

QUANTITATIVE CONCENTRATIONS OF SODIUM AND POTASSIUM RELEASED FROM BROWN COAL AND PINE WOOD IN A LAMINAR PREMIXED FLAME USING LIBS

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ABSTRACT

A quantitative point measurement of total sodium and potassium released during combustion of Australian Loy Yang brown coal particles (23 ± 3 mg) and pine wood pellets (63 ± 3 mg) has been performed using laser-induced breakdown spectroscopy (LIBS) in a laminar premixed methane flame at the equivalence ratio (Φ) of 1.287. Calibration was performed using droplets of sodium sulfite (Na_2SO_3) and potassium sulphate (K_2SO_4) entrained into the flame. This compensated for the absorption caused by atomic alkalis in outer seeded flame, which is significant at high concentrations. Hence quantitative release of sodium and potassium during the three phases of combustion, namely devolatilization, char and ash cooking, were obtained. The concentration of total sodium in the plume released from the combustion of pine wood pellets during the devolatilization reached up to 15 ppm. The strongest concentrations of total sodium and potassium released from burning coal and wood particles during char phase were found to be 21.3 and 2.4 ppm, 15.5 and 26.3 ppm, respectively.

Keywords: brown coal, pine wood, alkali elements, LIBS, quantitative measurement

INTRODUCTION

Alkali species, mainly sodium (Na) and potassium (K), released from combustion of coal and biomass cause substantial problems with the fouling and corrosion of heat exchange surfaces (Neville & Sarofim, 1985; Bryers, 1996). Hence, substantial effort has been invested to understand these processes with a view to solve these problems. The flue gases of biomass combustion have been investigated by applying mass spectrometry and scanning electron microscopy / energy dispersive X-ray (SEM/EDX), to stable products, such as alkali chloride, alkali hydroxide and sulphur dioxide (SO_2) (Dayton et al, 1995; Knudsen et al, 2004). Ash analysis has also been performed to

model combustion of coal and biomass (Chio & Kruger 1985; Gilbe et al, 2008). However, with these methods, it is not possible to investigate the unstable intermediate species of alkali species.

Laser diagnostic techniques can provide *in-situ*, non-intrusive measurements that are spatially and temporally resolved in extreme environments. Van Eyk et al. (2008) developed a quantitative planar laser-induced fluorescence (PLIF) to provide time-resolved measurements of atomic Na released from single burning coal particle during char phase. Saw et al. (2009) then applied the same technique to measure atomic Na released from black liquor combustion. However, the significant scattering that occurs in devolatilization leads to low signal-to-noise of PLIF during that stage at the combustion. Furthermore, PLIF measurements require a specific wavelength corresponding to the target species, which is a substantial constraint in seeding to measure multiple species simultaneously. Indeed it is presently unachievable to resolve simultaneously all of the key forms of Na and K by PLIF.

Laser-induced breakdown spectroscopy (LIBS) is an alternative and complementary technique that affects the possibility to measure the total amounts of multiple species in various types of samples, such as solid, liquid and gas. Yamamoto and co-workers reported that the Limit of Detection (LOD) of barium (Ba), beryllium (Be), lead (Pb) and strontium (Sr) in contaminated soil samples were 265, 93, 298 and 42 ppm, respectively (Yamamoto, 1996). Arca et al. (1997) also quantified Na, K, calcium (Ca), chromium (Cr) and chlorine (Cl) in drinking water. The LOD of LIBS applied inside the liquid was reduced due to lower temperature of plasma resulting from high heat lost. Dudragne & Adam (1998) reported that LIBS was applied to measure quantitatively sulphur (S), fluorine (F), chlorine (Cl) and carbon (C) in the atmosphere. Other studies (Stavropoulos et al, 2005; Stavropoulos et al, 2005; Mohy, 2009) evaluated C, oxygen (O), hydrogen (H) and nitrogen (N) in various equivalence ratios of laminar premixed methane flames using LIBS. Compositions of coal and wood particles have been investigated quantitatively by applying LIBS in solid-fuel particles (Mateo et al, 2007; Uhl et al, 2001). However, LIBS is yet to be employed to investigate the release of alkali species during combustion.

