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Influence of potassium chloride and other metal salts on soot formation studied using imaging LII and ELS, and TEM techniques

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ABSTRACT

An experimental investigation has been performed where the influence of metal salts on soot formation has been studied. By combining two-dimensional laser-induced incandescence (LII) and elastic light scattering (ELS), two-dimensional information could be obtained on soot properties in the flames. For these studies, seven metal salts (NaCl, $MgCl_2$, $AlCl_3$, KCl, $CaCl_2$, $FeCl_3$ and $ZnCl_2$) were dissolved in water and aspirated into a premixed ethylene/air flame. At lower flame heights, in the soot inception region, the LII signal (representing soot volume fraction) was marginally affected by all additives, whereas the ELS signal strongly decreased with increasing additive concentration for the alkali salts. At higher heights, in the soot growth region, the soot volume fractions were lowered for the addition of potassium, calcium and sodium chloride, in order of significance. Some of the salts ($MgCl_2$, $AlCl_3$ and $FeCl_3$) resulted in negligible influence on LII signals and slightly higher ELS signals throughout the flames, and we relate the increased ELS signals to salt particles propagating through the flame. Main focus in our study was on the addition of potassium chloride for which several parameters were investigated. For example, soot primary particle sizes were evaluated using combined LII and ELS, showing decreasing particle sizes for increasing concentrations of potassium, in reasonable agreement with particle sizes evaluated using transmission electron microscopy. Also, CARS thermometry showed slightly higher flame temperature, ~30 K, for the potassium-seeded flame compared to the reference flame.

1. Introduction

Soot emissions are known to have negative impact on human health [1] as well as on environment and climate [2]. A serious climatological effect is global warming, and knowledge on the impact of soot on this phenomenon has increased in recent years. Soot is now believed to be one of the main contributors, along with carbon dioxide and methane, to global warming [2,3]. This effect is mainly combustion-related due to the extensive use of fossil fuels. The future direction globally is toward replacing fossil fuels with renewable sources, e.g. by using biomass fuels in combustion and gasification. These fuels, however, show large variation in concentration of ash-forming compounds, of which metal compounds constitute the major part. For example, stem wood has low concentrations of these compounds. Bark, on the other hand, has metal concentrations of several percent [4]. The influence of various metals on the soot formation may, at least partly, explain why gasification of different biomass sources lead to various soot concentration levels under the same fuel-to-air ratios [5]. Hence it is of great interest to gain better understanding of the role of metal compounds in soot formation processes. In order to gain basic knowledge on characteristics in real-world gasifiers, simplified laboratory systems such as premixed and non-premixed flames can give valuable information, which is not distinguishable in large scale experiments.

It is well-known, since the middle of the last century, that metal additives could have a pronounced effect on soot formation [6]. In the subsequent decades after this observation, different additives were tested in gas turbines [7] as well as in diesel engines [8], and depending on the additive used, soot formation could be either promoted or reduced. One of the earliest systematic investigations with metal salts and salt solutions introduced to sooting flames was presented in 1971 by Cotton et al. [9]. In this work they investigated propane diffusion flames using gravimetric soot sampling and direct observations of flame height. The results showed that especially alkali and alkaline earth metals decrease the amount of soot significantly. In the following year, Salooja et al. [10] presented results based on sampling showing inhibition of carbon formation when metals were placed in the reaction zone of the investigated flame. In 1975, Bulewicz et al. [11] investigated the effect of metal additives on soot formation in diffusion flames

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of acetylene and propane using gravimetric sampling for soot concentration and TEM for particle sizing. They suggested that ionic species rather than neutral ones were responsible for the observed effects of either soot promotion or soot reduction.

The first measurements investigating the influence of salts on soot formation using optical diagnostics were presented by Haynes et al. in 1979 [12] for premixed ethylene flames and in 1981 for premixed benzene flames [13]. In these studies, soot concentration and particle sizes were evaluated from combined elastic light scattering and extinction measurements. In the paper from 1979, Haynes et al. showed that introducing alkali metals (Na, K, and Cs) to the flame significantly reduced the scattered light, where cesium showed the strongest effect, followed by potassium and then sodium. In comparison to the scattering measurements, the extinction measurements only showed small variations when adding alkali metals. By combining the data from extinction and scattering measurements, they concluded that particle sizes decreased markedly with increased concentration of the additive, especially for potassium. Of the investigated alkaline earth metals (Ba, Sr and Ca), only additives of barium to the sooting flame led to the same strong soot suppression effects as the alkali metals, while the additives strontium and calcium led to a decrease in scattering of the same magnitude as the decrease in extinction. Similar measurements were performed in benzene flames seeded with a variety of metals including several alkali and alkaline earth metals [13]. The results showed the same trends as for the measurements performed in ethylene flames.

