## **Supporting information**

## Dynamics of soot surface growth and agglomeration by enclosed spray combustion of jet fuel

by

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The experimental set-up used here, Fig. S1, was almost identical to that used previously [9]. Now, the bottom quartz glass tube was exchanged with a steel tube containing five evenly spaced, sealable holes to allow for soot sampling and temperature measurements with a straight sampling tube [32] and an R-type thermocouple, respectively.



Fig. S1: Schematic of the experimental set up used by [9] and modified here to allow for soot sampling and *T* measurements at HAB = 5, 10, 15, 20, 25 and 63 cm.

The diameter of the spray droplets,  $d_d$ , was measured using Fraunhofer laser diffraction spectrometry (SympaTec Heleos) in the absence of combustion, 6 cm above the nozzle (Figure S2) as a function of EQR at 1.88 (diamonds), 1.73 (squares), 1.59 (circles) and 1.46 (triangles). For safety reasons, ethanol was used instead of jet A1 for the majority of the spray measurements. However, ethanol droplets (open symbols) give nearly identical droplet size distributions to jet A1 fuel (filled circles). Here, the fuel flow rate is kept constant while the O<sub>2</sub> dispersion is increased to produced lower EQR. The range of conditions studied here produce large variations in the median droplet diameter,  $\bar{d}_d$ , from  $330 \pm 2 \mu m$  at EQR = 1.88 down to  $36 \pm 0.5 \mu m$  at EQR = 1.46. The droplet diameter changes only slightly at low EQR ( $50 \pm 1 \mu m$  at EQR = 1.59) then increases exponentially from EQR = 1.73 and higher. The correlation between the dispersion gas flow rate and the  $\bar{d}_d$  has been shown for similar spray reactors with ethanol [23] and water [S1].



Figure S2: The droplet size distributions of ethanol sprays at EQR = 1.88 (diamonds), 1.73 (squares), 1.59 (open circles), 1.46 (triangles) and a jet fuel spray at EQR = 1.59 (filled circles).

When the flame is ignited, droplets likely do not reach the room temperature sizes. The temperatures in the flame reach up to 1600 K (Fig. 1), well above the autoignition temperature, 483 K, of jet A1. Droplets of a jet A1 surrogate with  $d_d = 15 \mu m$  undergoing combustion evaporated within less than 1 ms, much shorter than the 12 ms residence time at HAB = 5 cm shown in Fig. S8. Below the autoignition temperature, the evaporation rate of a droplet can be estimated with the procedure from Hinds [49]. Briefly, modeling jet A1 as n-decane [27] which has a molecular weight,  $MW_{C10H22} = 142$  g/mol and chemical formula  $C_{10}H_{22}$ , the atomic diffusion volume,  $v_{C10H22}$ , can be estimated as 209 [S2]. The vapor pressure,  $P_{vap}$  of n-decane at T = 448 K can be estimated from the Antoine equation with coefficients valid from 368 K to 448 K [S2]:

$$log_{10}(P_{vap}) = 4.07857 - \frac{1501.268}{T - 78.67}$$
(S1)

Then, the diffusion coefficient, D, can be calculated as [S2]:

$$D = \frac{10^{-3} \cdot T^{1.75} \left(\frac{1}{MW_{C_{10}H_{22}}} + \frac{1}{MW_{air}}\right)^{1/2}}{P\left[\left(v_{C_{10}H_{22}}\right)^{1/3} + \left(v_{air}\right)^{1/3}\right]^2}$$
(S2)

where *P* is the pressure in atm, and the  $MW_{air}$  and  $v_{air}$  are 29 g/mol and 20.1 [S2], respectively. Finally, the droplet lifetime can be calculated as [49]:

$$t = \frac{\rho d_d^2}{8DMW_{C_{10}H_{22}}\left(\frac{P_{vap}}{T}\right)}$$
(S3)

where  $\rho$  is the density which at 448 K is 606 kg/m<sup>3</sup> [S3]. This results in a droplet lifetime of 17 ms assuming the median  $d_d = 36 \mu m$  at EQR = 1.46. While this is slightly longer than the time needed to reach HAB = 5 cm, at the true flame temperatures the droplet lifetime will be much shorter.

