

***In-situ* laser measurement of oxygen concentration and flue gas temperature utilizing chemical reaction kinetics**

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Combustion research requires detailed localized information on the dynamic combustion conditions to improve the accuracy of the simulations and hence improve the performance of the combustion processes. We have applied chemical reaction kinetics of potassium to measure local temperature and O₂ concentration in flue gas. Excess of free atomic potassium is created into the measurement volume by photofragmenting precursor molecule such as KCl or KOH that are widely released from solid fuels. The decay of the induced potassium concentration is followed with an absorption measurement using a narrow linewidth diode laser. The temperature and O₂ concentration are solved from the decay curve features using equations obtained from calibration measurements in temperature range of 800-1000 °C and in O₂ concentrations of 0.1-21 %. Local flue gas temperature and O₂ concentration were recorded in real time during devolatilization, char burning and ash cooking phases of combustion in single particle reactor with 5 Hz repetition rate. The method can be further extended to other target species and applications where the chemical dynamics can be disturbed with photofragmentation. © 2017 Optical Society of America

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Laser spectroscopy allows authentic nonintrusive analysis of combustion chemistry. Various methods based on absorption spectroscopy have shown to be simple and effective for chemical analysis in combustion environment. Wavelength modulation spectroscopy (WMS) and tunable diode laser absorption spectroscopy (TDLAS) have been used to analyze multiple different major combustion gas components O₂ [1], CO₂[2], H₂O[3], NO[4], CO[4] and temperature [2, 3, 5] as well as trace gas species such as gaseous potassium [6]. However, these methods have not been able to deliver localized information on flame temperature or O₂ concentration. Multiple methods, in addition

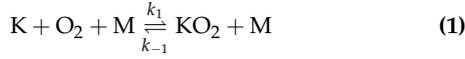
to conventional probe method [7], have been proposed to provide the desired localized temperature information on combustion flames and some of these techniques have also shown capability to map O₂ concentrations. Planar laser induced fluorescence (PLIF) has been used to obtain 2-dimensional single pulse measurement on temperature contours in flames [8] as well as do imaging of O₂ concentration [9]. Phosphorescence effect has also been used for temperature mapping by seeding the flame with thermographic phosphors [10]. Also use of scattering techniques has been introduced to temperature and molecular concentration mapping in flames [11].

Concern of environmental aspects and increasing price of fossil fuels are driving power production towards renewable and CO₂ neutral fuels, such as biomass. Biomass fuels contain alkali and chloride species whose fate in combustion processes has been under interest due their problematic nature in combustion boilers [12]. Monitoring of the alkali species has been tackled with absorption methods. Simultaneous measurement of potassium (K), potassium hydroxide (KOH) and KCl has been introduced with collinear photofragmentation and atomic absorption spectroscopy (CPFAAS) [13, 14].

In this letter, temporal behavior of flue gas temperature and O₂ concentration during combustion of biomass are measured using calibrated reaction dynamics of atomic potassium after a photofragmentation event. The measurement arrangement is analogous to CPFAAS [14]. It exploits the presence of the potassium chloride (KCl) and potassium hydroxide (KOH) in the flue gas. The excess of atomic potassium is created with a photofragmenting UV laser pulse, and the reaction rate back to the equilibrium is followed by absorption measurement of atomic potassium using a narrow linewidth continuous wave laser. Thus the method provides information from volume of fragmenting laser beam that contains KCl or KOH compounds in the gas phase. Calibration of the reaction parameters was carried out with KCl vapor in an oven, and the method was further applied in a single particle combustion reactor during black liquor droplet combustion. The technique provides temporal profiles of the flue gas temperature and O₂ concentration showing expected temporal behavior finally settling on the predefined furnace values. The short measurement path length of about 1 cm and fine temporal resolution indicates that this method can be utilized for temporal analysis of local parameters

in gas phase where photofragmentation can be induced.

