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# Experimental exploration of potassium compounds in the vicinity of a burning biomass pellet: From near-surface to downstream



Siyu Liu<sup>a</sup>, Wubin Weng<sup>a</sup>, Yong He<sup>a</sup>, Marcus Aldén<sup>b</sup>, Zhihua Wang<sup>a,\*</sup>, Zhongshan Li<sup>b</sup>

<sup>a</sup> State Key Laboratory of Clean Energy Utilization, Zhejiang University, Hangzhou 310027, P.R. China
 <sup>b</sup> Division of Combustion Physics, Lund University, P.O. Box 118, Lund S-22100, Sweden

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### ABSTRACT

The concentrations of gas-phase potassium hydroxide (KOH), potassium chloride (KCl) and atomic potassium (K (g)) were quantitatively measured from the near-surface to downstream area of burning pinewood pellets by a newly developed photofragmentation tunable diode laser absorption spectroscopy (PF-TDLAS) technique to reveal the original form of the released potassium. The novel arrangement of the PF-TDLAS system enabled a spatial resolution of  $\sim 1 \text{ mm}^3$ , which made it possible to obtain temporal release profiles of K(g)/KOH/KCl at different heights above the burning pellet surface. Surface temperature and mass loss of the wood pellet as well as the gas temperature at measurement points were measured simultaneously. During the devolatilization stage, the release of all three potassium species was observed, with each of them accounting for  $\sim 1/3$ ; while in char oxidation stage, the release of KOH was dominant, but the release intensity was strongly influenced by the local oxygen content. The results from different measurement heights showed there was a notable difference in potassium release profiles of different potassium species over the near-surface area, where the detected potassium forms were the best representative of the originally released forms of potassium. For a period of time during the devolatilization stage, only K(g) was detected in the near-surface area, and the concentration was significantly lower than the downstream area where KOH and KCl coexisted. This suggested that a large amount of potassium might leave the pellet as organic-K, which cannot be detected by the PF-TDLAS method. During char oxidation stage, the total potassium concentration at the near-surface area was also lower than the downstream area, but it was due to the lack of oxygen at the measurement position. A potassium release mechanism during the devolatilization stage of biomass combustion was proposed based on the experimental measurements, and the results also indicated the importance of spatially resolved measurement.

## 1. Introduction

Biomass is considered as a carbon-neutral fuel and a promising renewable alternative to fossil fuels in thermochemical conversion processes, such as combustion and gasification. However, the high content of potassium in biomass leads to ash-related issues in facilities, including slagging, fouling, and corrosion [1], which brings challenges to the utilization of biomass compared with traditional fossil fuels. Therefore, knowledge of the potassium release behaviors is crucial for addressing ash-related issues in biomass thermal conversion processes.

The potassium in biomass can be released in various forms, such as potassium atoms (K(g)), potassium hydroxides (KOH), and potassium chlorides (KCl), depending on fuel compositions and reaction environments. To develop the potassium release mechanism, it is indispensable

to measure these potassium species in the vicinity of burning biomass pellets. Several experiments have been conducted to study the release behaviors of potassium during biomass thermal conversion processes using optical techniques. For example, the release of total elemental potassium from burning biomass pellets has been studied using laserinduced breakdown spectroscopy (LIBS) [2], the release behaviors of potassium atoms have been investigated by tunable diode laser absorption spectroscopy (TDLAS) [3] and planar laser-induced fluorescence (PLIF) [2], the release of KOH and KCl has been measured by laser-induced photofragmentation fluorescence (LIPF) [3], collinear photofragmentation and atomic absorption spectroscopy (CPFAAS) [4], and photofragmentation tunable diode laser absorption spectroscopy (PF-TDLAS) [5]. Nevertheless, the initial release pathways of potassium remain unclear due to the limited information available about the

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<sup>\*</sup> Corresponding author. *E-mail address:* wangzh@zju.edu.cn (Z. Wang).

