In-situ quantification of alkali metals from biomass combustion by optical emission spectroscopy

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Abstract. In this study, an in-situ method was developed to quantify the alkali metal emissions and its speciation from the combustion of biomass in a 150 kWth furnace. An optical emission spectrometer was used to detect the spontaneous atomic emissions of the potassium and sodium in the flame. A calibration is performed to obtain the radiation intensities of potassium and sodium, which are precursive values needed to quantify each alkali metals’ relative ground state number densities. The results show that the spontaneous emissions of the alkali metals appear as doublet lines in the spectra. The calibrated radiation intensities for sodium were converted to relative values via Lorentzian fitting. The relative excited state number densities for sodium and potassium were within the range of 0.536 to 0.791 cm⁻³ and 23.468 and 30.320 cm⁻³ respectively. This shows that potassium vapours and its compounds were higher compared to sodium. These number densities will be compared to the sodium and content in the ash for further discussion and validation.

1. Introduction

To mitigate climate change and greenhouse gas emissions from heat and power generation, alternate and renewable sources of carbon are being utilized [1-3]. Biomass has higher alkali metals content, and the emitted form slags that causes operational issues at temperatures as low as 900°C [4]. The slag reduces heat transfer efficiency and leads to internal surface failures, leading to losses in revenue due to unplanned downtime. In addition, the alkali metal chlorides are corrosive [5, 6], and alkali metal sulphate form particulate matter [7-11].

Alkali metals are usually measured by various techniques, which include X-ray fluorescence (XRF) and energy dispersive X-rays (EDX) [12-14]. However, these methods are unable to measure the alkali metal emissions in the furnace where they are initially devolatilized. The spatial evolution of the alkali metal emissions in the furnace needs to be determined to provide a better understanding of reaction mechanisms, and can be provided by using optical emission spectroscopy. Erbel et al. [15] developed an excimer laser induced fragmentation fluorescence (ELIF) system to detect alkali metal emissions, but the method requires a laser system. Similar methods requiring laser or light excitation include laser induced breakdown spectroscopy (LIBS) [16, 17] and UV-light dependent in-situ alkali chloride monitor (IACM) [18].

This study presents a portable method that quantifies the alkali metal emissions based on the optical emission spectra of the flame from a 150 kWth furnace without requiring any light excitation. In addition to our previous study [19], the results will be used for further analysis by comparing the sodium and
potassium’s relative excited and ground state number densities with the sodium and potassium content in the ash were obtained.

2. Methodology

The portable method is based on the optical emission spectroscopy (OES) of the flames from a 150 kWth furnace, shown in Figure 1, using sawdust as fuel. The dimensions of the 150 kWth furnace are shown in Figure 1. A thermocouple in section 1, T1 (ref. Figure 1) measures the temperature where the OES was recorded. The OES was obtained using an AvaSpec Starline spectrometer that detects peaks from wavelengths of 200 to 1030 nm. The spectrometer has charged-coupled device (CCD) detectors, with a grating resolution of 1200 lines/mm. Further details of the spectrometer can be found in [19]. A probe measures optical emission spectra at a distance of 600 mm flame (ref. Figure 1 (a) and (b)). The probe in Figure 1(b) detects the radiation, and is transferred via an optical fibre into the spectrometer. The spectrometer contains prisms that breakdown the radiation into specific spectral components (i.e. the spontaneous atomic emissions) as a function of wavelength and displays it on a computer.

