Supporting information for

High-throughput generation of aircraft-like soot

by

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S1. Equivalence ratio calculation and range

The equivalence ratio of the flames at standard temperature and pressure (STP) was calculated accounting for the fuel flow rate (4.5 mL/min, 0.00038 mol/s), dispersion O_2 flow rate (1.5 – 3.0 L/min, 0.00112 – 0.00223 mol/s), sheath air flow rate (20 L/min, 0.01488 mol/s), and premixed flame flow rate (CH₄/O₂: 1.25/2.25 L/min, 0.00093/0.00167 mol/s). Jet A1 fuel is a complex mixture with no one chemical formula however, for this calculation Jet A1 was assumed to be composed of 11.6 carbon atoms and 22 hydrogen atoms on average (Dagaut and Cathonnet 2006). From this chemical formula the molar mass was calculated to be 161 g/mol. The density of Jet A1 at STP is 811 kg/m³ (Measurement Canada 2016).

A stoichiometric methane flame has the chemical equation:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O_2$$

Thus, in each case twice the molar flow of CH₄, \dot{m}_{CH4} , of O₂ is needed to fully combust the CH₄. This amount is subtracted from the O₂ available for combustion with jet fuel giving the 'net' molar flow of O₂. The O₂ required to combust the jet fuel under stoichiometric conditions was calculated given the stoichiometric ratio for hydrocarbon combustion:

$$C_{11.6}H_{22} + 17.1O_2 \rightarrow 11.6CO_2 + 11H_2O \tag{S1}$$

Thus, an O_2 /jet fuel ratio of 17.1 is needed to achieve stoichiometric conditions. From this the equivalence ratio at each dispersion O_2 flow rate is calculated as:

$$EQR = \frac{17.1}{\left(\frac{Net \ molar \ flow \ of \ O_2}{Molar \ flow \ of \ jet \ fuel}\right)}$$
(S2)

For example, EQR = 1.34 was calculated as follows: 2.5 L/min of dispersion O_2 is used for this EQR. Using the ideal gas law, where the density of a gas at STP is 22.4 L/mol, the molar flow of dispersion O_2 is:

$$\frac{2.5 L/min}{60 s/\min \cdot 22.4 L/mol} = 0.00186 mol/s$$
(S3)

The same calculation is used to determine the molar flow of CH_4 , premixed O_2 and sheath air of which 21% is assumed to be O_2 and 79% N_2 . The molar flow of jet fuel is calculated as:

$$\frac{4.5 \text{ mL/min}}{60 \text{ s/min}} \cdot \frac{811 \text{ kg/m}^3}{161 \text{ g/mol}} = 0.00038 \text{ mol/s}$$
(S4)

Subtracting the O₂ required for CH₄ combustion from the premixed O₂, dispersion O₂ and sheath O₂:

$$\left(\dot{m}_{premixed,02} + \dot{m}_{disp,02} + \dot{m}_{sheath,02}\right) - 2\dot{m}_{CH4} = 0.0048 \ mol/s \tag{S5}$$

Thus, the EQR is:

$$EQR = \frac{17.1}{\left(\frac{0.0048 \ mol/s}{0.00038 \ mol/s}\right)} = 1.34$$

The EQR ranging from 1.25 to 1.59 are investigated extensively. However, a larger range is possible with the spray combustion unit set up (Figure S1a). The upper limit, EQR = 1.90 (solid line) is due to the lowest dispersion O_2 flow rate that the mass flow controller could supply, 0.62 L/min.



Figure S1: Mobility soot size distributions a) at the maximum, 1.90 (solid line), and minimum, 1.15 (broken line) EQR which could practically be achieved and b) with the same EQR, 1.25, achieved using either the standard premixed O_2 (2.25 L/min) and dispersion O_2 flow of 3 L/min (double-dot dashed line), or 2.50 L/min of premixed O_2 and 2.75 L/min of dispersion O_2 (dotted line).

