Biomass Combustion:
Potassium and Sodium Flame Emission Spectra and Composition in Ash

Mooktzeng Lim†, Ahmad Zulazalan Shah Zulkifli, and Hamdan Hassan
(Received December 22, 2016)

The flame emission spectra were measured from the combustion of biomass in a boiler, from which the ratio of the alkali metals' number densities (sodium and potassium) were precursory derived. Fly and bottom ash samples were collected to determine their composition via scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDX). A comparison of the alkali metals' number density ratios (from the flame emission spectra) and the ash composition provided information on potential pathways for the alkali metals. The comparison also showed that the number density ratio can be taken as a tentative in-situ indicator of the alkali metals’ ratio. The ash composition also allowed the determination of several slagging and fouling indices.

Key Words
Biomass, Combustion, Alkali metals

1. Introduction
Biomass is increasingly used for providing heat and power, and its associated particulate emissions have been known to cause environmental, operational and health issues. Larger particulates can cause asthma attacks, while ultrafine particles (particulates which are smaller than 1 μm in size) are easier to inhale and reportedly can cause cardio pulmonary diseases and lung cancer 1) ~ 3). Particulates are formed through the nucleation of gaseous species, such as volatile organic compounds (VOC), semi-volatile organic compounds (SVOCs) and alkali metals 4). Alkali metals are emitted in the form of alkali chloride and hydroxide vapors from the fuel during the initial stage of combustion and undergo homogeneous nucleation to form initial particulates, and condenses when the temperature is lower to form ultrafine particles 5). The condensation temperature depends on whether the alkali metals are in the form of sulfates, chlorides or other compounds. Alkali sulfates (K2SO4 and Na2SO4) have been reported to condense at temperatures below 950 °C, while alkali chlorides (KCl and NaCl) condense at temperatures below 600 °C 6). Coarser particles (>PM10) have also been found to contain high amounts of potassium 7), and act as a link between the larger and finer particles. Alkali metals can act as adhesives that allow ash deposition on heat transfer surfaces 8). If the temperature is high enough, the alkali metals form low-melting substances by reacting with SiO2 and Fe2O3 contained in the ash deposits, thus decreasing the heat transfer efficiency. Alkali metals also react with SiO2 on a particulate level to form agglomerates 8).

The above review shows that alkali metals play a crucial role in the formation of particulates and slagging as a result of biomass combustion. Thus, the objective of this study is to characterize alkali metal emission from the combustion of biomass in two 1 MW Stoker boilers via optical emission spectroscopy. As mentioned earlier, the alkali metals' reactions are complex (some of which include devolatilization, nucleation, condensation, agglomeration, and slagging) and obtaining their reaction rates require controlled experimental conditions (e.g. injection of known quantities of alkali metals) and extensive chemical analyses at different locations of the boiler.

In this study, the reaction pathway of the alkali metals is preliminarily investigated by comparing the ratio of the alkali metals' emission signals from the optical emission spectra (OES) from the boiler's grate area with those from the ash samples. The method proposed here is unable to determine the reaction rates and therefore the
dominant reaction pathways, but the comparison of the ratio from the OES with those from the ash samples would be able to provide a tentative in-situ indicator of the pathways and estimated contents of the alkali metals.

2. Experimental Methods

The flame emission spectra is obtained from a biomass boiler using an AvaSpec-ULS2048 Starline spectrometer which has four channels capable to measure the flame’s optical emissions in the ultraviolet (UV), visible (VIS) and near infrared (NIR) regions. Each channel covers wavelengths of 200 to 458, 455 to 683, 680 to 974 and 870 to 1030 nm. All channels are equipped with 2048 pixel charged-coupled device (CCD) detectors, with a grating resolution of 1200 lines/mm, a slit width of 10 μm, and an instrumental wavelength resolution of 0.1 nm. Four channels of the spectrometer are connected to a 2 m four-furcated cable. The cable has a fiber optic probe at the end that is placed 600 mm from boiler grates’ viewport (which is 1000 mm from the bottom of the boiler) and detects the optical emissions from the radiating flames. An AvaSoft software displays and records the optical emissions in terms of spectral lines.