Quantitative LIBS requires calibration based on comparison of intensities of chosen spectral lines between trace species and standard samples. It is also necessary to account for the interferences of self-absorption, spectral overlapping and matrix effect, which dominate the accuracy of quantitative LIBS. The matrix effect only occurs in solid samples, so can be neglected in flame environment. The influence of spectral overlapping can be reduced by optimizing gate delay and gate width of a spectrometer. However, self-absorption cannot be avoided and becomes significant under high concentrations of target species. Nevertheless, it can be reduced by selecting other persistent spectral lines, for calibration, rather than the major resonant ones. For example, the chosen line for calibration of Fe(I) is 404.582 nm instead of 248.328 nm to avoid self-absorption in highly populated level of Fe (Walid, 2008). The LOD for quantitative LIBS can also be improved choosing appropriate reference wavelengths.

Due to special characteristics of LIBS, the quantitative release of total sodium and potassium performed as a point measurement in the flame can provide insight into estimation of the total amounts of alkali metals release during combustion of solid-fuel particles for further investigation. Besides, small solid-fuel particles were burned

individually to provide fundamental understanding of alkali metals release in a simplified combustion environment which can facilitate aspects of combustion simulations and eventually reduce pollutant release.

The aims of this paper are therefore to develop a technique for real-time quantitative measurement of Na and K released during combustion and to apply it to Australian Loy Yang Brown coal and pine wood pellets to provide time-resolved profiles. LIBS can provide insight of the quantitative release of Na and K into devolatilization of burning particles of coal and wood.

METHODOLOGY

Laminar Pre-mixed Burner

A laminar pre-mixed burner (Perkin Elmer), specifically designed for flame atomic emission spectroscopy (AES), was employed in this work. The burner contains a bottom chamber to premix air and fuel, connected to an upper honeycomb matrix of circular-shape and diameter of 23 mm. This central matrix was mounted within a concentric honeycomb of diameter in 45 mm. Air and fuel flow rates were controlled by mass flow controllers (MFCs, Bronkhorst). One MFC was utilized to control the flow rate of methane to 0.872 ± 0.006 ml_n (normal litre per minute), and two other MFCs, were used to control the main stream air and seeding air (for calibration). The total flow rates of the main stream air were 6.45 ± 0.03 ml_n, including 0.525 ± 0.015 ml_n of seeding air during calibration. A nebulizer was employed to produce droplets of salt solution with a nominal diameter of 1 μm (Van Eyk et al., 2008) in the calibration processes. A bottom outlet was designed to drain away any excess salt solution to avoid any influence on the mixing chamber.

Laser-Induced Breakdown Spectroscopy (LIBS)

The LIBS system shown in Fig. 1 was applied to measure the quantitative histories of total Na and K released into the plume by a single burning particle of coal particle (23 ± 3 mg, diameter of 2 mm) or pine wood (63 ± 3 mg, diameter of 3 mm) suspended on a platinum (Pt) wire at a height of 10 mm above the flat flame burner. The constituents of Loy Yang coal and pine wood pellets shown in Table 1 were analyzed by HRL technology Pty Ltd in Australia. A Q-switched Nd:YAG laser operating at the fundamental wavelength of 1064 nm (10 Hz repetition rate and pulse width of 8 ns) and equipped with an attenuator to vary the pulse energy provided a laser beam of 240 mJ per pulse. The laser beam was focused to a 1 mm dot size to generate a plasma with an elliptical measurement volume, at a position 10 mm above the burner surface during calibration or 10 mm above the fuel particles, by a quartz lens of 150 mm focal length. The emitted radiation was collected through a quartz lens of focal length 150 mm by a spectrometer which comprised a grating (300 grooves per mm) and an ICCD detector. A pulse generator (DG535) and an oscilloscope, respectively, were used to trigger the laser and to optimize the gate delay and gate width, reducing background noise, which was dominated by emission spectra of atomic Na, K and water. The optimized delay time and gate width were experimentally determined to be 45 and 5 μs, respectively, which eliminated line overlapping. Total Na and K were not measured simultaneously owing to the large wavelength difference between the D1 bands of Na(I) and K(I),

