

Experimental investigation of soot oxidation under well-controlled conditions in a high-temperature flow-reactor

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Abstract

A new setup is presented to study the oxidation of soot by molecular oxygen (O_2) in a flow reactor from 750–1150 K at atmospheric pressure. A laminar, premixed ethylene/air-flame with an equivalence ratio of 1.85 serves as the soot source and sampled flame gases with freshly produced soot are introduced highly diluted with nitrogen into the reactor, which is typically used to study the reaction kinetics of generic and technical fuels. Soot oxidation is then investigated under well-controlled conditions during continuously temperature-ramping with 6145 ppm of O_2 . Soot particles are characterized before and after oxidation by electrical mobility technique. Additional information about molecular flame species is obtained simultaneously by molecular-beam mass spectrometry. Only a few oxygenated species are formed during the oxidation process, while all hydrocarbon species are sampled directly from the flame, but show partly different oxidation behavior. Particle size distributions (PSDs) for a large temperature range and for two different inlet size distributions provide insights into soot oxidation kinetics. Particle sizes vary distinctly for the two investigated sampling positions and soot oxidation starts at different temperatures, but is clearly separated from flame species oxidation, which starts prior to soot oxidation at lower temperatures. Complete oxidation of soot particles is achieved at high temperatures for both sampling positions. Calculation of soot oxidation rates by O_2 and comparison with the Nagle-Strickland-Constable (NSC) equation indicates that our investigated flame-sampled soot is more reactive than graphitized soot. The presented dataset may help to validate existing soot models.

Introduction

Soot is formed by coagulation and growth of polycyclic aromatic hydrocarbons during incomplete combustion. Besides understanding the formation of soot, the kinetics of soot oxidation by molecular oxygen (O_2) and hydroxyl radicals (OH) is of crucial importance because of the high uncertainties of soot oxidation rates in existing soot models [1]. The NSC equation derives from measurements of oxidation rates of heated carbon rods by O_2 for temperatures from 900–2000°C and was later extended to 2400°C [2]. Vander Wal and Tomasek [3] have studied the soot oxidation by adding different soot aerosols obtained from pyrolysis into a

laminar flame and analyzing changes in particle diameter by transmission electron microscopy. In a recent study, Camacho et al. [4] have measured PSDs for the oxidation of nascent soot from ethylene, *n*-heptane, and toluene flames by O₂ from 1000–7800 ppm in a flow reactor for 950, 1000, and 1050 K. Oxidation rates from [3] and [4] were higher than predicted by the NSC equation. Here, we have studied the oxidation of soot produced from a C₂H₄/air-flame in a flow reactor for a wide temperature range.

Experiment

A laminar, premixed ethylene-air-flame at atmospheric pressure with an equivalence ratio $\Phi = 1.85$ and a total flow rate of 10 slm (1.14 slm C₂H₄, 8.86 slm air) is used as the soot source. The flame is stabilized on a McKenna burner with a water-cooled, porous bronze matrix (6 cm in diameter). To prevent flame-flickering a stainless-steel plate is placed 30 mm above the burner surface and the whole burner setup is also sideways enclosed. Additionally, a high co-flow of air (4 slm) shields the flame from the surrounded air. Flame gases and soot particles are sampled by a standard Dekati diluter based on ejection dilution, i.e., a high stream of N₂ (20 slm) flows around the ejector nozzle behind the sampling tube, which causes a pressure drop and gases at the tip of the sampling nozzle are sucked in and directly diluted. The nozzle of the diluter is made from stainless steel with an opening diameter of 4.5 mm and is introduced into the center of the flame at two different positions. First sampling position is directly above the burner with a distance of 5 mm from the burner surface to the center of the sampling nozzle. The second sampling position is at a height above the burner (HAB) of 25 mm in the exhaust gas region. A flow rate of 0.39 slm of sampled flame gases was measured by calibration with argon flowing through the burner matrix. This gives a dilution factor of 52.85 in our setup. The high dilution minimizes diffusion loss effects of sampled particles. For the soot oxidation process, O₂ (180 mg/min) is added together with N₂ behind the ejector nozzle. Nitrogen is preheated to 180°C and the diluter is also heated to 120°C to prevent condensation. Gas flows are precisely metered by Coriolis (C₂H₄, O₂, and N₂) and thermal mass flow controllers (air).