potassium species in the near-surface area of the burning biomass. This requires species-specific measurements with good spatial resolution. By using LIBS, the measurement points are generally located at a relatively far distance from the biomass surface to minimize the impact of plasma on biomass combustion. Additionally, the LIBS technique cannot provide information about specific potassium species. PLIF only provides information for atomic potassium and cannot capture the behaviors of the important potassium salts, e.g., KOH and KCl. Absorption-based techniques such as TDLAS, CPFAAS and PF-TDLAS are line-of-sight methods that do not provide spatially resolved information. While the LIPF technique can provide two-dimensional concentration distributions, the conventional LIPF, using an excimer laser (193 nm) to photodissociate potassium compounds, cannot distinguish between KOH and KCl. Notably, Weng et al. [6] recently achieved imaging of KOH distribution using the fourth harmonic of a Nd:YAG laser (266 nm). However, due to the significant interference from the broadband emission of polycyclic aromatic hydrocarbons (PAHs), concentrations of potassium compounds during the devolatilization stage were not captured.

Despite the lack of spatial resolution, CPFAAS and PF-TDLAS techniques allow for simultaneous quantitative measurements of three key potassium components, i.e., KOH, KCl, and K(g). Furthermore, there have been several reports [5,7] on the utilization of PF-TDLAS techniques under reducing conditions, which are likely the case during the devolatilization stage of biomass combustion. Recently, Liu et al. [8] developed the PF-TDLAS technique, which enables spatially resolved measurements of potassium compounds by arranging the photofragmentation laser and the TDLAS laser perpendicular to each other. Using this method, the temporal profiles of potassium concentrations at different positions can be obtained, allowing for quantitative investigation of potassium release and gas-phase chemistry during the biomass combustion process, especially for the near-surface area, as it is the region where the detected potassium forms are the best representative of the originally released forms of potassium species from within the pellet.

In the present study, a spatially resolved PF-TDLAS method similar to the one described in [8] was employed to capture the temporal concentration profiles of K(g)/KOH/KCl at various heights above the surface of individually burning pinewood pellets. Special attention was given to the vicinity very close to the pellet surface, specifically, with 0.5 mm above the surface. Based on the experimental results, a comprehensive discussion on the potassium release behaviors was carried out, and a possible release mechanism of potassium during the devolatilization stage of wood combustion was proposed.

### 2. Experimental setup

Concentrations of potassium species were measured in the plume of a single pinewood pellet burning in a hot flue gas provided by a multi-jet burner. Details of the multi-jet burner have been reported by Weng et al. [9]. A homogeneous hot gas flow was provided at the burner outlet with an area of  $85 \times 45 \text{ mm}^2$  and a flow speed of  $\sim 1 \text{ m/s}$ . A stabilizer was placed 35 mm above the burner outlet, as shown in Fig. 1(b). The hot flue gas adopted in the present work for wood combustion has a temperature of  $\sim 1750 \text{ K}$  with an uncertainty of about  $\pm 3 \%$  [9]. Taking into account heat losses through thermal radiation and heat conduction, the gas temperature was selected to keep the pellet temperature consistent with that of the grate-firing system, which is one of the most prevalence technology of biomass combustion [10]. The contents of the reactive species, O<sub>2</sub>, H<sub>2</sub>O and CO<sub>2</sub> were around 4.5 %, 13.1 % and 6.6 %, respectively.

Cylindrical pinewood pellets with a weight of  $\sim 300$  mg and a size of  $\sim 6 \times 10$  mm (diameter  $\times$  length) were used in the experiments. The properties of the pinewood samples are presented in Table S1 in the supplement. For each measurement, the wood pellet was held by two ceramic rods (diameter of 1 mm) and placed with its center at a height of 5 mm above the outlet of the multi-jet burner. In addition, the ceramic



**Fig. 1.** (a) Schematic of the PF-TDLAS system, inset shows an example of the photofragmentation-induced K-atom absorption (PF-induced absorption). (b) Details of the burner head and the arrangement of the photofragmentation and diode laser beams. (c) The front view photo of the burning pinewood pellet at the devolatilization stage with schematic of measurement points adopted in this work. M: mirror, DM: dichroic mirror, BS1: beam sampler, BS2: beam splitter, AF: attenuating filter, IF: interference filter, CL: cylindrical lens, A: aperture, SL: spherical lens, HB-PD: high bandwidth photodiode, LB-PD: low bandwidth photodiode.

rods were fixed on a weight scale (FZ-120i, A&D Company) to monitor the mass loss history of the individual wood pellet with a precision of 1 mg. Meanwhile, the surface temperature of the burning pellet was monitored using a two-color pyrometer with a similar setup presented by Weng et al. [3]. The thermal radiation signal of the burning wood pellet was captured by an ICCD camera with a stereoscope. Two interference filters, centered at the wavelength of 515 nm and 652 nm, were mounted before the stereoscope. The ratio of the radiation intensity at these two wavelengths were used to derive the surface temperature after calibration.