Fig. S3 shows the mobility size distributions of soot at HAB = 63cm with (squares) and without (circles) a thermocouple inserted at HAB = 10 cm. While the mobility and primary particle size distributions in the main text were measured in the absence of a thermocouple, this indicates that the thermocouple does not affect the fuel evaporation and subsequent soot aerosol dynamics.



Fig. S3: Mobility size distributions of soot produced at EQR = 1.59 and sampled at HAB = 63 cm with (squares) and without (circles) inserting a thermocouple at HAB = 10 cm. The shade shows the reproducibility of the measurements [9].

Fig. S4 shows the temperature profile from a premixed ethylene flame with EQR = 2.5 [26] (broken line). The flame was reproduced using a McKenna burner [39] and the gas compositions and flow rates given in [31]. The temperature profile measured here using a thermocouple (symbols) is in excellent agreement with that obtained in literature [31] (broken line). The flame *T* was obtained from the measured thermocouple temperature,  $T_t$ , corrected for radiative losses based on the following energy balance [26]:

$$h(T - T_t) = \varepsilon_t (T_t^4 - T_w^4) \tag{S4}$$

where *h* is the convective heat transfer coefficient,  $\varepsilon_t$  is the emissivity of the thermocouple and  $T_w$  is the temperature of the tube walls. The same  $\varepsilon_t$  is used for *T* measurements in both premixed and spray flames as the same thermocouple was used in all conditions. The flame heat transfer coefficient, *h*, is given by [S4]:

$$h = \frac{Nu \cdot k}{d_h} \tag{S5}$$

where Nu is the Nusselt number, k is the thermal conductivity of the gas mixture and  $d_h = 42$  mm is the diameter of the enclosure [9]. The k of the gas mixture is derived iteratively using MATLAB based on an initial  $T = T_{bead} + 50$  K, the k at that temperature [S3] and assuming a mixture of CO<sub>2</sub>, H<sub>2</sub>O and N<sub>2</sub> calculated based on the chemical mass balance after combustion of ethylene and jet A1 fuels in the premixed and spray flame, respectively. Details of this calculation are described in the SI of [9] for the spray flame. A Nu = 2 is used for the premixed flame, as is commonly done [26]. For the turbulent spray flame, Nu is obtained from [S5]:

$$Nu = 0.431 Re^{0.5}$$
(S6)

where the spray flame *Re* is [S4]:

$$Re = \frac{\rho v d_h}{\mu} \tag{S7}$$

with  $\rho$ , v and  $\mu$  as the fluid density, velocity and dynamic viscosity, respectively. The  $\rho$  and  $\mu$  are derived iteratively similarly to k based on the assumed mixture of CO<sub>2</sub>, H<sub>2</sub>O and N<sub>2</sub>. The velocity at the exit of the spray flame nozzle,  $v_i$ , is approximately equal to the speed of sound, 343 m/s, as the pressure drop across the nozzle is maintained slightly above the critical pressure ratio for a sonic flow [23]. As HAB increases, v is estimated by [S6]:

$$v = v_i \sqrt{\frac{1}{HAB}}$$
(S8)

Using Eqs. 2 - 4, Nu = 60 - 67 is obtained at HAB = 5 - 63 cm and EQR = 1.46 - 1.88 of the spray flame. Equation (S4) has been used for *T* measurements in premixed [31] and spray [23] flames. This validates the present temperature measurements, as well as the radiative loss correction used here [31].



Fig. S4: Temperature data from a premixed ethylene flame [31] (broken line) compared to the same flame recreated with the experimental set up used in this work (symbols).

To ensure a sufficient number of primary particles (PPs) were counted to obtain a reliable value of  $\bar{d}_p$ , the median was plotted as a function of number of particles counted, Fig. S5. Always, an asymptote was reached by about 200 counted, in agreement with literature [39].



Fig. S5: The evolution of  $\bar{d}_p$  as a function of the number of PPs counted for HAB = 63 cm and EQR = 1.88 (dotted line), 1.73 (broken line), 1.59 (solid line) and 1.46 (dot-broken line).

Fig. S6 shows the volume fraction,  $f_v$ , of soot at EQR = 1.46 (triangles) and 1.59 (circles) as a function of HAB. The  $f_v$  was calculated based on mass mobility measurements reported in [9] and number concentrations measured by SMPS.