Under lean combustion conditions reaction



plays an important role in determining the dynamics of atomic potassium [15–17]. In stable conditions, Eq. 1 is in equilibrium state in which the forward and reverse reaction rates are equal. This equilibrium state is described by an equilibrium constant that can be defined using the minimum of Gibbs's free energy

$$\ln K_{eq} = -\Delta G/RT. \quad (2)$$

The equilibrium constant determines the ratio of partial pressures of reactants and products for Eq. 1 with relation

$$K_{eq} = \frac{[\text{KO}_2]p^0}{[\text{K}]_0^{\text{res}}[\text{O}_2]}, \quad (3)$$

when ideal behavior of Eq. 1 is assumed. Addition of atomic potassium with photofragmentation from KCl or KOH leads the reaction to proceed forward with reaction rate k_1 to revert to the equilibrium state. Generally, the concentration of the induced potassium $[\text{K}]_0$ decays exponentially

$$[\text{K}] = [\text{K}]_0 \exp(-k_1 t). \quad (4)$$

The reaction rate k_1 has been found to be function of temperature and O_2 concentration with the relation $k_1 = 1.2417 \times 10^{-9} [\text{O}_2] T^{-0.733} \text{ cm}^3 \text{ K molecules}^{-1} \text{ s}^{-1}$ in temperature range of 477–1050 °C [15]. However, in temperatures over 800 °C the atomic potassium concentration decays in double exponential manner. In the first phase k_1 potassium forms reversibly potassium superoxide (KO_2) as described above. In the second phase k_2 , that is in range of two orders of magnitude slower decay than k_1 , the intermediate and/or the reactant diffuses irreversibly away from the volume of the fragmenting beam and the potassium concentration settles back to the initial surrounding equilibrium [15]. The second phase follows exponential

$$[\text{K}] = [\text{K}]_0^{\text{res}} \exp(-k_2 t), \quad (5)$$

where $[\text{K}]_0^{\text{res}}$ is the potassium concentration at the equilibrium of Eq. 1. As Eq. 1 is considered to be the only fast decay path for potassium, the concentration of induced KO_2 can be written as $[\text{K}]_0 - [\text{K}]_0^{\text{res}}$. It suggests that measurement of the reaction rate and the equilibrium concentration of the potassium atoms in Eq. 1 enables solving the temperature and O_2 concentration in the measurement volume.

The atomic potassium population was deviated from the steady state by photofragmenting KCl or KOH molecules that induced potassium atoms to the measurement volume. The precursor molecules, KCl or KOH, were fragmented using pulsed UV lasers emitting at 266 nm (FQSS 266-200, CryLas GmbH) or at 320 nm (NT342/1/UV, Ekspla Ltd.), respectively. The evolution of potassium concentration was followed with a narrow linewidth distributed feedback diode laser (Nanoplus GmbH) having emission wavelength locked to the potassium D2 absorption line at 766.5 nm using a reference potassium cell (SC-K-19 75-Q-W, Photonics Technologies). The probe beam was aligned using dichroic mirrors to overlap with the fragmenting beam in the desired measurement volume so that the relative potassium concentration changes due the fragmentation and the relaxation kinetics can be recorded as varying transmission of the probe beam. The temporal intensity of the probe beam was measured

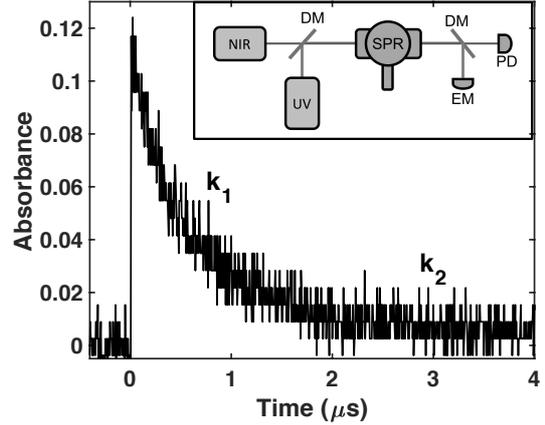


Fig. 1. Temporal evolution of probe laser absorbance. k_1 is the decay constant of the first phase and k_2 the decay constant of the second phase of the decay. Schematic presentation of used measurement arrangement is presented in the inset: Probe laser, NIR; fragmenting laser, UV; dichroic mirrors, DM; single particle reactor, SPR; energy meter, EM; photodiode, PD.

using amplified photodetector (PDA10A, Thorlabs) and a 12-bit oscilloscope (HDO6054, LeCroy).