In principle, a different mass flow controller or higher fuel flow rate could be used to achieve a higher EQR which should further increase the \bar{d}_m . On the other hand, the lower limit, EQR = 1.15 (broken line), 3.60 L/min dispersion O₂, was determined by the very low concertation of soot, < 1000 #/cm³. This value is after the same dilution described in the main text so it is possible that with less dilution this EQR could also be useful. However, without proper dilution the sampling system needs to be reconfigured to avoid overheating. Using

different O₂ flowrates in the premixed flame does not significantly affect the mobility size distribution when comparing the same EQR, Figure S1b. For example, increasing the O₂ flowrate in the supporting flame from 2.25 to 2.5 L/min and equally decreasing the dispersion O₂ flowrate (from 3 to 2.75 L/min) results in soot with similar a mobility size distribution but lower concentration than that made at the same overall EQR of 1.25 (Figure S1b). The range studied extensively from EQR = 1.25 to 1.59, covers the range of aircraft-relevant sizes at which sufficient mass could be collected for N₂ absorption and TGA.

S2. Thermal gravimetric analysis (TGA)

Figure S2 shows the normalized evolution of spray combustion soot at EQR = 1.59 (solid lines), 1.46 (broken lines), 1.34 (dot-broken lines), 1.29 (dotted lines) and 1.25 (double dot-broken lines) with mass loss under a) N₂ and b) air as a function of time. The mass lost under N₂, \bar{m}_{os} (up to 900 °C), is attributed to organic carbon (OC). Mass lost under air, \bar{m}_s (up to 900 °C), that occurs after N₂ is attributed to elemental carbon (EC). The temperature profile applied (thin solid lines) is shown on the right axis. In each case the temperature begins at 30 °C, then increases at a rate of 20 °C/min up to 900 °C where it remains for 10 minutes before returning to 30 °C at 20 °C/min.



Figure S2: Mass loss profiles a) in N₂ and b) in air of soot made at EQR = 1.59 (solid line), 1.46 (broken line), 1.34 (dot-broken line), 1.29 (dotted line) and 1.25 (double dot-broken line). The mass lost under N₂, \overline{m}_{os} , is attributed to OC. Mass lost under air, \overline{m}_s , that occurs after N₂ is attributed to EC. The resulting OC/TC are shown in Fig. 5. The evolution of temperature, *T*, as a function of time, *t* (thin solid line), is shown on the right-hand axis.

To ensure a sufficient number of primary particles (PPs) were counted to obtain a reliable value of \bar{d}_p , the geometric mean was plotted as a function of number of particles counted. Always, an asymptote was reached by about 200 counted, in agreement with the literature (Kelesidis et al. 2020).

The PPs of soot are polydisperse thus d_p can be represented more accurately as a particle size distribution as is shown in Figure S4 with d_p ranging from 5 to 30 nm. The exemplary TEM images illustrate significant necking between PPs indicative of surface growth. The images also illustrate the polydispersity of the PP sizes.



Figure S3: The evolution of \bar{d}_p as a function of the number of PPs counted for EQR = 1.59 (solid line), 1.46 (broken line), 1.34 (dot-broken line) and 1.29 (dotted line).

Liati et al. (2014; Fig. 3) provided histograms of the soot primary particle (PP) size distribution along with the respective mode $d_p = 20$ and 24 nm measured from aircraft engines at 65 and 100 % thrust, respectively. Similarly, Marhaba et al. (2019; Fig. 2) provide primary particle size distributions at 70, 85 and 100 % thrust with mode $d_p = 13$, 13.8 and 13.7, respectively. To facilitate the comparison of PP size distributions of aircraft soot obtained



EQR = 1.59, b) 1.46, c) 1.34, and d) 1.29. from various studies (Boies et al. 2015; Liati et al. 2014; Marhaba et al. 2019) the \bar{d}_p was obtained by fitting a lognormal distribution to the published raw data. Figure S5a shows the raw microscopy data from Liati et al. (2014; symbols) at 100 (circles) and 65% thrust

(triangles), along with their lognormal fittings used here that result in $\bar{d}_p = 18$ (broken line)

and 17.4 nm (solid line), respectively.