Fig. S6: The  $f_v$  as a function of HAB at EQR = 1.46 (triangles) and 1.59 (circles). The error bars represent the standard deviation between at least 10 scans of the SMPS.

Fig. S7 shows *T* as a function of Knudsen number, *Kn*, measured during enclosed spray combustion of jet fuel at EQR = 1.46 (symbols) and used as an input in DEM (line). The soot *Kn* was estimated from the measured *T* (Fig. S4) and  $\bar{d}_m$  (Fig. 2) at various HAB. As *T* drops with increasing HAB, *Kn* decreases from 80 to 4. The *T* used in DEM is varied as a function of *Kn* (line) to follow closely the *T* measurements of enclosed jet fuel spray combustion.



Fig. S7: Temperature, T, as a function of Knudsen number, Kn, measured during enclosed spray combustion of jet fuel at EQR = 1.46 (symbols) and used as an input in DEM (line).

Fig. S8 shows the evolution of *t* as a function of HAB at EQR = 1.59 (circles) and 1.46 (triangles) derived by DEM. At EQR = 1.46, *t* increases from about 12 ms at HAB = 5 cm up to about 400 ms at HAB = 63 cm. Increasing EQR to 1.59 enhances *t* by a factor of 3 on average. This can be attributed to the 25 % smaller dispersion  $O_2$  flowrate used at EQR = 1.59 compared to that at EQR = 1.46. This reduces also the maximum flame *T* by about 60 K (Fig. 1). The *t* enhancement obtained here is consistent with measurements in premixed flames [59]. There, *t* was enhanced by a factor of 2.5 by reducing the gas velocity by 21 %.



Fig. S8: Evolution of *t* as a function of HAB at EQR 1.59 (circles) and 1.46 (triangles).

Fig. S9 shows all of the experimental (symbols) and DEM derived (lines) mobility size distributions at EQR = 1.59 and 1.46 and at HAB = 5, 10, 15, 20, 25 and 63 cm.



Fig. S9: Experimental (symbols) and DEM-derived (lines) mobility size distributions at EQR = 1.59 (b, d, f, h, j) and 1.46 (a, c, e, g, i, k) at HAB = 5 - 63 cm.

Soot is composed of polydisperse PPs which are better represented by histograms. Their size distributions from TEM imaging are shown in Fig. S10 for EQR = 1.46, 1.59, 1.73 and 1.88 at HAB = 5, 10, 15, 20, 25 and 63 cm.



Fig. S10: Histograms of the PP diameters measured by TEM at HAB = 63 cm and EQR = 1.88 (a), 1.73 (b), 1.59 (c) and 1.46 (d). Inside the flame, PP size distributions are shown at HAB = 25 (e, f), 20 (g, h), 15 (i, j), 10 (k, l) and 5 cm (a, b) at EQR = 1.59 (e, g, i, k, m) and 1.46 (f, h, j, l, n).

The full Raman spectra of soot made at EQR of a) 1.59 and b) 1.46 are shown in Fig. S11 at HAB = 5, 10, 15, 20, 25 and 63 cm.



Fig. S11: Raman spectra of soot at EQR = 1.59 (a) and 1.46 (b) at HAB = 5, 10, 15, 20, 25 and 63 cm.

The organic carbon (OC) to total carbon (TC) ratios of soot produced at each EQR are shown in Fig. S12 using thermal gravimetric analysis (TGA) following the method of [S7] with more detail given elsewhere [9]. The OC/TC ratio decreases from EQR = 1.88 to 1.59 then begins to increase more quickly from 1.59 to 1.46. At even lower EQR, the OC/TC ratio further increases when measured with TGA [9].



Fig. S12: Organic carbon to total carbon (OC/TC) ratios at EQR = 1.46, 1.59, 1.66, 1.73, 1.88.

In order to further probe the graphitization of soot, high resolution TEM (HRTEM) was used to image the graphene layers making up the primary particles as shown in Fig. S13.



Fig. S13: Exemplary HRTEM images of soot produced (from left to right) at EQR = 1.46, 1.59, 1.73 and 1.88 along with the respective median dp and mean D/G ratio.

## References

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