The newly developed photofragmentation tunable diode laser absorption spectroscopy (PF-TDLAS) technique, as described in detail by Liu et al. [8], was used to measure the concentrations of KOH/KCl/K(g) above the burning wood pellet. Schematic of the PF-TDLAS system is depicted in Fig. 1(a). Two Nd:YAG lasers (Brilliant B, Quantel) operating at the wavelength of 355 nm and 266 nm were used to photodissociate KOH and KCl, respectively. Both lasers operated at a pulse energy of 12 mJ with a pulse duration of 5 ns and a repetition rate of 10 Hz. The delay time between the two laser pulses was set to be 190 µs, allowing sufficient time for the photofragmentation-induced K atoms to fully recombined. The laser beams were collinearly aligned using a dichroic mirror and transformed into a laser sheet with a height of 8 mm and thickness of about 1 mm through a cylindrical lens. An aperture was employed to truncate the laser sheet to around 1 mm in height. Subsequently, the laser beam passed above the burning wood pellet, as shown in Fig. 1(b). Laser energies were monitored by photodiodes placed before and after the measurement zone. As the laser beam passed through the measurement zone, additional potassium atoms in the ground state were generated. TDLAS technique was employed to monitor both this portion of atomic K and the K atoms originating from the burning biomass.

For TDLAS measurement, an external cavity laser (DL 100, Toptica) controlled by a scan control module (SC 110, Toptica) was utilized to provide a continuous wave laser at 766.49 nm, with a scan range of 16 GHz and a scan rate of 10 Hz. The laser had a power of about 5 mW with a beam diameter of 1 mm. The diode laser beam passed orthogonally to the photofragmentation laser, as illustrated in Fig. 1(a) and (b), enabling a spatial resolution of approximately 1 mm<sup>3</sup>, depended by the overlap volume. The transmitted diode laser beam was then separated using a beam splitter. The majority (90 %) of the light was focused onto a high

bandwidth photodiode (HB-PD) to monitor the photofragmentationinduced K-atom absorption signal as shown in Fig. 1(a). The remaining light as well as a small portion of the diode laser beam before the passage was separately directed onto a low bandwidth photodiode (LB-PD) to monitor the atomic K released from the wood pellet. The concentration of K atoms ( $N_K$ ) released from the burning wood pellet was calculated based on the Beer-Lambert law,  $N_K = \alpha(\nu)/(\text{L}\cdot\sigma(\nu))$ , where  $\alpha(\nu)$  is the absorbance, *L* is the optical path length and was assumed to be 0.02 m in this work,  $\sigma(\nu)$  is the absorption cross section of K atoms. The uncertainty of the TDLAS system was estimated to be ~5 %, as described by Weng et al. [11].

The concentrations ( $C_{KM}$ ) of KOH and KCl were calculated based on equations given by Sorvajärvi et al. [12]:

$$C_{KM} = -\ln\left(1 - \alpha_{max}\frac{h\nu}{\eta}\frac{A}{\sigma_{K}E_{in}}\right)\frac{kT}{p}\frac{1}{\sigma_{KM}L_{pf}},$$
(1)

$$C_{KM} = \alpha_{max} \frac{A}{E_{in}L} \frac{h\nu}{\eta} \frac{kT}{p} \frac{1}{\sigma_K \sigma_{KM}} \frac{\ln(E_{in}/E_{out})}{1 - E_{in}/E_{out}},$$
(2)