The optical emissions are from thermal excitation of molecules or atoms of an element, and arise from the energy released when the electrons transition from a higher to lower energy atomic orbital \(^{9-11}\). As the electron transitions to the lower energy levels or states, energy is released. The amount of energy released is distinctive as it corresponds to the energy difference between the two atomic orbitals for an element. The energy released from the transition is displayed as discrete spectral lines at certain wavelengths. From the wavelengths, the elements or molecules can be identified. In the case of biomass combustion, atomic emissions from alkali metals of sodium and potassium are usually detected, as is shown in the Results section.

The ratio of Na/K OES emission signals is then compared to those in the ash samples. Fly ash samples are collected from filters in the flue gas path that exits from the top of the boiler, while bottom ash samples are collected from the grate. The ash samples are analyzed in a Hitachi SU8020 scanning electron microscope (SEM) at an accelerating voltage of 15 kV and at a working distance of 15 mm. Single particle analysis was performed with the SEM that is coupled to a energy dispersive x-ray spectrocope (EDX) that has a Bruker XFlash Beryllium 6/60 detector (8386 series). The X-ray spectra were acquired for 60s.

In addition, several slagging indices were determined to characterize the harmfulness of biomass combustion. The total alkali content is total content of the alkali metal oxides in the ash samples \((K_2O + Na_2O)\), while the base-to-acid \((B/A)\) ratio and silica index are determined via the weight fraction of the following oxides\(^{12,13}\):

\[
\text{Total alkali content} = \frac{[K_2O] + [Na_2O]}{100} \quad (1)
\]

\[
\text{B/A ratio} = \frac{[CaO] + [MgO] + [Fe_2O_3] + [K_2O] + [Na_2O]}{[SiO_2] + [Al_2O_3] + [TiO_2]} \quad (2)
\]

\[
\text{Silica index} = \frac{[SiO_2]}{[SiO_2] + [Fe_2O_3] + [CaO] + [MgO]} \quad (3)
\]

3. Results and Discussion

3.1 Atomic emission spectra from flames of biomass combustion

Fig. 1 shows the optical emission spectra of the flames from biomass combustion. Fig. 2 (a) shows a close up of the atomic emission spectra from sodium at wavelengths of 588.95 and 589.54 nm, while Fig. 2 (b) shows a close-up of potassium’s atomic emission spectra at 766.42 and 769.93 nm.

The peaks detected at these wavelengths represent the energy released from a photon as the respective elements’ electron transition from a higher to lower energy
The transitions are represented by atomic term symbols, which refer to the energy levels or states of the electron, and are indicated by a super-script, a capitalized letter, a sub-script, which represent the multiplicity, total orbital angular momentum quantum number, and the total angular momentum quantum number respectively. These numbers indicate the number of possible states for the orbital’s orientation, the shape of the orbital, and the orientation of the orbital respectively. For the sake of brevity, the readers are referred to the literature for the derivation of the atomic term symbols\(^{10,11,14,15}\).

The peaks for the sodium spectral lines mentioned earlier represent electronic transitions from the \(3s\) \(^2S_{1/2}\) to \(3p\) \(^2P_{3/2,1/2}\) states respectively, while the peaks for the potassium spectral lines represent electronic transitions from \(4s\) \(^2S_{1/2}\) to \(4p\) \(^2P_{3/2,1/2}\) states respectively. The notations \(3s, 3p, 4s,\) and \(4p\) refer to the atomic orbitals where the valence electrons are. The latter terms (\(^2S_{1/2}, \, ^2P_{3/2,1/2}\)) are the atomic term symbols mentioned earlier.

### 3.2 Sodium-to-potassium ratio

From the atomic emission spectra of the flame in Fig. 2, the first peak of the atomic emissions of sodium and potassium (with the highest emission intensity) was taken to determine the ratio of Na/K. The ratio from two biomass boilers is determined as \(0.12 \pm 0.03\). The values are higher than the averaged Na/K ratios for fly ash and bottom ash samples from SEM-EDX analyses, ranging from 0.009-0.024, as shown in Fig. 3. The difference suggests that the potassium emission signal is lower than sodium’s, resulting in a higher Na/K ratio from the OES.