The obtained PD-voltage curves were converted to absorbance and further to concentration c by applying Beer-Lambert law

$$\alpha L = \sigma c L = -\ln[I(t)/I(t < 0)]. \quad (6)$$

However, note that the absolute concentration is not important as only relative change in concentration is considered and, hence, also line broadening effects can be neglected. Figure 1 shows an example of temporal absorbance curve. The fragmenting UV pulse is launched at $t = 0$ resulting a rapid increase in absorbance. The peak of the curve indicates the initial induced potassium atom population $[\text{K}]_0$ in the measurement volume. In the obtained absorbance curve, the decay constant k_1 is equivalent to reaction rate k_1 and can be determined through fitting an exponential function to the first phase of the measured decay curve. The equilibrium concentration $[\text{K}]_0^{\text{res}}$ of potassium in the predominant conditions is determined by fitting an exponential function to the second phase of the decay curve and extrapolating it to $t = 0$.

The theoretical dependencies were validated with calibration measurements using a quartz tube furnace. KCl powder was set inside the sample cell in 10 cm long glazed combustion boat. The atmosphere in the sample tube was controlled using a mass flow controller (5850S, Brooks Instruments) diluting dry synthetic air with nitrogen. The tube was flushed for 5 min before each measurement with desired gas mixture. The gas flow was closed 2 min before the measurement to let the gaseous KCl partial pressure reach its equilibrium. The precursor molecule was chosen to be KCl due its easy behavior even in high temperatures. KOH reacted strongly with the sample tube which interfered the measurements. Few successful measurements with KOH showed that the reaction path of the free gaseous potassium does not depend on the precursor molecule and therefore the calibration done with KCl can be also used for temperature and O_2 concentration measurement in flue gas using KOH molecules.

The factor $-\Delta G/R$ of Eq. 2 was measured by varying the temperature with fixed O_2 concentration to determine the tem-

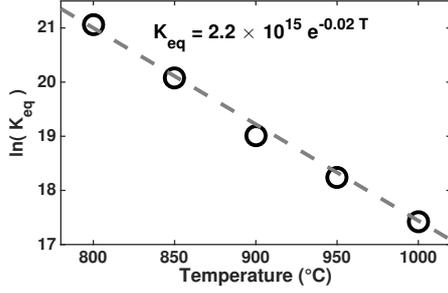


Fig. 2. Logarithm of the equilibrium constant K_{eq} measured in 21 % of oxygen in temperature range of 800-1000 °C

perature dependency of the equilibrium constant. The obtained graph is shown in Fig. 2 with K_{eq} being defined by Eq. 3. In temperatures lower than 800 °C, Eq. 1 does not yield to large enough equilibrium concentration $[K]_0^{res}$ that would be detectable with the arrangement used in these experiments. This causes the equilibrium measurement to focus only to high temperature conditions. Fitted function for equilibrium constant as a function of temperature was $K_{eq}(T) = 2.2 \times 10^{15} \exp(-0.02T)$. This also confirms the theoretically anticipated relation between K_{eq} and T .