In a review paper by Howard and Kausch [14] from 1980, they discuss three main mechanisms for how different additives impact the soot formation in flames. The first mechanism, also known as an ionizing mechanism, occurs mostly for metals which ionize significantly in the flame due to their low ionization potential, e.g. sodium and potassium. It is speculated that this ionization may lower the coagulation and nucleation rates resulting in lower soot concentrations and smaller sizes. Investigations of additives showing behavior according to the first mechanism can be found in, for example, the work presented earlier by Haynes et al. [12] and also by Bonczyk et al. in [15,16]. For example, Bonczyk [16] shows a clear correlation between decreasing particle sizes and lower ionization potential in his studies using various alkali additives. In the second mechanism presented in [14], the additives together with the flame gases create hydroxyl radicals which lower the amount of soot and precursors of soot. The second mechanism affects the flame for additives such as barium, calcium and strontium. Measurements in flames using, e.g., calcium and barium additives have been performed both by Haynes et al. [12] and by Bonczyk et al. [17] showing decreased concentrations of soot. The third mechanism affects the soot formation in flames when metals such as manganese, iron, cobalt, and nickel, are used. These metals are speculated to increase the oxidation rate of soot late in the flame (secondary flame zone). Only marginal effects are often found in the primary flame zone.

It is not certain that a specific metal always affects soot formation in a distinct way, since the effect may be related to, for example, flame type and in what configuration the metal is introduced to the flame. As an example, in studies of iron additives to flames, the effect on soot formation has depended strongly on how the iron atom was bonded in a molecule before entering the flame, see for example [18–22]. In a TEM study conducted by Wong [19], it was found that ferrocene only had a marginal influence in reducing the particle sizes of the soot, while ferric acetylacetonate significantly reduced the soot particle sizes. In work by Hahn and Charalampopoulos [20], where they studied the effect of iron pentacarbonyl additive, they conclude that iron will nucleate as iron oxide prior to soot inception and thereby provide a location for soot inception and deposition, which could explain the measured increase in soot concentration found. Feitelberg et al. [22] also showed results from extinction and scattering measurements that indicate an increase in soot volume fractions for added ferrocene. They discuss why well known soot suppressors, such as iron and manganese, could result in an increased soot concentration. A plausible explanation is that initially when the flame is fuel-rich, the additives may increase the amount of soot, while it can catalyze the soot oxidation later in the flame.

In the present work the influence on the soot formation of seven metal salts aspirated into a premixed ethylene/air flame has been investigated, where a limited part was presented previously [23]. The work focuses on the use of advanced optical methods, and for the first time laser-induced incandescence (LII) has been used for study of the influence of additives on soot formation. The LII technique allows extraction of two-dimensional information of soot volume fractions. Also elastic light scattering (ELS), extinction measurements, and transmission electron microscopy (TEM) have been used, the latter to study the morphology of sampled soot. In our previous paper by Simonsson et al. [23], we presented results from laser measurements showing a significant decrease in soot volume fraction when adding potassium chloride, while there was only a marginal influence, a slight increase, on the soot volume fraction resulting from adding iron (III) chloride to the flame. The optical results indicated that the soot particles were smaller for the potassium-seeded flames, which were also supported by TEM measurements. In the present paper, more extensive results are presented from the seeding of all seven salts along with further evaluation of the results of potassium chloride. For the potassium chloride-seeded flames we present evaluated soot primary particle sizes based on combined LII and ELS measurements, and a discussion of how measurements of the depolarization scattering ratio can be used to estimate the influence of fluorescence from PAHs and soot precursors on the ELS signal. Furthermore, measurements by coherent anti-Stokes Raman spectroscopy (CARS) were performed to study the influence of potassium on the flame temperature. We also discuss scattering effects from the salt particles themselves as well as study the soot oxidation effects caused by the more diffusion-like flame at the edges of the investigated premixed flame.

2. Theoretical considerations

In this work, mainly three laser diagnostic techniques have been used; laser-induced incandescence (LII), elastic light scattering (ELS) and extinction. In this section, these techniques will be briefly described and some theory needed for evaluation will be presented.

Laser-induced incandescence is a technique for soot concentration measurements, where the energy of the incident laser pulses is absorbed by soot particles, resulting in an increase in temperature to about 4000 K and thereby also increase of the Planck radiation [24,25]. This increased Planck radiation from the heated soot on top of the natural flame luminosity is called the LII signal. The LII signal has been shown to be approximately proportional to the soot volume fraction when applied in flames [26]. However, using LII by itself cannot measure quantitative soot volume fractions without being calibrated using a secondary technique. In the present work, extinction has been used to calibrate the LII signal to soot volume fractions. LII can also be used for temperature measurements using 2-color pyrometry [27], and for particle size measurements from fitting of experimental LII signal decay curves using theoretically modeled curves [28,29].

Extinction is a line-of-sight technique, where the laser intensity attenuation, in this case caused primarily by absorption in soot particles, is measured. The initial intensity, I_0, and the transmitted intensity, I, can be used to evaluate the extinction coefficient,