Mapping the Operation of the Miniature Combustion Aerosol Standard (mini-CAST) Soot Generator

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Introduction

Soot aerosol derived from combustion processes have been previously shown to affect the Earth's radiation budget via direct absorption and scattering of solar radiation and by acting as cloud condensation nuclei (CCN) or ice nuclei (IN) to form clouds. In addition, ultrafine soot particles and associated polycyclic aromatic hydrocarbon (PAH) compounds likely pose significant health risks to the public. Consequently, much work in recent decades has focused on quantifying the properties of both ambient soot and that directly emitted from combustion sources. Relevant properties include soot concentration, size and morphology and the presence of inorganic and organic coatings on the soot surface. Investigating the role of each of these properties in determining climate and health impacts directly from ambient measurements is challenging, in part, because of low ambient mass loadings and because soot often coexist with atmospheric aerosol with a high degree of chemical complexity. Consequently, laboratory studies are needed to deconvolve these dependencies. A crucial component in these studies is having a reliable and reproducible combustion aerosol generator. A promising commercially-available generator is the Jing Ltd. Miniature Combustion Aerosol Standard (mini-CAST), which generates soot using a nitrogen-quenched, non-premixed, propane diffusion flame. While a number of previous studies have examined aspects of mini-CAST soot properties at a single or several operational conditions, a detailed examination of soot properties over the range of burner operation has not be conducted to date. This motivates the present study.

Methods

Soot from the mini-CAST was characterized by a variety of aerosol instruments, which are shown in Table 1. The mini-CAST fuel, quench, and dilution flows were held constant at the manufacturer-recommended flow rates (0.06 slpm, 7.5 slpm, and 20 slpm, respectively), while the oxidation air and mixing N_2 flow rates were varied to measure the soot size and concentration at over 200 different flow rate set points; a smaller sample size was examined for the other soot property measurements.

Table 1: Summary of Instruments Used to Characterize the mini-CAST soot.

Instrument	Measurement
TSI, Inc. Scanning Mobility Particle Sizer (SMPS)	Particle size distribution, number concentration
Aerodyne High-Resolution, Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS)	Non-refractory aerosol chemical composition
EcoChem Photoelectric Aerosol Sensor (PAS2000)	Surface polycyclic aromatic hydrocarbon (PAH) concentration
Droplet Measurement Technologies Cloud Condensation Nuclei Counter (CCNC)	Size-resolved CCN activation and growth kinetics
Veeco Multimode V Atomic Force Microscope (AFM)	Single-particle morphology, imaging
Kanomax Aerosol Particle Mass Analyzer (APM)	Particle mass, density
Sunset Labs Elemental Carbon – Organic Carbon (OC/EC) Analyzer	Organic/elemental carbon speciation, composition

Summary of Results

Measurements of particle size were found to be fairly constant and reproducible over a period of weeks to months (standard deviation < 7-10%), while number concentration varied by two-fold due, in part, to soot accumulation in the flow system. Particle size modes ranging from 10 nm to 130 nm were achieved by varying the burner flow rates to effect a change in flame chemistry.

OC-EC analysis from bulk filter measurements and PAS2000 analysis show a significant variation in residual PAHs coating the soot surface over the range of measured sizes, with the largest organic fractions found at fuel rich and very fuel lean conditions. Analysis of these soot coatings with an Aerodyne HR-ToF-AMS shows the O:C ratio of the organic coatings increases with decreasing burner flame equivalence ratio, which in turn, results in a slight increase in the CCN-derived aerosol hygroscopicity ($\kappa \sim 0\text{-}10^{-2}$; Petters and Kreidenweis, 2007). Measurements of soot density with the APM and single particle morphology with the AFM suggest that the organic-rich soot found produced by high flame equivalence ratios is thickly coated. The coating fills in the irregular structure of the soot agglomerate, producing large globules that have a higher effective density than the soot particles produced at lower equivalence ratios.

Overall, these results indicate that the soot produced by the Mini-CAST has properties similar to the range of properties previously reported in the literature for real world diesel and aircraft engine soot. However, we also find that the OC:EC ratio of the soot is directly related to the soot mode size, which prevents production of small soot diameters with low OC fractions (typical of, e.g., aircraft engine soots), unless a thermal denuder or catalytic stripper is used to post-process the soot stream in order to remove a portion of the organic coating.