Temperature and O_2 concentration dependencies of the reaction rate constant k_1 are presented in Fig. 3 and in Fig. 4. In the calibration measurements, the reaction rate constant k_1 shows linear behavior against inverse of the temperature with $k_1 = 1.73 \times 10^{10} T^{-1} - 1.10 \times 10^7$ at the range of 600-1000 °C. Also, the reaction rate k_1 behaves linearly as function of O_2 concentration in partial pressures over 10^{-3} . In lower partial pressures the reaction between potassium and O_2 becomes slow enough to other decay mechanisms to affect to the measured decay constant diverting the measured points off from the linear curve. The linear fit $7.48 \times 10^7 [O_2] - 1.95 \times 10^{-9}$ in O_2 partial pressures over 10^{-3} was used due the uncertainty of the decay processes in lower partial pressures. Effect of major combustion gases CO_2 and H_2O to the potassium decay curve was also studied but no change in the curve features were found. The obtained calibration functions are compiled into a pair of equations to solve temperature and O_2 concentration utilizing potassium kinetics

$$\begin{cases} \frac{([K]_0 - [K]_0^{res}) p^0}{[K]_0^{res} [O_2]} = 2.2 \times 10^{15} \exp(-0.02T) \\ 1.73 \times 10^{10} T^{-1} - 1.10 \times 10^7 = 7.48 \times 10^7 [O_2]. \end{cases} \quad (7)$$

The obtained pair of equations was applied to solve the temporal behavior of temperature and O_2 concentration of flue gas in a single particle reactor. The reactor is a quartz glass tube with tube diameter of 5 cm placed inside an electrically heated oven [18]. The fragmenting laser beam and the probe beam were aligned through the front and back view ports of the reactor as shown in the inset of Fig 1. Black liquor (570) droplet was used as sample fuel. The sample droplet placed to a platinum hook was inserted from the side port and set to the center of the reactor. Laser beams were aligned to pass the fuel 7 mm above the droplet where the interaction length of laser beam with released KCl and KOH was approximated to be 1 cm corresponding the size of the flame. The gas flow rate was set to 220 (standard)L/h and the combustion gas components N_2 and O_2 were blended with Bronkhorst mass flow controllers. The O_2 concentration in

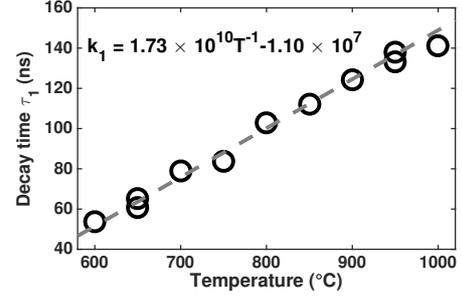


Fig. 3. Decay time of induced potassium concentration $\tau_1 = 1/k_1$ as function of temperature measured in 21 % of O_2 .

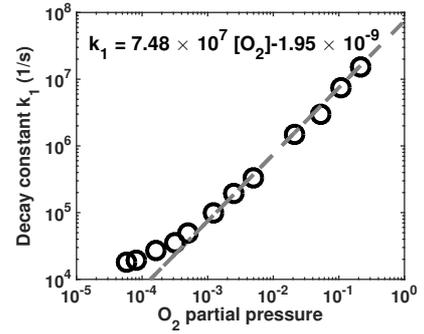


Fig. 4. Decay constant of induced potassium concentration k_1 as function of O_2 partial pressure is linear in pressures over 10^{-3} . The measurement was done in furnace temperature of 600 °C.

the combustion gas was measured with gas analyzer (AO2020 ABB) to be 11.13 %. KOH was used as precursor molecule to induce the atomic potassium to the measurement volume in the single particle reactor measurements due its availability in black liquor flue gas throughout the measurement. The time traces of temperature and O_2 concentration recorded during devolatilization, char burning and ash cooking phases in combustion temperature of 950 °C are shown in Fig 5. The method is validated in temperature range from 800 °C to 1000 °C with the calibration measurements done in tube furnace. The measured time traces are within this range through char burning and ash cooking providing well resolved temporal local information. During ash cooking phase, the temperature in measurement volume recovers close to the level of set furnace temperature averaging on 961 °C with standard deviation of 9 °C. Also the O_2 concentration recovers to the set level averaging at 11.6 % with standard deviation of 0.4 %. The obtained measures agree well with the set values of the reactor. The systematic deviation in temperature measurement might originate from different locations of furnace controlling thermocouple measurement points and different temperature profiles in the two furnaces. Also, the furnace O_2 concentration is measured from exhaust gas so the measurement location is far away from the flame zone and may lead to a small difference in the results. During devolatilization, the flue gas temperature rises above the calibrated range. However, measured temperature agrees well on surface temperature measurements done for a black liquor droplet [19]. The obtained curves in Fig 5 proposes the methods potential to measure temperature and O_2 concentration in dynamic combustion environment.

