Real-time release of Na, K and Ca during thermal conversion of biomass using quantitative microwave-assisted laser-induced breakdown spectroscopy

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ABSTRACT

Power production with thermal conversion has met new challenges due the global pressure to use CO_2 neutral and renewable fuels, e.g. recycled fuel and biomass. Many of these fuels contain high concentrations of elements, such as alkali metals and chlorine, that together are harmful for boiler structures and may cause operational problems. Therefore, detailed quantitative information on release behaviour of the problematic elements, potassium and sodium, is required. For this, a new burner, which allows linear calibration of laser induced breakdown spectroscopy (LIBS) measurement towards higher concentrations relevant for the release studies during thermal conversion of biomass, was designed. The analytical performance of conventional LIBS measurement is significantly improved by introducing microwave radiation to the laser-induced plasma. An enhancement of linearity and up to 60-fold improvement of limit of detection (LOD) was observed with microwave-assisted LIBS (MW-LIBS) in comparison to conventional LIBS. The LOD of Na, K and Ca were 10 ppb, 19 ppb and 16 ppb, respectively. In-flame MW-LIBS measurement was applied to record time-traces of K, Na and Ca during thermal conversion of a poplar pellet. This is the first demonstration of Microwave near-field applicator injected MW-LIBS for gas phase measurement. With broad dynamic measurement range, the proposed method can be applied to extensive research of elemental release behaviour of different fuels. In addition to combustion studies, the MW-LIBS method can be extended to study trace-elements in gas phase in different fields of industry and science.

1. Introduction

Concern of environmental aspects and the increasing price of fossil fuels are driving the power production towards renewable and CO_2 neutral energy sources. This has increased the interest on using low quality fuels, such as communal waste and biomass, for power production. However, these fuels are problematic for combustion boiler operation due to high release rate of alkali compounds [1]. KCl and NaCl have been found to cause severe slagging and fouling in the boiler structures that may lead to operational problems and unplanned shutdowns [2]. Detailed information on the release behaviour of the alkaline compounds is required and it has been under extensive research.

Multiple online methods are used to study the metal species in reactive flows and are extensively reviewed by Monkhouse. [3] Atomic absorption techniques, atomic absorption spectrometry (AAS) [4], differential optical absorption spectrometry (DOAS) [5], and their

applications [5,6,7], offer element or molecule specific information but are limited to their specific species present in gas phase. In many combustion applications, it would be in interest to measure the total concentration of an elemental specie. This can be achieved with atomic emission methods, such as excimer laser-induced fragmentation fluorescence (ELIF) [8] or laser-induced breakdown spectroscopy (LIBS) [9] that, however, have limited operational range due the difficulties in calibration for broad measurement range.

LIBS has become one of the leading online elemental analysis techniques. Its ability to provide multi-element analysis, requirement of minimal or even no sample preparation, applicability to solid, liquid, and gas phase, and stand-off capability are the clear advantages of LIBS [11] when compared to other elemental analysis techniques, such as inductively coupled plasma (ICP) analysis methods and X-ray fluorescence (XRF) technology [12]. In recent years, LIBS technique has been widely applied in field of combustion diagnostics. For instance,

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equivalence ratios in laminar premixed flame [13,14], non-premixed flame [14,15], and turbulent partially premixed flame [14,16] were all measured by LIBS. Besides the laboratory flames mentioned above, LIBS has also been utilized for equivalence ratio measurements in spark-ignited engines [17,18]. In addition of the equivalence ratio detection, LIBS was employed for in situ measurement of temperature in partially premixed flame [19].

Measurement of alkali metals in high temperature gases has been under extensive study. Molina et al. [20] studied the effect of the ambient gas to the LIBS signal and found that significant attenuation of the alkali metal LIBS signal occurred, when the stoichiometry of the gas surrounding the spark changed from fuel lean to fuel rich. He et al. [21] have been studying the effect of O_2 and CO_2 to the temporal behaviour of alkali metal release from coal particles and Zhang et al. [22] have recorded the potassium release during combustion of pine wood using LIBS. The LIBS results have also been applied in modelling of the alkali release from biomass fuels [23]. However, in the reported studies the calibration ranges have been limited to concentration of approximately 10 ppm [10,21,22] and this has been hindering extensive alkali release measurements from biomass fuels with more abundant alkali concentrations. Therefore, in order to make the in-flame LIBS detection of alkali metals more accurate and reliable, new LIBS calibration methods, which are able to provide linear calibration curves covering the practical high alkali metal concentration ranges in flame, are urgently needed.

The calibration of laser induced plasma emission signal is associated on the curves of growth, i.e. calibration curves. The curves are expressed to describe the relation between the intensity of the emission and the analyte number density in the plasma [11]. Ideally the calibration curve shows linear relation between the wavelength-integrated emission line intensity and the analytic concentration, and indeed, this is the case in optically thin environment, i.e. when self-absorption is negligible. In optically thick conditions, the linear dependency of the emission on analyte number density is lost due to self-absorption. In the most extreme case the collected analyte emission line is deteriorated by self-reversal effect. Compromises in the analytical performance have to be done to overcome these problems causing the nonlinearities in the curve of growth. Self-absorption either forces to focus on low concentration conditions or leads to a choice of another analyte emission line that is less prone to self-absorption [24]. The lines that are less influenced by the self-absorption usually originate from higher energy levels and therefore the use of these lines for the detection compromises the limit of detection (LOD) in conventional LIBS measurements. Recent development on microwave-assisted LIBS (MW-LIBS) has shown that, in addition to improvement of LOD, microwave assistance is capable to reduce the self-reversal and self-absorption in the plasma plume [25]. This is highly beneficial when measuring high elemental concentration samples that are prone to self-absorption.