where  $\alpha_{max}$  is the maximum K-atom absorbance caused by photofragmentation, h is the Planck's constant,  $\nu$  is the frequency of the photolysis laser,  $\eta$  is the fragmentation efficiency and is equal to 1 for both KOH and KCl,  $\sigma_K$  and  $\sigma_{KM}$  are the absorption cross sections of K atoms and KOH/KCl, respectively, A is the cross-section of photolysis volume (~ 1 mm<sup>2</sup> in the present work), k is the Boltzmann constant, T is the gas temperature, p is the pressure,  $E_{in}$  and  $E_{out}$  represent the power of photofragmentation laser before and after the burner,  $L_{pf}$  is the path length for photofragmentation laser (1 mm in the present work). Eq. (1) is valid only when the attenuation of the photofragmentation laser energy can be considered negligible. Otherwise, Eq. (2) should be employed. In this work, Eq. (1) was satisfied most of the time, however, during the devolatilization stage of wood combustion, a clear attenuation of the photofragmentation laser energy was observed. Therefore, Eq. (2) was utilized in this stage. An uncertainty of 15 % was estimated for the KOH and KCl concentration measurements, according to the work of Liu et al. [8] and Sorvajärvi et al. [12].

As presented in Eq. (1) and (2), the gas temperature was necessary to determine the concentration of KOH/KCl. However, the gas temperature of the plume above the burning wood is not the same as the surrounding gas temperature [13]. Viljanen et al. [14] reported that the decay process of the photolysis-induced K-atom absorbance could be fitted by a double exponential curve, where the first decay time constant could represent local temperature. Therefore, in this work, the first decay time constant of the 355 nm photolysis-induced K-atom absorbance profile was used to determine the gas temperature at the measurement point. Temperature calibration was conducted prior to the experiment through a series of well-designed flames seeded with KOH solution. The flame temperatures varied from 1290 to 1950 K with a fixed oxygen concentration at around 4.5 %. Details of the calibration flame conditions are shown in Table S2 in the supplement. The calibration curve is shown in Fig. 2. Nevertheless, the decay time constant was also affected by the oxygen concentration, which varies a lot during the devolatilization stage. Therefore, in this work, the method was only used to determine the gas temperature during the char oxidation and ash cooking stage.

The concentration profiles of K(g)/KOH/KCl and gas temperatures at different heights in the center of the plume above the burning pellet surface were measured through adjusting the height of the intersection of the photofragmentation laser and diode laser, as presented in Fig. 1 (c). Four different heights above the pellet surface, i.e., 0.5 mm, 4 mm, 10 mm, and 15 mm, were adopted. At least three consecutive measurements were conducted for each case and an averaged result was used for further analysis.



**Fig. 2.** Calibration curve of gas temperatures using the first decay time constant of the photofragmentation-induced K-atom absorbance. Inset shows decay curves at two different temperatures.

## 3. Results and discussion

Photos of the burning wood pellet at six different residence times are shown in Fig. 3(a). The bright flames were evident in the devolatilization stage, which was attributed to the combustion of volatiles released from the pellet. Then the flame disappeared in the following char oxidation and ash cooking stage. Meanwhile, the pellet size began to shrink in the char oxidation stage and stayed relatively constant in the ash cooking stage. A convincing separation of the combustion stage was obtained based on the temporal release profiles of KOH as presented in Fig. 3(b), and the surface temperature and mass loss profiles of individual burning wood pellets as a function of residence time depicted in Fig. 3(d). For the wood samples used in the present work, three distinct combustion stages, i.e., the devolatilization stage, char oxidation stage and ash cooking stage, can be identified through both the temporal behaviors of KOH release and profiles of pellet surface temperature and mass loss. The duration of each stage determined based on these profiles shows good consistency with the devolatilization stage lasting about 65 s, followed by the char oxidation stage lasting about 460 s, and the ash cooking starting and lasting until the end. Additionally, mass loss results indicated that at the end of the devolatilization stage, there was an approximately 82 % mass loss of the pellet, which was close to the volatile content (83.3 %) in the sample. This suggested that the separation could effectively distinguish the devolatilization stage and the char oxidation stage. Fig. 3(b) shows the temporal release profiles of gasphase KOH at 4 mm and 0.5 mm above the burning pellet surface. The concentration was calculated through Eq. (1) and (2) based on the local gas temperature as shown in Fig. 3(c). It was observed that consistent results, e.g., curve shapes, absolute values, and stage durations, were obtained from three repeated experiments of each pellet. However, for the time series of KOH concentration at different heights above the burning pellets, there are obvious differences, characterized by the shape of the KOH concentration profiles in the devolatilization stage and the duration and KOH release intensity in the char oxidation stage. These differences will be further discussed in the following part. The gas temperature profiles of the measurement points are presented in Fig. 3 (c). The gas temperature at the position closest to the pellet surface exhibited similar values and trends to the pellet surface temperature (cf. Fig. 3(d)). As the distance increased, the gas temperature became closer to the temperature of the surrounding hot gas.