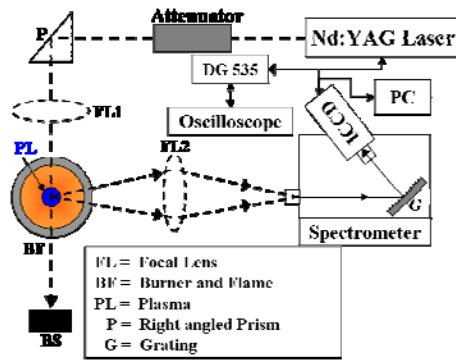


Fig. 1. Experimental arrangement used to perform LIBS for the measurement of Na and K during the combustion of coal and wood particles.

Table 1. Composition of Loy Yang coal and pine wood

%(Dry ash free basis)	Loy Yang coal	Pine wood
C	67.80	51.30
H	5.20	6.00
N	0.57	<0.01
S	0.24	0.02
Cl	0.06	0.09
O(By difference)	26.13	42.59
%Ash basis		
SiO ₂	12.90	43.30
Al ₂ O ₃	31.40	0.97
Fe ₂ O ₃	6.70	0.82
TiO ₂	0.70	0.15
K ₂ O	0.77	5.70
MgO	12.20	8.30
Na ₂ O	11.30	4.90
CaO	5.60	24.8
SO ₂	16.90	3.90

which are out of the range covered by the chosen grating. Nevertheless, commercial spectrometer products, such as the Echelle spectrometer (Walid, 2008), are capable of measuring multiple elements simultaneously. Although Na and K were not measured simultaneously, this choice leads to improve resolution and LOD.

Calibration Method

Measurements of Na and K using LIBS were converted quantitatively by applying a calibration process. Unlike conventional calibration methods reported in the literature (Drogoff et al, 2001; Sabsabi et al, 2003) based on the relative intensities of the spectral lines of the reference and trace elements, the present calibration curves were based on the intensities of atomic lines corresponding to the concentrations of seeded Na and K. Various concentrations of potassium sulphate (K₂SO₄) and sodium sulphite (Na₂SO₃) were entrained into the flame. The distribution of alkali salt in the flame was assumed to be uniform. Mass flow rate (v_m) was calculated as the product of the concentration of alkali salt (C_s) and the consumption rate of salt solution (v_s), as shown in Eq. 1(a). In order to calculate v_s , the volumes of salt solutions before and after 4 hours consumption with constant seeding air flow rate of $0.525 \pm 0.015 \text{ ml}_n$ (described in the section of laminar pre-mixed burner) were measured. Condensed salt solution was taken into account by feeding it back to the nebulizer system directly. Hence the molar flow of alkali salts in the flame (v_{ms}) was obtained shown in Eq. 1(b), where M is molar mass of salt and a_m is molar ratio of alkali ions in the salt. It can be seen on Eq. 1(c) that the total gas flow rate (v_f) at flame temperature T_f , is a function of v_g (flow rate of methane), v_a (flow rate of air), and T_r (room temperature). Then, using the ideal gas equation, the molar flow rate through the flame is obtained, as presented in Eq. 1(d). The concentration, C , of Na or K in the flame are represented in parts per million (ppm), as calculated in Eq. 1(e). According to Eq. (1), two linear calibration equations of the concentrations of sodium and potassium were thus obtained.

$$\begin{aligned}
 v_m &= C_s \times v_s \\
 v_{ms} &= a_m \cdot v_m / M \\
 v_f &= (v_g + v_a) \times T_f / T_r \\
 v_{mf} &= P \cdot v_f / R \cdot T_f \\
 C &= v_{ms} / v_{mf}
 \end{aligned}
 \tag{Eq. 1:(a - e)}$$