The sampled aerosol should be quickly transferred to the reactor to minimize changes in PSD. Therefore, the outlet of the diluter is connected by a flexible stainless steel line (950 mm in length, 16 mm in diameter) to the reactor inlet which is heated to 80°C. Depending on the aerosol temperature, the transfer time is no longer than 0.5 s. All gases are also premixed before entering the reactor. There is a 4-way cross mounted at the reactor inlet to measure continuously stable flame gases by quadrupole mass spectrometry (QMS) and the PSD at the beginning and the end of the temperature-ramping by scanning mobility particle sizer (SMPS). At the outlet of the reactor, the molecular gas phase composition is measured continuously by molecular-beam mass spectrometry (MBMS) and the PSD by SMPS. The temperature inside the reactor is varied between 750–1150 K. Soot experiments starts at the high temperature where total oxidation is achieved and

temperature then decreases with a cooling rate of 200 K/h. The high-temperature flow reactor is coupled to the MBMS and is typically used for investigation of technical fuels. The reactor and the MBMS are described in detail elsewhere [5, 6]. Briefly, the oven has three temperature zones with total heated length of 1000 mm, but all zones are set to same temperature for our experiment. To prevent emerging of particles at higher temperatures, the ceramic tube was replaced by a quartz tube. This limits the maximum temperature to 1350 K. Total length of the used quartz tube is 1500 mm with inner diameter of 43 mm. The residence time of the particles inside the heated length is approx. 1–1.5 s depending on the studied temperature for the soot oxidation. Gases are sampled at the outlet of the reactor by a quartz nozzle (opening diameter < 50 μm) to determine the molecular gas phase composition by MBMS. Sampled molecules are ionized by electron impact ionization (11.4 eV) and separated in the reflectron time-of-flight mass spectrometer (Kaesdorf) with the high mass resolution of 3000.

The measurement of stable flame gases (H_2 , H_2O , C_2H_2 , and CO_2) and the diluent gas (N_2) with the QMS at the inlet of the reactor allows of monitoring the initial gas phase composition and ensures the long-term stability during the soot oxidation experiments. If the sampling nozzle starts clogging, signal intensity of sampled flame gases (e.g., acetylene or CO_2) will drop while stability of the dilution gas shows general stability of the sampling process. For the flame with $\Phi = 1.85$, the signal intensities of the flame gases decrease slightly over time.

Because it is necessary to use nitrogen as diluent gas for the SMPS, detection of CO is not possible neither with QMS ($R = 300$) or MBMS ($R = 3000$). The used SMPS (TSI, Model 3938) with the electrostatic classifier (TSI, Model 3082) consists of four parts. The impactor at the inlet of the SMPS is 0.071 cm in diameter and removes very large particles. The adjusted inlet flow is 1.5 L/min. An X-ray source is used as neutralizer to make sure that all particles have a uniform and known bipolar charge distribution. All particles will be positively-charged. The differential mobility analyzer (DMA, TSI, Model 3085A) classifies the positively-charged particles in an electric field depending on their electrical mobility. By applying different voltages, certain particle size classes will pass the DMA and all particles are considered as monodisperse in size. A PSD of 1.5–150 nm can be measured depending on the sheath gas flow. A condensation particle counter (CPC) is connected to the outlet of the DMA to determine the particle concentration. SMPS scan time was 120 s.

Results and discussion

Complete soot oxidation series were measured three times for both sampling positions and good reproducibility is achieved. The sampling process of flame gases and soot particles is also stable enough for continuously temperature-ramping for the adjusted Φ of the flame. Addition of O_2 to the aerosol does not change the initial PSD and all measured particles are generated in the flame as measurements with a HEPA filter have shown. The signal from the SMPS was nearly zero with

the HEPA filter between the reactor inlet and the diluter indicating that no particles are released from the reactor at higher temperatures as observed for ceramic materials.