Figure S5: Raw microscopy data (symbols) and lognormal fits (lines) of the primary particle size distribution measured by Liati et al. (2014) from aircraft engines at a) 100 (circles, broken line) and 65 % (triangles, solid line), as well as by Marhaba et al. (2019) at b) at 100 (circles, dot-broken line), 85 (diamonds, dotted line) and 70 % (squares, double dot-broken line).

Similarly, Figure S5b shows the raw microscopy data from Marhaba et al (2019;

symbols) at 100 (circles), 85 (diamonds) and 70 % (squares) thrust along with their lognormal fittings that result in $\bar{d}_p = 13.6$ (broken line), 13.7 (dotted line) and 12.7 nm (double dotbroken line), respectively.



Figure S6: The soot d_p as a function of d_m obtained here by interfacing mass-mobility data from enclosed spray combustion at EQR = 1.59 (circles), 1.46 (triangles), 1.34 (diamonds) and 1.29 (squares) with a power law (Kelesidis et al. 2020) in comparison to that measured for soot from open spray combustion (Kholghy and DeRosa 2021; inverse triangles) as well as to an empirical power law obtained from engine data (Olfert and Rogak 2019; solid line & shaded area).

The mass concentration, M, of soot estimated from an aethalometer depends on the assumed mass absorption cross-section (*MAC*) which depends on particle chemical composition and size (Kelesidis et al. 2021). The *MAC* originally used by Ess and Vasilatou (2019), 7.77 m²/g at 880 nm, does not account for the OC/TC and causes a systematic underestimation of the M for soot with low OC/TC, i.e. aircraft-like soot. Figure S7 shows the M from the enclosed unit studied here (circles) and an open one (Kholghy and DeRosa 2021; squares), along with the corrected miniCAST M (open triangles) and the ones directly from Ess and Vasilatou (2019; filled triangles).



Figure S7: The mass concentration of soot produced by an enclosed (circles) and open (Kholghy and DeRosa 2021; squares) spray combustion unit, as well as a 5201 miniCAST with corrected (Ess and Vasilatou 2019; open triangles) and raw (Ess and Vasilatou 2019; filled triangles) mass concentrations using the manufacturer's default $MAC = 7.77 \text{ m}^2/\text{g}$ at 880 nm as a function of \bar{d}_m .

S5. Molar flow rate of spray combustion unit and miniCAST

The molar flow rate, \dot{m} , can be calculated as:

$$\dot{m} = \dot{v} \cdot \frac{\rho}{MW} \tag{S6}$$

where \dot{v} is the volumetric flow rate, ρ is the density and *MW* is the molecular weight. These values for spray combustion and miniCAST soot are listed in Table S1 assuming a chemical equation of C_{11.6}H₂₂ for Jet A1 (Dagaut and Cathonnet 2006). Based on these, the molar flows are $\dot{m}_{jetfuel} = 0.02$ mol/min and $\dot{m}_{propane} = 0.003$ mol/min.

Table S1: Properties of fuel used for the enclosed spray combustion unit (this work) and a			
miniCAST (Ess and Vasilatou 2019) which use Jet A1 and propane, respectively.			
	ψ̇́ (mL/min)	ho (kg/m ³)	MW (g/mol)
Enclosed unit, Jet A1	4.5	804	161.4
miniCAST, propane	60 - 70	1.882	44.09

S6. Nitrogen adsorption isotherms

Specific surface area (SSA) and pore size distributions are estimated from N_2 adsorption isotherms, shown in Figure S8, by the Micromeritics Tristar II Plus software.



Figure S8: The N_2 adsorption isotherms for soot at EQR = 1.59 (solid line), 1.46 (broken line), 1.34 (dot-broken line) and 1.29 (dotted line).

References

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