Without controlled extensive sampling and chemical analyses, the true reasons for the discrepancy may not be known. However, one of the reasons for the discrepancy could be due to the location from where the OES was taken, which is the boiler’s grate area. Potassium has been reported to have a higher diffusivity than sodium\(^8\)\(^{17}\), and potassium could diffuse to the particle surface at a faster rate than sodium. Then potassium is emitted as vapors into the area above the bed of fuel. Literature has also suggested that the maximum rate of potassium release occurs after devolatilization\(^18\), which is located above the bed of fuel. Since the OES in this study is captured from the grate area, the spectra could be emission signals from the bed of biomass which undergoes a slower char reaction compared to devolatilization\(^18\). Char reaction decomposes carboxylic acids groups, carbonates and sulfates in the biomass to release gaseous potassium, but this release reportedly accounts for approximately 10% of the total potassium release. Thus, it could be possible that the OES from the biomass...
grate area is a representation of the char reaction, where the potassium emission signal is lower. Obtaining the OES from above the grate area could give a better indication of the potassium content.

Another possibility for the difference is that potassium could have formed ash melts such as silicates or aluminosilicates directly in the burning char particles. The formation of ash melts would decrease the amount of potassium vapors released, further reducing the emission signal of potassium. However, the reaction rate of silication and aluminosilication relative to char reaction and devolatilization is uncertain and further investigation is required.

The above reactions could be of several pathways which resulted in lower potassium emissions signal and hence a higher than expected Na/K ratio compared to that from the ash samples. However, as mentioned in Section 1, the intensities of Na and K spectral emissions are only precursory in-situ indicators of the respective atoms’ content, and an accurate representation of the contents can only be obtained by controlled experiments via impregnation in the biomass prior to combustion. In this study, the control of the alkali metal contents in the biomass was not possible.

Sulfur oxide was detected in the fly ash samples as shown in Table 1, a possibility that alkali metals have condensed on particulate matter to form sulfates. No sulfur content was detected in the bottom ash, possibly because the temperatures in the lower furnace areas are higher than the condensation temperature of 950 °C, preventing any alkali sulfation reactions. As mentioned earlier, potassium could have formed silicates or aluminosilicates with the char particles in the grate area. Chlorine was not detected in the ash samples as these exists mainly as alkali chloride vapors, but could have nucleated or condensed on particulate matter, as is discussed later.

Fig. 3 shows that the Na/K ratio for fly ash is lower than that of bottom ash. This is due to higher potassium content in the fly ash, as shown in Fig. 4, thus decreasing the Na/K ratio. This finding is similar to those in literature, where the alkali metals are initially released as gaseous species and condenses on fly ash. The higher potassium content in fly ash also suggests that potassium chloride vapors in the flue gas stream that has not undergone sulfation to condense on fly ash could nucleate or condense at lower temperatures to form ultrafine particulates. This study did not investigate particulate matter emissions, and further studies are required to determine their potassium content.

### 3.3 Slagging and fouling indices

Due to the higher potassium content in fly ash, the total alkali content and base-to-acid ratios is higher as well, as shown in Table 1. This indicates that fly ash will have a higher tendency to foul downstream equipment and heat transfer surfaces. The silica index for all ash samples are high enough for the alkali metals to form alkali silicates or alkali aluminosilicates. The propensity for the silication and alumina-silication reactions is higher in the lower furnace area, as indicated by the higher silica index of the bottom ash. Thus, the potassium could be contained within the silicate or aluminosilicate melts, hence the lower potassium content in bottom ash (Fig. 4).

### 4. Conclusion

The study showed that the ratio of the alkali metals’ emission signals (Na/K) was higher than that from the ash samples. Notwithstanding the necessity for further experiments to accurately determine the ratios, there are several possible pathways which could contribute to the discrepancies in the ratio. The location from which the OES was taken is in the grate area where the bed of biomass undergo a slower char reaction, which could release potassium vapors at a slower rate compared to devolatilization above the bed of biomass. Potassium could
also form ash melts with the burning char particles, thus potentially reducing the emission signal. The lower potassium emission signal increases the ratio of Na/K.

Potassium vapors emitted from combustion in the form of chlorides or hydroxides could undergo sulfation or condensation to form particulate matter as well. At temperatures below 950°C the potassium sulfates condense fly ash in the upper regions of the furnace, but further investigation is required to determine their composition, with focus on the potassium content.

As mentioned earlier, without controlled experiments, an accurate determination of the alkali metals’ pathways and content is not possible. However, the method proposed in this study could use the Na/K ratio from the atomic emission spectra as a tentative in-situ indicator. By comparison with the ratios from the ash samples, several of many possible reaction pathways were identified.

Acknowledgement

The authors would like to acknowledge Saidatul of the Materials Characterization Lab who assisted in the ash analysis and Dr. Leo Matsuoka of Hiroshima University who have contributed towards the improvement of this manuscript. The authors would also like to acknowledge the funding from Tenaga Nasional Berhad (TNB).

