



Full length article

Experimental investigations of potassium chemistry in premixed flames



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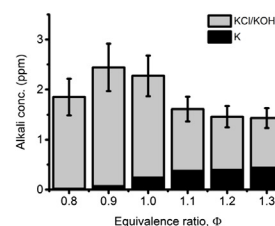
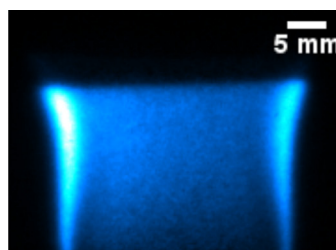
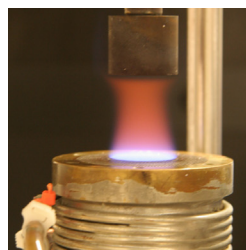
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HIGHLIGHTS

- Optical measurements of alkali species in premixed laminar flames seeded with KCl.
- Quantitative species concentrations have been evaluated from experimental data.
- Measurements show good agreement with predictions of a chemical mechanism.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 21 February 2017

Received in revised form 3 May 2017

Accepted 4 May 2017

Available online 16 May 2017

Keywords:

Combustion
Alkali formation
Optical diagnostics

ABSTRACT

Quantitative potassium species concentrations have been measured in alkali-seeded premixed methane-air flames of different stoichiometry. Potassium chloride (KCl) and hydroxide (KOH) were measured by broadband UV absorption spectroscopy and laser-induced photofragmentation fluorescence, while atomic potassium was measured using tuneable diode-laser spectroscopy. In addition, laser Rayleigh scattering was employed for temperature measurements. Investigations were made for different alkali-seeding levels and chlorine loads resulting in KCl/KOH concentrations up to ~30 ppm and concentrations of K atoms at ppm levels. Experimental results were compared with predictions from a chemical mechanism used in a homogenous reactor model. The observed trends, decrease in KCl and KOH concentrations and increase in K-atom concentrations with flame equivalence ratio, were well reproduced in simulations and are compared with results reported in literature. In addition, possibilities using the experimental methods for further investigations of alkali-related combustion phenomena and detailed model validation of alkali chemistry are discussed.

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1. Introduction

Increased attention to limited fossil fuel resources and the impact of combustion emissions on climate, environment, and health continuously promotes efforts to implement sustainable concepts for future energy supply. Even though solar- and wind based systems have been introduced, combustion remains a major supply of energy worldwide, which has motivated use of renewable biomass fuels [1]. While combustion of such fuels is considered to produce no net CO₂ and thereby have reduced impact on

global warming, it still has substantial impact on the environment [1]. Moreover, the chemical composition of biomass fuels introduces new challenges to achieve combustion with minimum wear of power plant units and minimum pollutant emissions [2].

Biomass from wood or crops contains alkali species (mainly potassium) as well as chlorine and sulfur [3–6], and formation of alkali compounds during combustion is of high practical importance since corrosive alkali chlorides cause severe problems in boilers and furnaces [2,7]. In addition, deposits formed on surfaces such as heater and steam tubes contribute to problems with fouling and slagging [8]. Thus, detailed knowledge on alkali release and formation processes during combustion is crucial for efficient uti-

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lization of biomass fuel while also minimizing problems during power plant operation.

Trace-level species, such as alkali and chlorine [3], in the fuel are many times neglected in combustion models, but have nevertheless been found to have rather strong impact on the overall combustion process, affecting the fuel oxidation process as well as formation of NO_x [9]. According to the discussion in the review by Glarborg [9], this has mainly been attributed to the ability of these reactive species to participate in chain-branching or chain-terminating chemical reactions resulting in production or consumption of flame radicals such as H and OH. In combustion chemistry, potassium atoms are reported to consume flame radicals such as O and H forming potassium hydroxide (KOH), which in turn establishes rapid equilibrium with potassium chloride (KCl) [9]. The combustion chemistry of potassium and chlorine is also coupled to that of sulfur via the ability to transform potassium chloride to less harmful alkali sulfates [10]. Thus, in addition to understanding pollutant formation of alkali species, knowledge on their impact on the overall combustion process and coupling with each other via the flame radical pool is necessary for development of models for biomass fuel combustion. Such combustion can be carried out under a variety of conditions, including co-combustion with coal [11], flameless combustion at very lean conditions [12], or oxy-fuel combustion in an atmosphere augmented with CO₂ [13]. Comprehensive combustion models are therefore required for predictions of relevant quantities such as species concentrations.

Detailed studies of alkali chemistry in flames allow for development of chemical mechanisms, which enable predictions of alkali formation under different combustion conditions. Experimental data acquired under well-defined conditions are crucial for further development and validation of such mechanisms. For example, a study including experiments as well as kinetic modelling of sodium-species in hydrogen flames has been presented by Hynes et al. [14]. For potassium, early investigations have included studies on its effect on flame inhibition [15] but also potassium kinetics in premixed methane flames [16]. A rather recent study was made to investigate the effect of sulfur addition on potassium-species formation [17]. In addition to studies of gaseous fuels, detailed characterization of potassium release has also been carried out for single particles of coal [18] and biomass [19].