The temporal profiles of potassium concentrations at the center of the plume with different heights above the pellet during the devolatilization stage and char oxidation & ash cooking stage are presented in Fig. 4 and Fig. 5, respectively. The average results of three measurements at each height are used and the corresponding standard deviations are presented. At the devolatilization stage, as shown in Fig. 4, all three potassium species, i.e., KOH, KCl, and atomic K, were observed. The profiles of KOH and KCl exhibited similar shapes and absolute values,



**Fig. 3.** (a) Images of the wood pellet combustion at different combustion stages. (b) Temporal KOH release profiles of individually burning wood pellets in the center of the plume at a height of 4 mm and 0.5 mm above the pellets, respectively (three replicates for each case). (c) Temporal profiles of gas temperatures at different heights above the burning wood pellet as a function of residence time. (d) Pellet surface temperature and mass loss profiles of individual pellet as a function of residence time. I: devolatilization stage, II: char oxidation stage, III: ash cooking stage.

while the concentration of atomic K was relatively lower. It should be mentioned that the results for KOH and KCl were spatially resolved, whereas the results for K atoms were from line-of-sight measurements. Consequently, the actual concentration of K atoms at the measurement point located in the center of the plume was typically higher than the measured results, which was an average of the given measurement height. The flux of potassium species, as depicted in Fig. 6, indicated that at the devolatilization stage, potassium atoms accounted for nearly one-third of the released potassium.

From the beginning to  $\sim 20$  s at the devolatilization stage, all three potassium species started to release. The occurrence of KCl and atomic K



**Fig. 4.** Temporal profiles of (a) KOH, (b) KCl, and (c) atomic K concentrations at different heights above burning wood pellets during the devolatilization stage.



**Fig. 5.** Temporal profiles of (a) KOH, (b) KCl, and (c) atomic K concentrations at different heights above burning wood pellets during the char oxidation & ash cooking stage.



**Fig. 6.** (a) Potassium flux at different heights above the burning wood pellet at a residence time of 40 s, 380 s, and 1000 s, respectively. Inset shows horizontal distributions of normalized KOH concentration measured at different radii.

began almost simultaneously, while the release of KOH occurred  $\sim$ 5 s later than these two species. Since the surface temperature during this period, as shown in Fig. 3(d), was below 700 K, which was much lower than the evaporation temperature of KCl and KOH, the current potassium release might be attributed to other reasons. van Lith et al. [15] associated the release of potassium under 500 °C to the decomposition of organic structure and suggested that the resultant potassium was probably in the form of KOH. However, the experimental results of the present study didn't entirely match their conclusions. Considering K atoms could also be generated through the decomposition of organically associated potassium [3], a considerable level of K atoms was also detected in the experiment. This portion of K atoms might quickly react with HCl, which was observed to release at a low temperature (< 500 °C) [16], forming KCl that was also detected in this temperature range. Another phenomenon observed during this period was the concentrations of KOH and KCl measured at a height of 0.5 mm were significantly higher than those measured at higher heights. Considering the accuracy of the potassium concentration relied on the temperature measurement and the gas temperature close to the pellet surface area was observed lower than that at higher position [17], one possible explanation was the calculated concentration at 0.5 mm overestimated and at higher position underestimated the actual value, as the gas temperature used during the devolatilization stage was fixed at 1200 K as reported by Weng et al. [13].

During the period from 20 to 50 s, neither KOH nor KCl was observed at 0.5 mm, while at downstream positions, the temporal profiles of KOH/KCl concentration at various heights displayed a similar trend, characterized by an initial increase followed by a subsequent decrease. Meanwhile, the concentration of atomic K remained at a comparable level to that at different heights. This indicated that, in addition to the potassium atoms, a large amount of potassium left the pellet surface in an unknown form and subsequently transformed to KOH or KCl at the downstream area. The PAH signal measured in the work of Weng et al. [13] indicated that a significant amount of PAH was generated in this period, which represented a strong release pattern of organic species. Besides, Jones et al. [18] suggested that the released K may be bound to or entrained in the organic volatiles during the devolatilization stage. Thus, potassium released in the form of a specific organic species, which could not be detected by the PF-TDLAS method, could potentially give an explanation.