The irradiance calibration was performed to obtain the calibrated intensity [µW/cm2/nm], which is determined from the measured optical emission spectra. The calibrated intensities are not absolute values as the sources radiation are distributed over the measurement length (i.e., 600 mm). The calibration was to mitigate the sensitivity dependence of the spectrometer on the wavelength. After the irradiance calibration, a Lorentzian function is used for fitting the peaks in the spectrum to determine the integrated emission intensity Iobs for each peak [20]. The emission intensity Iobs is related to the number density of the excited states nu by the following form:

\[ \varepsilon I_{obs} = I_{ul} = h\nu n_u A_{ul} \]  

(1)

where Iul is the absolute intensity in terms of [W/m²], ε is a coefficient derived from geometrical factors in the experiment, h is the Planck’s constant (6.62×10⁻³⁴ Js), ν is the frequency (ν = c/λ, where c is the speed of light, 3×10⁸ m/s and λ is the peak wavelength), nu is number density of the excited state, and Aul is the Einstein A coefficient which represents the probability of spontaneous emission for a particular atom from upper to lower energy states (the subscripts u and l represent the upper and lower energy states respectively). The coefficient ε is not determined, and the number density (nu) in terms of relative values are used. A detailed explanation for the use of relative values is presented in the Results and Discussion section.

3. Results and Discussion

Figure 2 shows an example of the optical emission spectrum from biomass combustion. Figure 3(a) shows the Na emission peaks at wavelengths of 589.16 and 589.60 nm for D2 and D1 transitions, while Figure 3(b) shows the K emission peaks at 766.71 and 770.10 nm for its’ respective D2 and D1 transitions. The peaks for the Na spectral lines represent electronic transitions from the 3p3P3/2,1/2 to 3s2S1/2 states respectively, while the peaks for the K spectral lines represent electronic transitions from 4p3P3/2,1/2 to 4s2S1/2 states respectively. A more detailed explanation of the atomic term symbols are reported elsewhere [21-24].

The calibrated intensity Iul of the sodium emission peaks are 0.68 and 0.61 µW/cm² for the D2 and D1 transitions respectively. The Iul of the potassium peaks are 11.24 and 10.48 µW/cm² for the D2 and D1. As the radiation from the flame is distributed over the distance of the optical probe from the flame, and the radiation may vary spatially. Calibration of the intensity with respect to the spatial distribution is not possible due to safety reasons. Thus, the quantification the alkali metals is based on relative values of the number densities, and the absolute intensities obtained from the spectrometer needs to be converted to obtain the relative radiation intensities.
The peaks in Figure 2 are fitted with the Lorentzian function [20] to obtain the relative intensities for potassium and sodium.

Figure 1. (a) Top view schematic of a 150 kW pulverized fuel furnace and spectrometer location (b) Photograph of spectrometer’s probe and the 150 kW furnace’s optical window for measurement of the OES

Figure 2. An example of the optical emission spectrum from flames of sawdust combustion with $T_1=960$ K
From Eq. (1), the relative $n_u$ for sodium D$_2$ and D$_1$ transitions are approximately 0.536 and 0.791 cm$^{-3}$ respectively; for potassium D$_2$ and D$_1$ transitions, the relative $n_u$ values are approximately 23.468 and 30.320 cm$^{-3}$. This shows that the emissions of alkali metals in the form of potassium vapours and its compounds are higher compared to sodium. This is because of the inherently higher potassium content in typical biomass such as wood. However, potassium’s volatility is higher [25], causing it to devolatilize even where biomass feeding into a reactor has seized [15]. Therefore, these number densities will be compared to the sodium and potassium content in the ash for further discussion and validation of the portable and in-situ method.

**Figure 3.** Expanded emission spectra of Fig. 2 around 589 nm for sodium (a) and around 770 nm for potassium (b).
4. Conclusion

This study shows preliminary results from an in-situ method that was developed to quantify the alkali metal emissions and its speciation from the combustion of biomass based on optical emission spectroscopy. The relative excited number densities for sodium D$_2$ and D$_1$ transitions are 0.536 and 0.791 cm$^{-3}$ respectively; for potassium D$_2$ and D$_1$ transitions, the relative $n_e$ values are 23.468 and 30.320 cm$^{-3}$. This shows that the emissions of alkali metals in the form of potassium vapours and its compounds are higher compared to sodium. This is because of the inherently higher potassium content in typical biomass such as wood. However, potassium has a higher volatility compared to sodium, and the number densities need to be compared to the sodium and potassium content in the ash for further validation and discussion of the in-situ method.

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