RESULTS AND DISCUSSIONS

Figure 2 illustrates the process by showing the flame during the various stages of the experiment. The orange colour of the Na is evident in the seeded flame used for calibration (Fig. 2a), the presence of soot during devolatilization is evident from the white orange (Fig. 2b), but not in the other stages, and the elliptically shaped plasma generated by the LIBS is evident in all stages. The visually distinct features of each stage of combustion were used to identify them following earlier work (Van Eyk et al. 2008; Saw et al. 2009), direct measurements and to estimate the duration of each phase, namely devolatilization (τ_d), char (τ_c) and ash cooking (τ_a) phases.

The fundamental equation used to calibrate the method is shown in Eq. (2),

$$\ln(I_{\text{exp}}) = \ln(\alpha) + \beta \cdot \ln(C_x) \quad (2)$$

where I_{exp} is the experimental intensities of alkalis; β is the coefficient of self-absorption; C_x is the concentration of alkalis in the seeded flame and α is an empirical constant. Calibration curves are linear while self-absorption is very small ($\beta = 1$). Hence a linear relationship between I_{exp} and C_x can be obtained, as shown in Eq. (3). However,

$$I_{\text{exp}} = \alpha \cdot C_x \quad (3)$$

the raw calibration curves are non-linear, as shown in Fig. 3, indicating significant absorption effects are present. The absorption effect in conventional LIBS measurements can be considered to result from self-absorption, which is not avoidable. The chosen wavelengths of sodium and potassium for calibration in Fig. 3 are 589.592 and 769.896 nm (D1 lines), respectively. These are the main resonant lines and can be expected to lead to significant self-absorption while high concentrations of alkali species are employed. Self-absorption for LIBS is the intrinsic property owing to the plasma quenching. Elements in the center of plasma are in various energy states and, due to the lower temperature outside the plasma, elements intend to stay in the major electronic energy states which emit the main resonant spectral lines. Therefore the significant absorption for target elements occurs in high population level outside the plasma. However, self-absorption in the present experiment might not be the only source of non-linearity.

Due to the specific arrangement of the present LIBS measurement, as shown in Fig. 4, LIBS plasma is located inside the seeded flame and radiation through a lens is collected by the spectrometer. Signal trapping, owing to the absorption of atomic Na and K in outer seeded flame, should be considered prior to self-absorption because signal

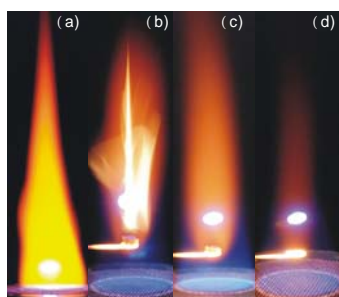


Fig. 2. LIBS plasma in stages of (a) seeded flame (b) devolatilization (c) char (d) ash.

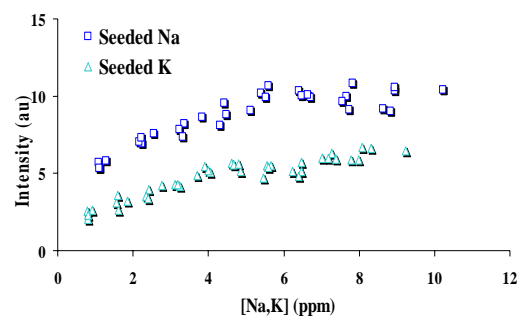


Fig. 3. The raw non-linear calibration curves of LIBS in seeded flame.

trapping intrinsically occurs before radiation is collected. This also indicates the weak persistent lines are not detectable owing to strong signal trapping during high concentrations of alkali salts were employed. Therefore the D1 lines of Na and K were chosen instead of other persistent lines.