At the end of the devolatilization stage, as the pellet surface temperature exceeded 1000 K, the evaporation of potassium salts, e.g., KCl and KOH, might occur and become another source of the released potassium, as indicated by the reappearance of KOH and KCl release at a height of 0.5 mm. Also, the concentration of KOH and KCl at higher positions could be under-predicted as a result of the relative higher gas temperature at higher heights.

The temporal profiles of potassium concentrations at the char oxidation & ash cooking stage are shown in Fig. 5. The KOH and KCl profiles also presented similar trends, however, the concentration of KCl was much lower than the one of KOH. Previous studies have found that for the low chlorine-containing biomass like wood, nearly all chlorine would be released at a temperature above 700 °C [15]. Hence, the potassium release at the char oxidation stage was dominated by KOH, generated by the oxidation of char bound potassium. However, there was still a small amount of KCl observed during this stage. Knudsen et al. [19] attributed the release of KCl to the capturing effect of the char layer during the devolatilization stage. Subsequently, at the char oxidation stage, the captured KCl could be released into the gas phase again, along with the reaction of char oxidation. Therefore, the KCl presented similar release behaviors to KOH during this stage.

Another interesting phenomenon observed in the experiment was the relatively lower concentration of KOH and KCl measured at a height of 0.5 mm during the char oxidation stage. The situation was different from the one in the devolatilization stage, as there was no organic volatile release in this stage. In the char oxidation stage, previous study [20] indicated that for wood combustion, K release mainly arose from the decomposition of char-K to the inorganic phase and subsequent evaporation. Hence, the concentration of K near the pellet surface should be highest, which was inconsistent with the experimental results of the present work. One possible reason for the difference could be the lack of oxygen at the measurement point, which was evident from the relatively dark color observed in the char image shown in Fig. 3(a), and the relatively long reaction duration of the char oxidation stage, as shown in Fig. 5. The discrepancy might be attributed to the presence of the pellet, which obstructed the diffusion of the hot flue gas generated by the multi-jet burner to the measurement point that near the top surface of the pellet. At a higher height, the hot gas flow converged, resulting in a high concentration of potassium species at higher height. The K-atom profile at the height of 0.5 mm also presented a distinct pattern at the char oxidation stage. The K-atom concentration reached its maximum at the beginning of this stage and continuously decreased. Meanwhile, the K-atom concentration profiles at higher heights exhibited a similar trend to KOH and KCl. This further supported the fact that the reaction conditions near the center of the pellet surface were different from those other locations. The results also indicated that, considering factors such as the flow field distribution around burning particles would also influence potassium release characteristics, spatially resolved measurements, especially two-dimensional measurements, are of significant importance for obtaining accurate potassium release rates, developing release mechanisms, and validating numerical simulations. Except for the results at 0.5 mm, a decreasing trend in KOH/KCl concentrations was observed during the whole combustion process with increasing measurement heights. Given the rapid equilibration between potassium species, this decrease in KOH/KCl concentrations indicated the influence of gas diffusion.

The potassium fluxes at different heights above the burning wood pellet at various residence times representing the devolatilization stage, char oxidation stage, and ash cooking stage, respectively, are shown in Fig. 6. The fluxes of potassium were obtained by integrating the product of K species concentration and velocity with different radii. The radial concentration distribution was measured using PF-TDLAS method with measurement points at varying radii, and the velocity distribution was calculated through a 3-D steady-type simulation using ANSYS FLUENT. Further details about the simulation procedure can be found in our previous study [21]. As can be seen, the measurement results of potassium species at a height of 0.5 mm during the devolatilization stage and char oxidation stage were quite different from the other positions, which has been discussed in depth above. These differences indicate that the measurement location has a significant impact on observing the

potassium release behaviors. The results obtained from different locations may lead to different conclusions, thus affecting the accuracy of the established release mechanisms and models. This highlights the importance of developing measurement methods with capability of spatial resolution. Except for the results at the height of 0.5 mm, the flux of the total potassium species at different heights remains relatively constant for a certain combustion stage. This validates the reliability of our measurement method. During the devolatilization stage, it was observed as the height increasing, the proportion of K atoms gradually decreased, indicating the transformation from atomic potassium to potassium compounds. During the char oxidation stage and ash cooking stage, an increase in measurement heights revealed a trend of a higher percentage of KOH, while the percentages of KCl and K atoms decreased. This phenomenon could be explained by the conclusion of Weng et al. [22], who found that with increasing temperature, as is the case in the present study (cf. Fig. 3(c)), the chemical equilibrium between KOH and KCl shifted towards the formation of KOH.