The calibration of LIBS signal is not alone affected by the elemental absorption properties but also the calibration sampling plays an important role. The complex nature of interaction between laser and sample and between plasma and sample leads to undesirable matrix-effects. These effects cause variations in plasma properties that are dependent on sample material properties and laser characteristics [11]. Therefore, the calibration sample properties have to match with the actual sample and this may be very difficult to achieve without extensive sample preparation, which would cut down one of the LIBS's advantages. The calibration sample arrangement is not as difficult in the case of gas phase, as it is in solid phase, as the measurement configuration parameters, e.g. lens-to-sample distance and the sample homogeneity, are easy to maintain. However, most elements, e.g. alkali metals and alkaline earth metals, are not commonly found in gas phase and therefore reliable calibration of metallic analytes to high concentration levels have found to be challenging. Controlled gas phase concentrations have been produced by evaporating salt compound containing the desired analyte letting the vapour pressure reach

equilibrium [26]. Even though the equilibrium method can produce considerable concentration of the analyte into the gas phase, it requires very stable atmosphere to reach the equilibrium. Therefore, this method is rarely suitable for LIBS applications. The salt can be also seeded into the measurement volume as aerosol. Aerosol is produced with nebulizer and carried with gas flow into a heated measurement volume where the aerosol is vaporized [10]. However, in the seeding method demonstrated by Hsu et al. [10] the aerosol is carried to the flame by the combustion gas that limits the ability to vary the amount of aerosol injected into the flame. High concentration calibration would require high number of aerosol droplets injected into the flame. In the former design variation in the carrier gas flow would lead variation in the flame properties that would compromise the validity of the calibration. On the other hand, changing the analyte concentration in the nebulized solution affects to the efficiency of nebulization, hence, may lead to nonreliable calibration of the measurement.

This paper addresses the issues in quantitative LIBS calibration related to combustion studies by using novel approach for analyte seeding. This was achieved by introducing aerosol containing the analye to centre of the flame only using novel burner design. The analytical performance was further improved introducing microwave-assistance to the laser induced plasma with a microwave near-field applicator (NFA) [27]. NFA injected MW-LIBS has previously been applied to solid [25] and liquid [28] phase measurements. This study is the first demonstration of NFA in gas phase measurement. MW-LIBS has the ability to reduce self-absorption in high concentration conditions and improve LOD [25]. LIBS and MW-LIBS performances are compared in terms of LOD and linearity of the calibration curves for K, Na, and Ca. The obtained calibration curves are applied to measure temporal release curves of K, Na, and Ca during thermal conversion of poplar pellet inside the flat flame to demonstrate the applicability of the method in a biomass combustion environment.

2. Experimental set-up

2.1. Calibration sample seeding and burner design

Fig. 1. shows a Hencken style flat flame burner with a single seeding tube in the centre. The burner was designed to provide a well-controlled combustion environment and suitable quantitative seeding of alkali salt solutions to the flame. The flat flame burner consists of an inner brass tube and an outer brass tube with the inner diameter of 23.4 mm and 40.5 mm, respectively. The inner brass tube is divided into two parts and connected by a fringe in the bottom part. The burner can be divided into four main parts, namely fuel jets, air co-flow, N_2 shroud flow, and seeding flow. There are 58 stainless steel hypodermic tubes with the diameter of 1 mm, which are fixed evenly on a stainless-steel disk in the connecting fringe. CH_4 is fed through a packed bed into all the tubes to ensure a uniform fuel flow in each tube. These tubes convey CH_4 to the outlet of the burner and emerged as the fuel ports on the surface of the honeycomb. The combustion air flows into the inner brass tube via side tubes and is conveyed upstream through a packed bed and a stainless-steel honeycomb, forming the co-flow. Each fuel jet is directly adjacent to 6 hexagonal air co-flows to form the uniform flat flame. The shroud N_2 flow is fed into the outer brass tube via side tubes and through a packed bed and a stainless-steel honeycomb to stabilize the inner flat flame. The central tube with a diameter of 1 mm was used to seed the salt droplets into the flame in the LIBS calibration system.

The seeding was realized using salt solutions that were nebulized and carried into the flame. An ultrasonic nebulizer was employed to produce a fog of droplets from different salt compound (KCl, NaCl or $CaCl_2$) solutions in a sealed tank. A flow of pre-mixed CH_4 and air passing through the tank carried the nebulized droplets via the central hypodermic tube that was drilled through the bottom of the inner brass tube into the centre part of the flat flame. The droplets were vaporized by the heat when injected into the flame. By changing the flow rate of