To correct for signal trapping and provide absolute concentrations of trace species, Beer-Lambert's law as presented in Eq. (4) has been widely used (Van Eyk et al. 2008;

$$\ln\left(\frac{I_{\text{act}}}{I_{\text{exp}}}\right) = \alpha(\omega) \cdot x \quad (4 - a)$$

$$\alpha(\omega) = n \cdot \sigma_a(\omega) \quad (4 - b)$$

Saw et al. 2009), where I_{act} and I_{exp} are respectively the actual (signal trapping compensated) and experimental (signal trapping affected) intensities of Na and K using LIBS, $\alpha(\omega)$ is the absorption coefficient at angular frequency ω , x is the absorption length within the flame, n is the number density of target species of atomic form in the flame with specific flame temperature and $\sigma_a(\omega)$ is the absorption cross-section of the trace species at angular frequency ω . It is well established that the coefficient of absorption can be determined by introducing Einstein coefficient for target species in the specific state (Hillborn, 1982). The conventional application of Beer-Lambert's law only considers one-dimensional absorption. The volumetric absorption effect in the present experiment, however, should be taken into account. Therefore Equation (4) needs to be modified, as shown in Eq. (5),

$$\ln\left(\frac{I_{\text{act}}}{I_{\text{exp}}}\right) = \sum \alpha(\omega) \cdot \sum x_i \quad (5 - a)$$

$$\sum \alpha(\omega) = \varepsilon \cdot C_x \cdot \sum \sigma_a(\omega) \quad (5 - b)$$

where Σ indicates volumetric calculations of $\alpha(\omega)$, x and $\sigma_a(\omega)$ described previously in Eq. (4). Here, Σx_i and $\Sigma \sigma_a(\omega)$ were respectively considered as the volume of a cone and the summation of absorption cross-section within the effective absorption volume. Σx_i was calculated as shown in Eq. (6)

$$\Delta v = \frac{1}{3} \cdot \pi \cdot r_{\text{cone}}^2 \cdot h_{\text{cone}} \quad (6)$$

where r_{cone} and h_{cone} are shown in Fig. 4. In addition, the absorption due to the number density (n) of atomic Na or K in the flame can be obtained in terms of the ratio, ε , estimated based on the flame temperature (~1500 K), multiplied by the salt concentrations, C_x , seeded into the flame. Therefore a modified Beer-Lambert's law was obtained, as shown in Eq. (7).

$$I_{\text{act}} = I_{\text{exp}} \cdot e^{\varepsilon \cdot C_x \cdot \Sigma \sigma_a(\omega) \cdot \Delta v} \quad (7)$$

The factor, ε , was estimated to be 0.020 and 0.018 for atomic Na and K, respectively, based on a temperature of 1500 K, estimated from the equivalence ratio of the flame. Equation (7) was used to correct the raw experimental intensities of total Na and K, to obtain two modified calibration curves, which are linear, for both of Na and K, as shown in Fig. 5. The lines of best fit of calibration equations are shown in Eq. (8) and (9), where I_{Na} and I_{K} are emission intensities of Na(I) and K(I) in D1 bands with LIBS, respectively; C_{Na} and C_{K} are molar concentrations in the seeded flame obtained from

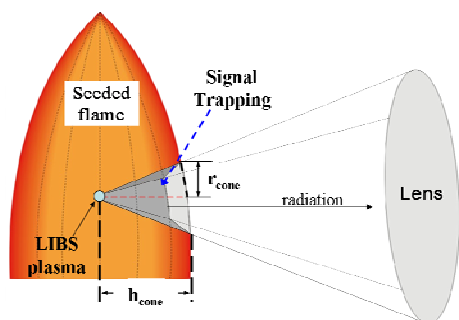


Fig. 4. Signal trapping occurs while LIBS plasma is applied inside seeded flame.

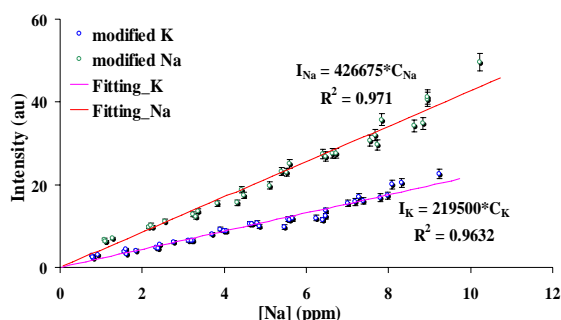


Fig. 5. The calibration curves of Na and K corrected for signal trapping in seeded flames using LIBS.

