing to remove potassium before combustion [28] and (2) addition of potassium sorbent additives to inhibit potassium release during combustion [29]. While both approaches have shown their potential to alleviate ash deposition and corrosion in biomass-fired furnaces, the additive approach appears more advantageous in that it saves water and the additives can be directly injected into boilers without any major reconfiguration. Previous studies on inhibition additives of potassium release have shown that additives with a high content of Al or Si are effective to reduce potassium release [29,30]. For example, Mason et al. [29] used flame emission method to investigated the effects of an aluminosilicate based additive on the release of potassium during biomass pellets combustion and the results suggest that high chlorine and/or low (Si + Al) facilitates the release of KCl or KOH to the gas phase, while high (Si + Al) helps to keep K in the solid phase. To achieve a deeper understanding of the inhibition mechanism of various additives, however, the potassium-release dynamics that interacts with these additives during biomass combustion are still required.

In order to bridge these research gaps and achieve a better understanding of the release characteristics of different forms of potassium compounds and the inhibition mechanisms of different additives, the present study employs the LIBS technique to obtain time-resolved profiles of potassium released from a burning biomass pellet mixed with four different additives. In addition, offline ICP analyses are performed along with the chemical fractionation method to reveal the transformation of different chemical forms of potassium compounds in the solid phase. A combination of online and offline measurements can provide us comprehensive physical insights into potassium release during