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Temporal release of potassium from pinewood particles during combustion

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ABSTRACT

The temporal release of K from single pinewood particles of four different initial masses (20–50 mg) in a Hencken burner was measured in-situ by laser-induced break down spectroscopy (LIBS). Particle temperature during the combustion was measured by two-color pyrometry. A calculation method was developed to determine the K release flux across the plume based on LIBS measurement and computational fluid dynamics (CFD) model. For all the 4 particle sizes, the temporal release rate of K showed a peak during devolatilization, a monotonous increase during char combustion and a monotonous decrease during the ash stage. It is found that the cumulative fraction of released K was below 4% in the devolatilization stage and ~20% in the char combustion stage. The particle mass did not have significant influence on the K release. The mechanism of the K release during the char combustion was analyzed, based on the initial portioning of K as inorganic K and organically-bound Char-K. The inorganic K releases mainly by thermal decomposition. The Char-K releases mainly by converting first to inorganic K when the char is burnt and then by releasing to gas phase from the inorganic K. A kinetic model for the release of K during pinewood char combustion was developed on this basis. The kinetic parameters for the release of K was found to be influenced by the initial partitioning between the inorganic K and the Char-K. The correlated initial proportion of inorganic K in pinewood char was found to be 0.37, while the correlated pre-exponential factor and the activation energy for K release were 12.5 1/s and 89.9 kJ/mol, respectively.

1. Introduction

Biomass is a promising fuel for its renewability and low net CO_2 emissions. However, it also contains inherent minerals such as K, Ca, Mg, Fe, Si, S, Cl and P, which lead to fouling, slagging and particulate emissions during thermal processing [1,2]. Of these elements, potassium is typically the most important fouling species [3]. Therefore, a better understanding of the transformation of K during biomass thermal conversion is needed to help to solve the technical problems arising from the use of biomass.

Previous measurements under different thermal conversion conditions have showed that the partitioning of K in gaseous and solid products is influenced by temperature [4–6], atmosphere [7], and the concentrations of Cl, Si, Ca in the fuel [5,6,8–12]. Similar experimental findings were also reported for Na transformations during the thermal conversion of coal [13–15]. Based on these findings, transformation mechanisms of K have been gradually developed. These reveal that the K in biomass is typically found in two forms, either as inorganic salts or organically bound to the carbonaceous matrix [2,4–7]. During thermal conversion, the inorganic K may be released to the gas phase by sublimation and decomposition, or may react with silica to form silicate [4–7,9]. The inorganic K may also be transformed into organic forms [4–7,9]. The organic K (Char-K) may decompose to release atomic K, or be oxidized to form inorganic K salts [5–7,9].

To further understand the transformation of K during biomass thermal processes, further investigation of the temporal release behavior of K is necessary. Recent advances in measurement science and technology now make this possible. For instance, molecular beam mass spectroscopy (MBMS) was applied to study the speciation of alkali metal release during switch-grass combustion [16], and feedstock and particle size influences on the alkali metal release during biomass gasification were also investigated

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Nomenclature

k_K	rate coefficient of K release (1/s)
$m_{char,0}$	initial mass of char (g)
$n_{K,0}$	initial total amount of K in char (mol)
$n_{K,oxidized}$	amount of oxidized Char-K in char (mol)
$n_{K,inorganic}$	amount of inorganic K in char (mol)
$n_{K,release}$	amount of K released from char (mol)
$n_{K,total}$	initial total amount of K in pinewood (mol)
r_0	radius of burner (mm)
r_p	radius of char (mm)
A_K	pre-exponential factor for K release (1/s)
E_K	activation energy of K release (kJ/mol)
C_K	K concentration (mol/m^3)
$C_{K,0}$	K concentration at the center of the measured plane (mol/m^3)
T_p	temperature of char particle (K)
α_K	cumulative fraction of released K
β	initial proportion of inorganic K in char
χ_{char}	char conversion
$\dot{\Phi}_K$	flux of K passing through a given height of the plume (mol/s)
$\dot{\Phi}_{gas,total}$	flux of plume gas (mol/s)