Eq. (1), and were utilized to quantitatively convert the time-resolved profiles of total Na and K released from burning coal and wood particles.

$$I_{Na} = 426.657 \cdot C_{Na} \quad (8)$$

$$I_K = 219.500 \cdot C_K \quad (9)$$

The linear calibration curves demonstrated good correlation of experimental data indicating the correction of signal trapping dominated the major absorption effect. The self-absorption indeed needs to be taken into account in conventional LIBS measurements. However, in the present experiment calibration curves demonstrate good linearity without considering self-absorption indicating the self-absorption is not significant. This paper demonstrates the feasibility of quantitative measurement of alkali species released from burning solid-fuel particles using LIBS. Therefore, the further correction of self-absorption would be carried out in the further experiments by employing very low concentrations of seeded salt solutions to improve the accuracy of the LIBS measurement.

The total releases of Na and K during devolatilization phase have been measured using LIBS, as shown in Fig. 6. The periods of coal and wood combustion during devolatilization, τ_d , were 12 and 22 seconds, respectively, consistent with those reported in previously using AES (Hsu et al, 2009). The peak emission of atomic Na from wood combustion during τ_d was roughly 30% of that at the end of char phase with AES. Total Na released from wood devolatilization, however, showed exceedingly strong, reaching up to the peak release of 15 ppm which was as significant as the strongest release at end of char phase, indicating that various forms of Na species were released. In addition, it was found during τ_d that total Na release from coal was also stronger than total K. Na species released during devolatilization of brown coal and pine wood, therefore, could significantly cause sticky deposit on the heat transfer surfaces (Neville & Sarofim, 1985; Bryers, 1996).

The profiles of Na and K released during char phase, as presented in Fig. 7, using LIBS were quantitatively investigated, showing that the release of K and Na were up to 2.4 and 21.3 ppm for coal, 26.3 and 15.5 ppm for wood, respectively. Due to wavelength range of the chosen grating, the releases of Na and K were not simultaneously measured. The results of LIBS in Fig. 7 and of AES in previous work (Hsu et al, 2009) demonstrated that the strongest releases of Na and K occurred at the end of char phase which consisted with the results presented in Ref. (Van Eyk et al., 2008; Van Eyk et al.,

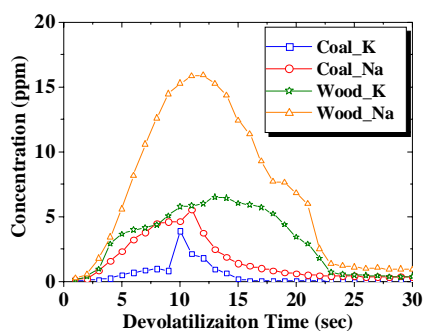


Fig. 6. The release of Na and K during τ_d using LIBS with equivalence ratio of 1.287.

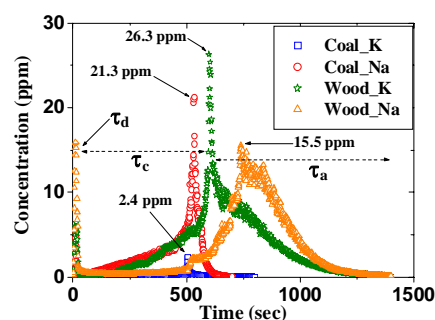


Fig. 7. Release of Na and K at three phases (τ_d , τ_c and τ_a) using LIBS under equivalence ratio of 1.287.