A release mechanism of potassium during the devolatilization stage of biomass combustion is proposed as shown in Fig. 7. Based on the experimental results, we subdivided the devolatilization stage into three sub-stages, corresponding to the three distinct time intervals during wood combustion in our experiment. Each sub-stage corresponded to different surface temperature intervals. While reaction durations may vary in different experiments due to diverse experimental setups, the surface temperatures determined the combustion progress and consequently the reaction stage. During the devolatilization stage, potassium could be released by decomposition of organic K or direct evaporation from inorganic K, depending on the fuel temperatures. Particularly, the experimental results indicate that a portion of potassium might be released in the form of organic K at a moderate temperature. The released atomic K or organic K could further react with surroundings and form KCl(g) and KOH(g) at the downstream area.

#### 4. Conclusion

In this work, a newly developed PF-TDLAS method was employed to obtain the quantitative temporal profiles of KOH/KCl/K(g) concentrations in the center of the plume at various heights above the burning pinewood pellet. Surface temperature and mass loss of the wood pellet as well as the gas temperature at measurement points were determined at the same time. The measurement results showed that, during the devolatilization stage, the release of all three potassium species was observed, with each of them accounting for around one-third, while during the char oxidation stage, the release of KOH was dominant, but the release intensity was strongly influence by the local O<sub>2</sub> content. Observation from different heights indicated that there was a significant difference in the potassium profiles of different potassium species with different heights, especially at the near-surface area of the burning pellet, where the detected potassium forms were highly likely to be the originally released form from the fuel pellet. During the devolatilization stage, there existed a period that only the release of K atoms can be detected in the near-surface area. Furthermore, the potassium fluxes at different heights indicated a discrepancy between the flux of released Katom and the total released K. This suggested the likelihood of organic potassium, which cannot be detected by the PF-TDLAS method, being released during this stage. However, the form of this organic potassium is still to be investigated. During the char oxidation stage, the observed low potassium concentration in the near-surface area was probably a result of the presence of pellet that hindered the diffusion of oxygen to the measurement position, which led to a reduction in the intensity of char oxidation. In addition, the variation of the potassium forms and concentrations at different positions highlighted the importance of developing spatially resolved methods. Based on the experiment results, a potassium release mechanism during the devolatilization stage of biomass combustion was proposed.



**Fig. 7.** A possible release mechanism of potassium during the devolatilization stage of wood combustion. The solid arrows and boxes represent potassium release path and the dash arrows and boxes represent potassium transformation path at downstream areas.

# Novelty and significance statement

The novelty of this research is the concentrations of multiple potassium species (KOH/KCl/K(g)) at the near-surface area of burning biomass pellets were quantitatively measured in-situ by a newly developed PF-TDLAS method for the first time. This is significant because it provides crucial insights into the original form of the released potassium from burning biomass pellets, which is indispensable for developing potassium release mechanisms, studying the aerosol formation mechanism, and addressing ash-related issues. However, previous measurement methods were unable to capture the release pattern of multiple potassium species at this area. From present experimental results, it was suggested that a large amount of potassium might leave the pellet in the form of organic K during the devolatilization stage, which was different from the previous studies. Based on the experimental measurements, a potassium release mechanism of biomass combustion during the devolatilization stage was proposed.

## Author contributions

- Siyu Liu, performed research, analyzed data, wrote the paper
- Wubin Weng, analyzed data, wrote the paper, reviewed the paper
- Yong He, reviewed the paper
- · Marcus Aldén, reviewed the paper
- · Zhihua Wang, reviewed the paper
- · Zhongshan Li, reviewed the paper

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.proci.2024.105583.

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