using MBMS [17,18]. It was found that the main K and Na containing species released during biomass combustion [16] or gasification [17,18] were KCl and NaCl. Later, measurements of the spontaneous emission of K from a burning willow particle with a spectrometer have found that the release of K during combustion can be divided into three stages: volatile combustion, char combustion and ash decomposition after char burnout [19]. Based on the assumption that KOH vaporizes from a spherical particle, a K release model has been developed to explain the K release during the char combustion stage [19]. The release of Na from coal combustion was found to be similar to that of K from biomass combustion. The atomic Na concentration field in the plume of single burning brown coal particle was measured by planar laser-induced fluorescence (PLIF), which revealed that the release of Na also occurs in three stages [20–22]. The decomposition of organic-Na in the char was assumed to lead to Na release during the char combustion stage and, based on this assumption, a Na release model was developed [23]. In recent years, Laser-induced breakdown spectroscopy (LIBS) has also been used to measure the alkali metal release during the combustion of single wood particles [24] and coal particles [25]. The behavior of the alkali metal release was observed to be similar to that found in previous studies. However, despite the significance of these findings regarding the final partitioning of K in the products and of their temporal release processes during thermal conversion, significant gaps in understanding remain. In particular, there is an absence of both detailed knowledge of the mechanisms of these processes and of predictive models of their behavior.

The present investigation aims to provide new measurement of the temporal release of K during the combustion of single pinewood particles and, from this, to identify the main release paths governing the release behavior. It further aims to develop a kinetic model of K release during char combustion, to propose the main pathways for K release, and to calculate the corresponding kinetic parameters.

2. Experimental

2.1. Samples and burner

Measurement were performed at the University of Adelaide. The pinewood particle used here was firstly produced by a pelletizer, and then polished into spherical shape with sandpaper. The composition of the pinewood particle was given in Table 1. Four sizes of pinewood particle were prepared with masses of 20.9 mg, 30.7 mg, 40.1 mg and 50.7 mg (with an accuracy of ±0.1 mg). The diameters of the particle were in the range of 3–4 mm. The particles were suspended by a Pt wire in the center of the flame at a height of 5 mm above a Hencken burner. The diameter of the Hencken burner was 20.4 mm. Methane and air were used as the fuel and oxidant, respectively. The gas composition at this location was calculated to be 73.1% N_2, 14.9% H_2O, 7.5% CO_2 and 4.5% O_2. The particle was positioned in a region with a flame temperature of $\sim$1650 K. A shroud gas of N_2 issuing from a circular pipe (diameter of 40 mm) concentric with the burner was used to stabilize the position of the flame (i.e. to avoid flicker). The emission of K from the burning particle was measured in the plume of the particle by laser induced breakdown spectroscopy (LIBS) and the char temperature was measured by a two-color pyrometry technique. The experimental system is shown in Fig. 1.

2.2. LIBS system

A Q-switched Nd:YAG pulsed laser (Quantel Brilliant B, 532 nm, 10 Hz) was used with a typical output of 90 mJ/pulse and 10 ns duration. The laser beam was focused with a 100 mm diameter, 200 mm focal-length lens to form a plasma spot, which was positioned 20 mm above the burner. The focusing lens was also used to collect the emitted plasma radiation and direct it to an optical fiber bundle. The optical fiber transmitted the emitted light to a spectrometer (Andor Shamrock, SR-500, with ICCD Andor iStar). A solution of K_2CO_3 was seeded into the flame in small nebulized droplets through the central tube (diameter 1 mm) of the Hencken burner to allow calibration of the 766.5 nm K emission line, following a similar calibration procedure described elsewhere [24]. The calibration fitting achieved a correlation coefficient of 0.996 in the range of 0–20 ppm, with a detection limit of 0.11 ppm. The overall accuracy of this system was better than ±12% in the calibration range.

Table 1
Composition of the pinewood.

Proximate analysis (wt%, dry basis)	
Volatile	76.1
Fixed carbon	23.1
Ash	0.8
Ultimate analysis (wt%, dry and ash-free basis)	
C	51.3
H	6.0
N	<0.01
S	0.02
O (by difference)	42.68
Main ash-forming elements (wt%, dry basis)	
Si	0.162
P	0.002
Cl	0.09
K	0.088
Mg	0.04
Na	0.029
Ca	0.142