A more detailed discussion of this poster can be found in the forthcoming paper by Moore et al. (in review).

References

Moore, R.H., et al. (in review) "Mapping the Operation of the Miniature Combustion Aerosol Standard (Mini-CAST) Soot Generator", submitted to *Aerosol Science & Technology*.

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Introduction and Motivation

- Combustion-generated soot affects Earth's radiation budget through direct absorption/scattering of solar radiation and by acting as cloud condensation nuclei (CCN) or ice nuclei (IN) to form clouds.
- Ultrafine soot particles and associated polycyclic aromatic hydrocarbon (PAH) compounds likely pose significant health risks to the public.
- Consequently, there is a need to quantify the properties of ambient soot and that directly emitted by combustion sources.
- Yet, atmospheric soot constitutes only a small fraction of the atmospheric aerosol (on a mass basis) and often coexist with other, chemically-complex ambient aerosol. This necessitates laboratory studies of soot processes.
- A crucial component in such studies is having a reliable and reproducible combustion aerosol generator. One promising, commercially-available technique is the Jing Ltd. Mini-CAST, which generates soot using a nitrogen-quenched, propane diffusion flame.

Experimental Setup

The Mini-CAST is shown in the upper left portion of Fig. 1. The soot first passes through a heated catalytic stripper or bypass line before being diluted with dry, particle-free air in the eductor. The dilution is controlled with an electrically-actuated proportional valve to ensure stable, reproducible concentration test points.
The soot is then chacterized by a comprehensive suite of aerosol instrumentation.

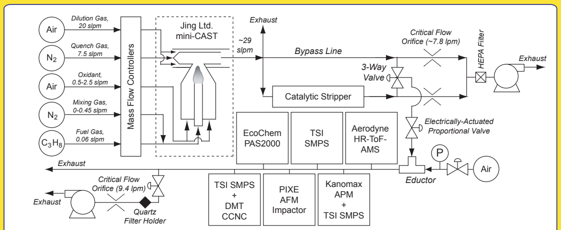

Figure 1: Schematic of the Jing Ltd. Mini-CAST and experimental setup.

Soot Size and Organic Fraction

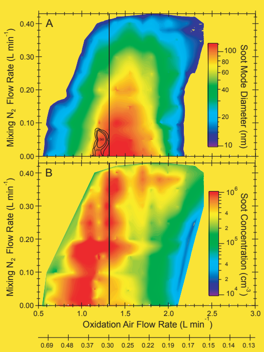

Figure 2: (A) Soot mode diameter and (B) soot concentration over the range of Mini-CAST operation. The black contours denote a region of bimodality, with the smaller mode diameter given in the contours (10-30nm).

- Soot size distributions (Figure 2a) and number concentrations (Figure 2b) depend on both oxidation air and fuel-N_2 mixing gas flow rates.
- Largest diameter soot observed during slightly fuel-lean flame conditions, while the highest soot number concentrations were observed during slightly fuel-rich flame conditions.
- Size and concentration are both strongly dependent on agglomeration/coagulation. Consequently, the magnitude of the reported values may change for different experimental setups; however, the overall trend should not change.
- Modal diameters are very consistent over a period of months (σ < 10%), while number concentrations are more variable (σ ~ 100%)

- Small soot particles have a greater organic to total carbon (OC/TC) fraction as shown in Figure 3a.
- OC/TC depends on soot mode size and *does not* depend on flame stoichiometry. This is shown in Figure 3b, which shows OC/TC as a function of oxidation air flow rate for constant size contours in Fig. 2a.
- This result is consistent with the mechanism of soot formation in a quenched diffusion flame, where quenching the flame early suppresses both the oxidation of organic PAHs to CO_2 and keeps the soot particle size small.
- Conversely, quenching the flame higher up in the burner allows both organic oxidation and particle growth reactions to produce large, mostly-elemental-carbon soot.
- Treating the soot with a 350 °C catalytic stripper is able to remove a portion of the organic coating (see Figure 3a).