2009). The quantitative measurement of Na and K using LIBS at the specific location revealed the instantaneous concentrations so that the entire emission of Na and K can be calculated if the fluxes of Na and K during combustion are determined. For ash cooking phase, due to high temperature cooking, Na and K are released from compounds depositing on the heat transfer surfaces. Major alkali compounds of ash from brown coal and pine wood (Knudsen et al, 2004) are generally alkali silicates, as shown in Table 1. Release profiles during ash cooking phase were consistent with alkali silicates which are highly temperature-resistant compared with other minor alkali compounds, such as alkali sulphates vaporized in the early stage of ash cooking (Knudsen et al, 2004; Glarborg & Marshall, 2005). Moreover, release profiles of ash cooking represented in Fig. 7 also revealed that K was more reactive than Na due to sharper slope. It is possible that Cl facilitated K release from silicates to form $KCl_{(g)}$ of which gas phase is thermodynamically stable above 1000 K (Knudsen et al, 2004).

CONCLUSION

A novel application of LIBS has been developed for quantitative measurement of sodium and potassium released from the burning particles of brown coal and pine wood applying calibration curves. Due to significant absorption effect caused by atomic alkalis in seeded flame surrounding the LIBS plasma, a correction was taken into consideration to compensate signal trapping of calibration curves which improved the accuracy of total Na and K conducted in the flame environment. The quantitative release of Na and K were up to 2.4 and 21.3 ppm for coal, 26.3 and 15.5 ppm for wood, respectively, at the end of char phase under the equivalence ratio of 1.287.

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REFERENCES

Arca, G, Gucci, A, Palleschi, V, Rastelli, S & Tognoni, E 1997, 'Trace element analysis in water by the laser-induced breakdown spectroscopy Technique', *Applied Spectroscopy*, vol. 51, no. 8, pp. 1102-1105.

Bryers, RW 1996, 'Fireside slagging, fouling, and high-temperature corrosion of heat-transfer surface due to impurities in steam-raising fuels', *Progress in Energy and Combustion Science*, vol. 22, pp. 29-120.

Chio, S & Kruger, CH 1985, 'Modelling coal particle behavior under simultaneous devolatilization and combustion', *Combustion and Flame*, vol. 61, pp. 131-144.

Dayton, DC, French, RJ & Milne, TA 1995, 'Direct observation of alkali vapor release during biomass combustion and gasification. 1. Application of molecular beam mass spectrometry to switchgrass combustion', *Energy & Fuels*, vol. 9 pp. 855-865.

Drogoff, B, Le, Margotb, J, Chakera, M, Sabsabi, M, Barthelemy, O, Johnstona, TW, Laville, S, Vidal, F & Kaenel, Y, von 2001, 'Temporal characterization of femtosecond laser pulses induced plasma for spectrochemical analysis of aluminum alloys', *Spectrochimica Acta Part B*, vol. 56, pp. 987-1002.

Dudragne, L & Adam, P 1998, 'Time-resolved laser-induced breakdown spectroscopy: Application for qualitative and quantitative detection of fluorine, chlorine, sulfur, and carbon in air', *Applied Spectroscopy*, vol. 52, no. 10, pp.1321-1327.

Gilbe, C, Öhman, M, Lindström, E, Boström, D, Backman, R, Samuelsson, R & Burvall, J 2008, 'Slagging characteristics during residential combustion of biomass pellets', *Energy & Fuels*, vol. 22, pp. 3536-3543.

Glarborg, P & Marshall, P 2005, 'Mechanism and modeling of the formation of gaseous alkali sulfates', *Combustion and Flame*, vol. 141, pp. 22-39.

Hillborn, RC 1982, 'Einstein coefficients, cross sections, f values, dipole moments, and all that', *American Journal of Physics*, vol. 50, pp. 982-986.

Hsu, LJ, Alwahabi, ZT, Nathan, GJ, Li, ZS & Aldén M 2009, 'Study of the release of atomic sodium and potassium from Loy Yang coal and biomass in a laminar pre-mixed methane flame', *Proceedings of Australian Combustion Symposium*, pp. 211-214.