Figure 1 shows measured PSDs before (inlet) and behind (outlet) the reactor for the two sampling positions. All measured PSDs are log-normal or close to log-normal distributions. Sampling at 5 mm gives a small distribution with median mobility diameter of 12 nm while the higher sampling position at 25 mm provides a larger distribution with median mobility diameter of 28.5 nm. The PSD changes from unimodal to bimodal at the reactor inlet when vary the sampling position from 5 to 25 mm. A similar observation was also done by Stirn et al. [7] for an ethylene/air flame with $\Phi = 1.9$ where this transition was observed at a HAB of 14 mm. PSD also changes from bimodal to unimodal when passing the reactor at pyrolytic conditions and high temperatures. At room temperature the PSD stays bimodal at the reactor outlet. We also observed that the absolute concentration of the soot particles (without any oxidation process) is smaller at the reactor outlet in comparison to the inlet. For the small distributions, a significant particle loss has to be stated when passing the reactor (up to 60%). At the high sampling position, the particle loss is only 15%. Median diameter changes only slightly for both positions. A loss of sampling efficiency of approx. 20% must be also stated over time. Camacho et al. [4] investigated the oxidation of nascent soot from laminar flames in a flow reactor with shorter residence times (0.20–0.22 s) and did not mentioned a particle loss.

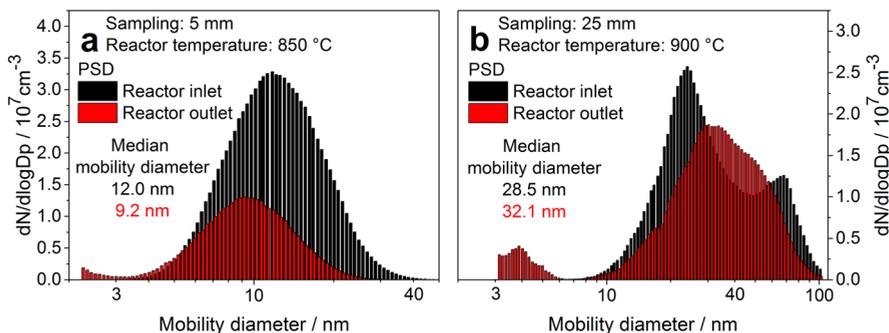


Figure 1. PSDs at the reactor inlet (black) and outlet (red) for two sampling positions (5 and 25 mm) in the flame with $\Phi = 1.85$.

PSDs of the soot oxidation with 6145 ppm O_2 for both sampling positions (5 and 25 mm) are shown in Figure 2 as function of the oven temperature. Oxidation of small soot particles starts at lower temperatures (approx. 940 K), while it is 990 K for the larger particles. All soot particles are almost oxidized above 1100 K. PSD shifted to smaller diameter when soot oxidation starts which can be clearly seen for the large distribution. Soot oxidation rates ω for the oxidation of soot by O_2 can be calculated based on a simple shrinking sphere model according to equation (1).

$$\frac{dm}{t} = \omega \cdot A \quad (1) \quad \omega = \frac{\rho}{2} \cdot \frac{dD}{t} \quad (2)$$

Soot oxidation takes place at the particle surface A and is expressed as mass loss dm over time t . If the density of the soot ρ is constant, the soot oxidation rate ω can also be expressed by equation (2) considering the change of the particle diameter dD over time. For our experiment, t is the residence time of the particles in the heated length of the reactor where the oxidation takes place and dD is the difference of the initial median mobility diameter of the PSD at the inlet of the reactor and the median mobility diameter of the PSD at the outlet of the reactor. Soot density was estimated to be 1.8 g/cm^3 , which is a typical value for soot between nascent soot [4] and amorphous carbon [3]. Figure 3 shows the calculated oxidation rates in comparison to the NSC equation for the oxidation of graphitized soot from [2]. Our results show that the investigated soot is more reactive than graphitized soot similar to the results of Camacho et al. [4] who studied nascent soot.

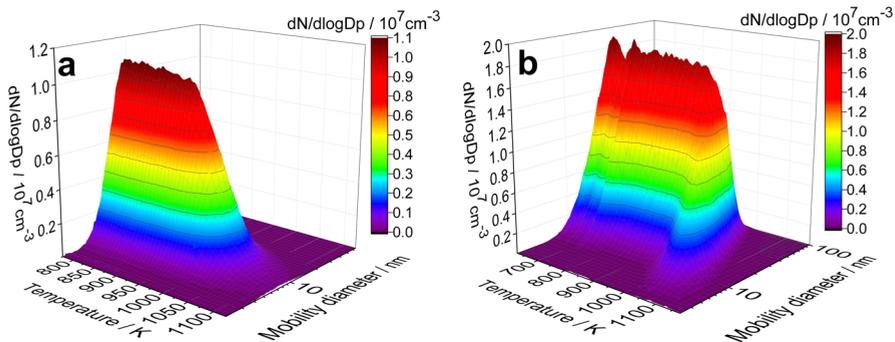


Figure 2. PSDs of the soot oxidation experiments in the temperature range of 750–1200 K and for sampling positions of 5 mm (left) and 25 mm (right).