References

1) Kappos, A. D.; Bruckmann, P.; Eikmann, T.; Englert, N.; Heinrich, U.; Hoppe, P.; Koch, E.; Krause, G. H. M.; Kreyling, W. G.; Rauchfuss, K.; Rombout, P.; Schulz-Klemp, V.; Thiel, W. R.; Wichmann, H. E., *International Journal of Hygiene and Environmental Health*, 207, 399 (2004)
2) Naeher, L. P.; Brauer, M.; Lipsett, M.; zelikoff, J. T.; Simpson, C. D.; Koenig, J. Q.; Smith, K. R., *Inhalation Toxicology*, 19, 67 (2007)
3) Pope, I. C.; Burnett, R. T.; Thun, M. J. *et al.*, *JAMA*, 287, 1132 (2002)
4) Sippula, O.; Hytönen, K.; Tissari, J.; Raunemaa, T.; Jokiniemi, J., *Energy & Fuels*, 21, 1151 (2007).
5) Garcia-Maraver, A.; Zamorano, M.; Fernandes, U.; Rabaçal, M.; Costa, M., *Fuel*, 119, 141 (2014)
6) Winikka, H.; Gebart, R.; Boman, C.; Boström, D.; Nordin, A.; Öhman, M., *Combustion and Flame*, 147, 278 (2006)
7) Vicente, E. D.; Duarte, M. A.; Tarelho, L. A. C.; Nunes, T. F.; Amato, F.; Querol, X.; Colombi, C.; Gianelle, V.; Alves, C. A., *Atmospheric Environment*, 120, 15 (2015)
8) Niu, Y.; Tan, H.; Hui, S. e., *Progress in Energy and Combustion Science*, 52, 1 (2016)
9) Pearse, R. W. B.; Gaydon, A. G., *Identification of molecular spectra*; Chapman & Hall Ltd., London, 1941
10) Harvey, D., *Modern Analytical Chemistry*, McGraw-Hill, 1999
11) Metcalfe, E., *Atomic absorption and emission spectroscopy*, John Wiley, 1987
12) Vamvuka, D.; Kakaras, E., *Fuel Processing Technology*, 92, 570 (2011)
13) Niessen, W. R., *Combustion and Incineration Processes: Applications in Environmental Engineering*, CRC Press, London, 2010
14) Sindhu, P. S., *Fundamentals of molecular spectroscopy*, New Age International Ltd., New Delhi, 2006
15) Kuhn, H.; Fosterling, H.; Waldeck, D. H., *Principles of physical chemistry*; John Wiley & Sons, New Jersey, United States of America, 2009
16) Baxter, L. L.; Miles, T. R.; Miles Jr, T. R.; Jenkins, B. M.; Milne, T.; Dayton, D.; Bryers, R. W.; Oden, L. L., *Fuel Processing Technology*, 54, 47 (1998)
17) Thy, P.; Lesher, C. E.; Jenkins, B. M., *Fuel*, 79, 693 (2000)
18) Fatehi, H.; Heb, Y.; Wang Z.; Li, Z. S.; Bai X. S.; Aldé, M.; Cen, K. F., *Proceedings of Combustion Institute*, 35, 2389 (2015)
19) Paneru, M.; Babat, S.; Maier, J.; Scheffknecht, G., *Fuel Processing Technology*, 141, 266 (2016)
20) Mason, P. E.; Darvell, L. I.; Jones, J. M.; Williams, A., *Fuel*, 182, 110 (2016)
21) Singh, J.; Kumar, R.; Awasthi, S.; Singh, V.; Rai, A. K., *Food Chemistry*, 221, 1778 (2017)
22) Zhang, J.; Han, C.-L.; Yan, Z.; Liu, K.; Xu, Y.; Sheng, C.-D.; Pan, W.-P., *Energy & Fuels*, 15, 786 (2001)
23) Liao, Y.; Cao, Y.; Chen, T.; Ma, X., *Bioresource Technology*, 194, 196 (2015)
24) Wu, D.; Wang, Y.; Wang, Y.; Li, S.; Wei, X., *Renewable Energy*, 96, Part A, 91 (2016)
25) Fournel, S.; Palacios, J. H.; Morissette, R.; Villeneuve, J.; Godbout, S.; Heitz, M.; Savoie, P., *Applied Energy*, 141, 247 (2015)