Knudsen, JN, Jensen, PA & Dam-Johansen, K 2004, 'Transformation and release to the gas phase of Cl, K, and S during combustion of annual biomass' *Energy & Fuels*, vol. 18, pp. 1385-1399.

Mateo, MP, Nicolas, G & Yanñez, A 2007, 'Characterization of inorganic species in coal by laser-induced breakdown spectroscopy using UV and IR radiations', *Applied Surface Science*, vol. 254, pp. 868-872.

Mohy S. Mansour, Hisham Imam, Khaled A. Elsayed, Wafaa Abbass 2009, 'Local equivalence ratio measurements in turbulent partially premixed flames using laser-induced breakdown spectroscopy', *Spectrochim. Acta Part B*, vol. 64, pp. 1079-1084.

Neville, M & Sarofim, AF 1985, 'The fate of sodium during pulverized coal combustion', *Fuel*, vol. 64, pp. 384-390.

Sabsabi, M, Detalle, V, Harith, MA, Tawfik, W & Imam, H 2003, 'Comparative study of two new commercial echelle spectrometers equipped with intensified CCD for analysis of laser-induced breakdown spectroscopy', *Applied Optics*, vol. 42, no. 30, pp. 6094-6098.

Saw, WL, Nathan, GJ, Ashman, PJ & Alwahabi, ZT 2009, 'Assessment of the release of atomic Na from a burning black liquor droplet using quantitative PLIF', *Combustion*

and Flame, vol. 156, pp. 1471–1479.

Stavropoulos, P, Michalakou, A, Skevis, G & Couris, S 2005, ‘Laser-induced breakdown spectroscopy as an analytical tool for equivalence ratio measurement in methane–air premixed flames’, *Spectrochimica Acta Part B*, vol. 60, pp. 1092-1097.

Stavropoulos, P, Michalakou, A, Skevis, G & Couris, S 2005, ‘Quantitative local equivalence ratio determination in laminar premixed methane–air flames by laser induced breakdown spectroscopy (LIBS)’, *Chemical Physics Letters*, vol. 404, pp. 309-314.

Uhl, A, Loegel, K & Kreuchwig, L, 2001, ‘Fast analysis of wood preservers using laser induced breakdown spectroscopy’, *Spectrochimica Acta Part B*, vol. 56, pp. 795-806.

Van Eyk, PJ, Ashman, PJ, Alwahabi, ZT and Nathan, GJ 2008, ‘Quantitative measurement of atomic sodium in the plume of a single burning coal particle’, *Combustion and Flame*, vol. 155, pp. 529-537.

Van Eyk, PJ, Ashman, PJ, Alwahabi, ZT and Nathan, GJ 2009, ‘Simultaneous measurements of the release of atomic sodium, particle diameter and particle temperature for a single burning coal particle’, *Proceedings of the Combustion Institute*, vol. 32, pp. 2099-2109.

Walid Tawfik Y. Mohamed 2008, ‘Improved LIBS limit of detection of Be, Mg, Si, Mn, Fe and Cu in aluminum alloy samples using a portable Echelle spectrometer with ICCD camera’, *Optics & Laser Technology*, vol. 40, pp. 30-38.

Yamamoto, KY, Cremers, DA, Ferris, MJ & Foster, LE 1996, ‘detection of metals in the environment using a portable laser-induced breakdown spectroscopy instrument’ *Applied Spectroscopy*, vol. 50, no. 2, pp. 222-233.

BRIEF BIOGRAPHY OF PRESENTER

Li-Jen Hus has a bachelor and a master of science in physics, from 1995 to 1999 and 1999 to 2001, respectively, in Chung Yuan Christian University (CYCU), Taiwan. The major topic was about the synthesis of carbon nanotubes (CNTs) and measurement of physical properties. The current education is the Ph. D in Chemical Engineering of Adelaide University since July 2006. The research topic is the alkali metals released from burning solid-fuel particles using laser diagnostic techniques. During the five years working, a patent has been filed that a manufacturing technique was used to improve the yield of CNTs using arc-discharge.