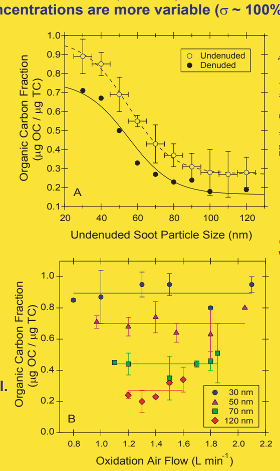

Figure 3: Organic carbon fraction as a function of (A) particle size and (B) oxidation air flow rate along constant size contours shown in Fig. 2a. Denuded soot were treated with a catalytic stripper at 350 °C prior to sampling.

Soot Coating Chemical Composition / Hygroscopicity

- Flame studies indicate that organic PAHs are formed early in the flame, and that these species are oxidized to CO_2 and elemental carbon in the oxidation regions of the flame.
- PAHs are easily photoionized, and measurements of the Mini-CAST soot with an EcoChem Photoelectric Aerosol Sensor (Figure 4) indicate that the highest PAH loadings in the soot occur under fuel-rich conditions.
- This suggests that the PAHs are oxidized to more-functionalized compounds under fuel-lean conditions -- a hypothesis that is supported by measurements of the coating O:C and OM:OC ratios with an HR-ToF-AMS (Figure 5).
- The increased degree of oxygenation of the soot coatings under fuel-lean conditions causes the soot particles to act as CCN at supersaturations consistent with insoluble, but hydrophilic particles (Figure 6).
- Only a small fraction of large soot particles are CCN-active (indicating that the soot is externally-mixed). No soot particles are CCN at Q_{oxi} < 1.5 L min (Figure 7).

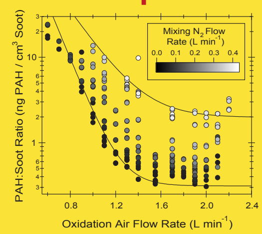

Figure 4: PAH mass concentration measured by the EcoChem PAS2000 normalized by the total soot volume concentration from the SMPS.

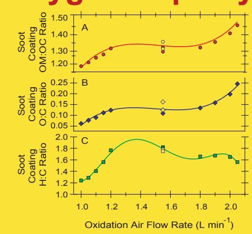

Figure 5: Soot coating oxidation state as determined by the HR-ToF-AMS. Q_{mix} = 0 L min^{-1} for all the solid markers and 0.15 and 0.30 L min^{-1} for open markers.

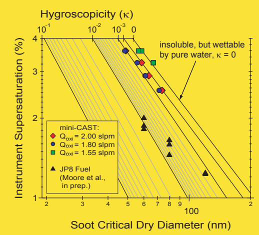

Figure 6: CCN-derived critical supersaturation-diameter relationship for multiple Mini-CAST conditions. Data are overlayed on the hygroscopicity matrix of Petters and Kreidenweis (2007). Shown for comparison is the CCN activity of soot from an APU burning JP-8 fuel.

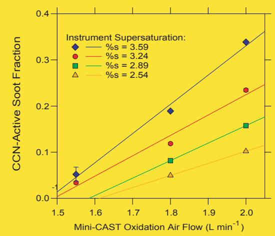

Figure 7: CCN-active soot fraction at multiple supersaturations and Mini-CAST operating conditions. Q_{mix} = 0 L min-1 for all conditions.

Soot Density and Morphology

- Single particle analysis using Atomic Force Microscopy (Figure 8) is consistent with bulk measurements showing that the soot produced under fuel-rich and very fuel-lean flame conditions is thickly coated with organics.
- Under slightly fuel-lean conditions, an organic coating is still present, but individual primary particles are more easily discernable with diameters on the order of 30 nm (Figure 8b).
- Bulk effective density measurements (Figure 9) show that the soot density decreases as the oxidation air increases from fuel-rich to fuel lean conditions.
- Density versus mobility size curves follow the characteristic power-law dependence with mass-mobility exponents ~ 2.4-2.6 (Sorenson, 2011).
- Density and AFM measurements show that soot produced under fuel-lean conditions is more "fluffy"