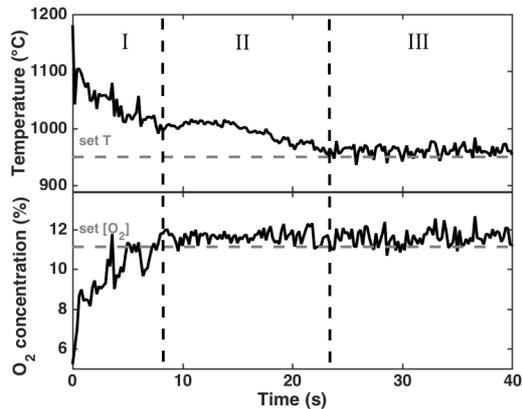


Fig. 5. Temporal behavior of temperature and O_2 concentration measured from black liquor (570) flue gas in single particle reactor. The set temperature of the reactor was $950\text{ }^\circ\text{C}$ and the set O_2 concentration in combustion gas was 11.13% . Dashed lines divide the different phases of combustion: I de-volatilization, II char burning and III ash cooking.

The demonstration in single particle reactor shows the applicability of chemical reaction kinetics based temperature and O_2 concentration measurements. By altering the beam path configuration of the lasers from collinear to intercepting, the measurement method can provide localized temperature and O_2 concentration data as the obtained absorption signal is formed only in the beam overlapping volume. In this work, the method was applied to a flue gas flow that was 1 cm wide but by increasing the fragmenting laser pulse energy, the interaction length of absorption can be further shortened. This allows spatially more specified measurements in larger combustion environments. The perpendicular laser beam configuration has already been demonstrated in tube furnace by Sorvajärvi et al. [15]. The range of measurement targets can also be extended by choosing different precursor molecules for the fragmentation, e.g. metal halides [20] and halogenated carbon molecules [21]. Metal halides are relatively easy to fragment due their accessible fragmentation energy and their volatility in reasonable temperatures. Another interesting type of chemical species for photofragmentation are the metal hydroxides [13, 22]. The presented method offers a tool for simultaneous concentration, temperature and O_2 monitoring for example NaOH that is used in many industries as chemical base. It is beneficial to have precursor molecule from which one of the fragments would be atomic since this allows use of strong atomic absorption. In conditions where the induced atomic concentration reaches an equilibrium state with the surrounding, the temperature and reactive compound concentrations can be measured using similar method as presented in this letter.

In conclusion, a novel approach for in-situ flue gas temperature and O_2 concentration measurements using chemical reaction kinetics is introduced. The potassium reaction kinetics with the ambient oxygen was calibrated in temperature range of $800\text{--}1000\text{ }^\circ\text{C}$ and in O_2 concentrations of $0.1\text{--}21\%$. The method was applied to measure temperature and O_2 concentration in flue gas released from black liquor droplet and it showed good agreement with the reference values within the calibration range and also in temperatures up to $1100\text{ }^\circ\text{C}$. Alkali compounds are widely present in many solid fuels used for power production [12, 23], therefore, with the spatial scalability and ability to mea-

sure in dynamic environment, the proposed method can be used in many combustion applications to obtain localized information on temperature and O_2 concentration. The method has also great potential to be used with other types of precursor molecules and applications, which opens new possibilities in different fields of industry and science.

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