Mole fraction profiles of small combustion intermediates were measured by MBMS and some of them are shown in Figure 3 in comparison with the total number concentration of soot particles for sampling at 25 mm. All detectable hydrocarbons have a mole fraction profile showing typical fuel behavior (e.g., C_2H_2 , C_6H_6) and are directly sampled from the flame, while oxygenated species like CH_2O or CH_2CO are intermediates formed within the oxidation process. The lower sampling position is in the reaction zone of the flame where combustion intermediates are formed and mole fraction of sampled acetylene is significantly higher as at 25 mm. As a result, intermediates which are formed during the oxidation process in the reactor like formaldehyde are also observed in higher concentrations. One of the species with highest observed mass in detectable amounts was C_{10}H_8 . Largest observed oxygenated species was on $m/z = 94$ and can be related to phenol. Soot oxidation is clearly separated from the flame species

oxidation and starts at higher temperatures. It was also observed that some sampled flame species have different oxidation behavior, e.g., oxidation of C_2H_2 starts a little earlier than oxidation of C_6H_6 .

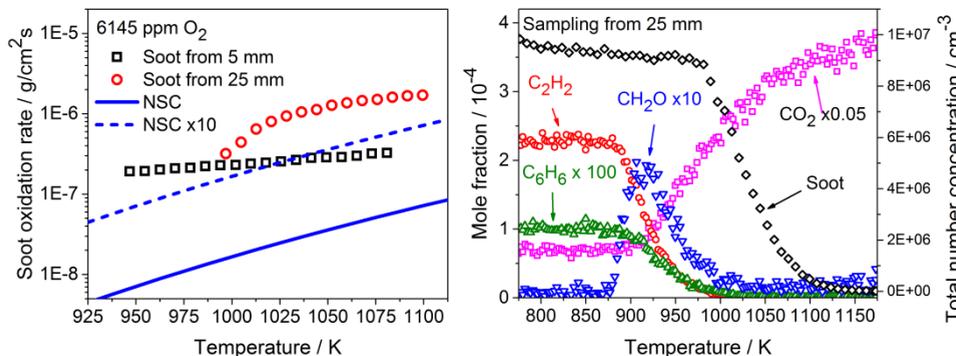


Figure 3. Soot oxidation rates in comparison with the NSC equation (left) and mole fraction profiles of molecular gas phase species in comparison with total number concentration of soot particles (right).

Conclusions

A laminar, premixed ethylene/air-flame was used as a soot source to investigate the oxidation of soot particles under well-controlled conditions between 750–1150 K and at atmospheric pressure. The flame with an equivalence ratio of 1.85 gives a reproducible data set for soot oxidation at two sampling positions including PSDs and species mole fractions. Small soot oxidation products (e.g., formaldehyde, ketene) and sampled molecules from the flame (e.g., acetylene, benzene) were quantified by MBMS. Calculated soot oxidation rates show that our investigated soot is more reactive than graphitized soot. The presented dataset for the oxidation of soot obtained from two different flame positions and for a wide temperature range may help to validate existing soot models.

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References

- [1] H. Guo, P.M. Anderson, P.B. Sunderland, *Fuel*, 172 (2016) 248-252.
- [2] J.R. Walls, R.F. Strickland-Constable, *Carbon*, 1 (1964) 333-338.
- [3] R.L. Vander Wal, A.J. Tomasek, *Combust. Flame*, 134 (2003) 1-9.
- [4] J. Camacho, Y. Tao, H. Wang, *Proc. Combust. Inst.*, 35 (2015) 1887-1894.
- [5] P. Oßwald, M. Köhler, *Rev. Sci. Instrum.*, 86 (2015) 105109.
- [6] M. Köhler, P. Oßwald, D. Krüger, R. Whitside, *J. Vis. Exp.*, (2018) e56965.
- [7] R. Stirn, T.G. Baquet, S. Kanjarkar, W. Meier, K.P. Geigle, H.H. Grotheer, C. Wahl, M. Aigner, *Combust. Sci. Technol.*, 181 (2009) 329-349.