According to the work presented by Slack et al. [16], potassium participates in chemical reactions involving O₂, atomic hydrogen, the hydroxyl radical (OH), and water when introduced in a flame. The potassium species involved in these reactions are atoms, potassium hydroxide, potassium oxide (KO), and potassium dioxide (KO₂). Moreover, fuel-rich combustion conditions result in increased formation of atomic potassium via reactions between potassium hydroxide and hydrogen atoms. Conversely the levels of potassium hydroxide are increasing at lean conditions favoured by the availability of oxygen and water. If potassium is introduced together with chlorine in a flame, additional reactions will be included involving species such as atomic chlorine, hydrogen chloride, and potassium chloride [20]. Corresponding investigations of combustion in flames burning hydrogen or propane with sodium and chlorine added, show similar trends with increasing levels of alkali atoms at higher equivalence ratios while chloride and hydroxide concentrations decrease [20].

This paper presents potassium species concentration measurements in alkali-seeded premixed methane-air flames. The methods employed for species concentrations measurements include broadband UV absorption spectroscopy [21], laser-induced photofragmentation fluorescence [21,22], and diode-laser absorption spectroscopy [21,23]. Multiple optical diagnostic techniques have been employed for separate measurements in this work due to the large dynamic range of concentrations encountered in the

investigated flames. However, combined measurements of K atoms, KOH, and KCl have been presented previously by Sorvajärvi et al. [24]. Measured potassium species concentrations are compared and the dependence on flame equivalence ratio is analysed and discussed in terms of results previously reported in literature. The obtained results can be further employed for future validation and refinement of alkali flame chemistry models.

2. Experimental

2.1. Optical diagnostics

Laser-induced photofragmentation fluorescence (LIPF) measurements were made using an ArF Excimer laser (Compex 102, Lambda Physik), which provided pulses at a wavelength of 193 nm with 25 ns pulse duration and output pulse energy of 50 mJ. The laser beam was focused using cylindrical lenses of focal lengths $f = 1000$ mm and $f = 500$ mm, which combined with an arrangement of razorblades resulted in a 20 mm vertical sheet. The photofragmentation-induced fluorescence signal was detected with an intensified CCD camera (PI-MAX I, Princeton Instruments) equipped with an $f = 50$ mm objective (Nikkor $f/1.4$). A bandpass filter centred at 766 nm (50 mm dia., OD 4, FWHM 10 nm, Edmund Optics) was used for suppression of scattered laser radiation.

The evaluation of alkali species concentrations from the photofragmentation fluorescence signal has been described in detail in a previous publication [25]. In brief, the signal, F , is given by Eq. (1)

$$F = \frac{\Omega}{4\pi} \epsilon_F A \frac{A_{fi}}{A_{fi} + Q} TN \quad (1)$$

where Ω is the detection solid angle, l the probe volume length, ϵ_F the detection efficiency for the fluorescence signal, and A is the probe volume cross section area. The fluorescence quantum yield is given by $\frac{A_{fi}}{A_{fi} + Q}$ where A_{fi} is the Einstein coefficient for spontaneous emission and Q the collisional quenching rate.

The transmission factor T accounts for fluorescence losses due to absorption, so-called trapping, which in this case is generated by atomic potassium formed in the flame chemistry. To determine this factor, spectra of the potassium D₁ line at 769.9 nm were obtained from tuneable diode laser absorption measurements, discussed in the following. The spectral line was fitted by a Voigt profile with a Gaussian width of 0.11 cm⁻¹ and a Lorentzian width of 0.05 cm⁻¹. An average integrated absorption cross section for the two 4²P transitions was determined from spectroscopic data in literature [26] to 8.36 · 10⁻⁶ cm² s⁻¹ and the peak absorption cross section for the fitted lineshape was then calculated to 1.6 · 10⁻¹¹ cm². Using this quantity, the transmission factor T was calculated according to the Beer-Lambert absorption law under optically thick conditions [27,28] described more in detail in the [Supplementary Material](#). The calculation requires the absorption cross section, given above, the concentration of K atoms, and the absorption path length as input parameters. Values of K-atom concentrations were determined from data of tuneable diode laser absorption measurements, while a path length of 1 cm was estimated for the passage to the detector in the central region of the flame.

Coefficients for spontaneous emission and data on collisional quenching have been obtained from literature [26,29]. The beam cross section area A , is determined by dimensions of the of the focused laser sheet, which had a height of 20 mm and a width estimated to 200 μm. The solid angle and detection efficiency can be retrieved by calibration using the Rayleigh scattering signal.

The quantity N in Eq. (1) is the concentration of K atoms generated in the excited 4²P states by photofragmentation of potassium compounds and the concentration of these compounds, N_{KCl} , is

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