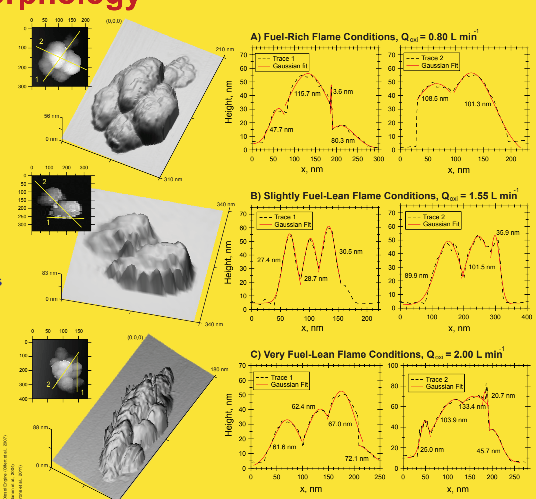

Figure 8: Atomic force microscopy images of single, soot agglomerates at three different Mini-CAST conditions. Height profiles are shown to the right for two, linear traces denoted by the lines in the top-down view insets. The dashed lines reflect the measured traces, while the solid lines are Gaussian fits to each clearly discernable peak. For each peak, the full Gaussian width at half maximum (FWHM) was computed and is reported beside each peak.

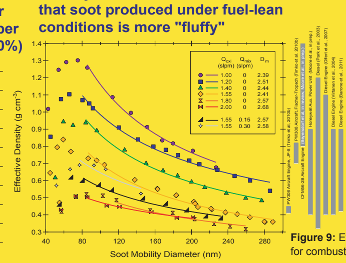

Figure 9: Effective density of Mini-CAST soot. Shown for comparison are the density ranges reported for combustion soot in the literature.

Summary and Conclusions

- Very fuel-rich or fuel-lean conditions produce organic-dominated soot with mode diameters of 10-60 nm, while slightly fuel-lean conditions produce larger diameter, lower organic fraction soot (70-130 nm).
- Moving from fuel-rich to fuel-lean conditions increases the O:C ratio of the soot coating, which causes a small fraction of particles to act as CCN near the Kelvin limit (κ ~ 0-10^{-2}).
- The properties of Mini-CAST soot overlap with the range of values previously reported in the literature for real-world aircraft and diesel engine soots (see Table 1 and Figure 9).

Table 1: Summary of Mini-CAST soot properties and those reported for aircraft and diesel engine combustion particles.

Property	Mini-CAST Soot Generator: Fuel-Rich, High OC	Fuel-Lean, Low OC	Fuel-Lean, High OC	Aircraft Engine	Diesel Engine
Q_{oxi}, L min^{-1}	0.6-1.1	1.1-1.8	1.8-2.2		
Q_{mix}, L min^{-1}	0	0	0		
Number Mode Diameter, nm	10-60	70-130	10-60	10-60 [i,q]	20-120 [c,o,s]
Number Concentration, cm^{-3}	10^7-10^8	10^7-5x10^7	10^6-10^7	10^{14}-10^{17} [†,g,h,j]	10^5-10^9 [s]
OC/TC Fraction, %	50-90	30-50	50-90	30-90 [r]	30-80 [n,o]
Organic Coating O:C Ratio	0.05-0.08	0.08-0.15	0.15-0.25	0.1-0.2 [p]	0.025-0.03 [k,t]
Hygroscopicity (κ)	Not CCN	0	0-10^{-3}	10^{-3}–5x10^{-2} [m,f]	0-10^{-2} [l]
Effective Density, g cm^{-3}	0.8-1.3	0.45-1.1	0.3-0.5	0.3-0.9 [e,f]	0.3-1.2 [a,b,c,d]

† Computed assuming 2.5% CO_2 mixing ratio at the engine exhaust plane and 3160 ppm CO_2 (kg fuel)$^{-1}$
[a] *Park et al.* [2003], [b] *Olfert et al.* [2007], [c] *Virtanen et al.* [2004], [d] *Barone et al.* [2011], [e] *Timko et al.* [2010b], [f] *Moore* [in preparation], [g] *Herndon et al.* [2005], [h] *Anderson et al.* [1998], [i] *Lobo et al.* [2007], [j] *Timko et al.* [2010a], [k] *Aiken et al.* [2008], [l] *Tritscher et al.* [2011], [m] *Popovicheva et al.* [2010], [n] *Shah et al.* [2004], [o] *Kerminen et al.* [1997], [p] *Robinson* [2011], [q] *DeWitt et al.* [2010], [r] *Cheng et al.* [2009], [s] *Kittelson* [1998], [t] *Kroll et al.* [2012]

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For complete reference information please see the extended abstract.

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