The evolution of species concentrations in turbulent premixed flames crossing the soot inception limit

H. Shariatmadar^a, F. Hampf^{a,b}, R. P. Lindstedt^{a,*}

^a*Department of Mechanical Engineering, Imperial College, London, SW7 2AZ, UK*

^b*German Aerospace Center (DLR), Stuttgart 70569, Germany*

Abstract

The current study quantifies the impact of equivalence ratio and rate of strain on the spatial distribution of major species and soot precursors in premixed turbulent ethylene flames crossing the soot inception limit. A back-to-burnt (BTB) opposed jet configuration is used to provide accurate control of the turbulent and chemical timescales. The upper nozzle features fractal grid generated turbulence and premixed ethylene/air mixtures with flames stabilised against well-defined hot combustion products emerging from the lower nozzle. The study combines simultaneous PAH/CH₂O-PLIF and elastic light scattering (ELS) with probe sampling. Gas chromatography-mass spectrometry (GC-MS) and gas chromatography-thermal conductivity detection (GC-TCD) were used to quantify concentrations of major species and poly-aromatic hydrocarbons (PAHs). The laser based diagnostics show that the rate of strain exerts a dominant impact on the growth of soot particles with low turbulent Reynolds numbers ($50 \leq Re_t \leq 94$) used to promote soot formation. The probe measurements indicate that acetylene, 1-methylnaphthalene (1-MN), $m/z = 154$, $m/z = 276$ and benzo(a)pyrene correlate with soot formation and that the equivalence ratio is the controlling PAH growth parameter. It is further shown that the spatial extent of the PAH containing reaction zone exceeds three integral length scales.

Keywords: Soot formation, Turbulent flames, Laser diagnostics, Poly-aromatic hydrocarbons, Probe sampling

Supplemental material: (i) Uncertainty analyses (ii) Mass spectra (iii) Laminar flame data (iv) Tables with species concentrations

*Corresponding author. Tel: +44 20 7594 7039

1. Introduction

Particulates generated from practical combustors feature complex chemical compositions that include polycyclic aromatic hydrocarbons (PAHs) [1–3]. Such emissions present health hazards [4, 5] and are subject to restrictions in aircraft and automotive industries [6–8]. For instance, particles from diesel exhaust include significant quantities of the Group 1 carcinogen benzo(a)pyrene (B(a)P) [9]. Such species are capable of efficiently bonding to, and be transported with, atmospheric particles [10]. The control of soot emissions from practical devices requires an understanding of the controlling parameters leading to their formation in turbulent flows [11].

Using laminar diffusion flames, Mercier et al. [12] concluded that soot nucleation coincided with the location of PAH dimers. However, the study [12] featured laser-induced incandescence (LII) at a wavelength of 1064 nm, suitable for measuring mature rather than incipient soot particles, and, accordingly, the study does not provide clear evidence of a contribution of non-covalently bound PAH dimers to soot inception in flames. Johansson et al. [13, 14] showed that larger species can grow ahead of lighter ones and that PAH radical combination reactions provide fast routes for mass growth. Liu et al. [15] attribute the dominant reaction product to PAHs with 5-membered rings and such structures were directly observed by Schulz et al. [16] and Commodo et al. [17] using high-resolution atomic force microscopy (AFM) in a premixed C₂H₄–air flame. Liu et al. [18] showed the importance of coalescence of moderate-sized (planar) PAHs into cross-linked three-dimensional structures as a probable pathway to soot nucleation. The studies by Liu et al. [15, 18], Schulz et al. [16] and Commodo et al. [17] pro-

26 vide results that are consistent with Johansson et al. [13, 14], supporting the
 27 role of resonance-stabilized radicals, predominantly formed from 5-membered
 28 ring structures, in the growth of covalently bound cross-linked adducts and
 29 soot inception. Tielens et al. [19] and Mao et al. [20] concluded that weak
 30 intermolecular interactions and van der Waals forces are responsible for bond
 31 formation arising from the majority of binary collisions between PAH radi-
 32 cals. However, experimental investigations can lead to a contrary conclusion
 33 for different flame conditions [21, 22]. Furthermore, numerous theoretical
 34 studies suggest that closed-shell PAH dimers have very short lifetimes under
 35 flame conditions except for species much larger than normally observed in
 36 flames [23–28]. Mass growth can result from direct PAH adsorption¹ onto
 37 the soot surface [30–32]. In addition, Dworkin et al. [33] concluded that the
 38 predominant surface growth mechanism depends on combustion conditions.
 39 Lindstedt and Waldheim [34] used a sectional model to show that it is nec-
 40 essary to account for the collision efficiency change when moving from PAHs
 41 to the van der Waals enhanced limit associated with particulates.

42 The complex interactions of gas-phase and soot chemistry with turbu-
 43 lence is of particular concern given the comparatively long chemical timescales
 44 associated with soot formation and must be addressed using turbulent flame
 45 studies [35, 36]. Examples include the KAUST [36] and Adelaide [37, 38] jet
 46 diffusion flames. In the KAUST flames, soot particles size distributions were
 47 measured using a probe technique, while the Adelaide group applied laser
 48 diagnostics, including laser induced incandescence (LII), to measure soot vol-

¹The term adsorption is preferred to condensation in light of the terminology review
 by Michelsen et al. [29]

ume fractions. The latter study showed that the rate of strain and the flame volume exert a dominant influence. Extensive optical diagnostics have been used to study premixed turbulent sooting flames in the DLR swirl burner with flow velocities, soot volume fractions, PAH locations, temperatures and OH radical concentrations determined in a series of studies e.g. [39, 40]. The studies show that the spatial distributions of soot, PAH and OH are strongly dependent on the properties of the flow field.

Mueller and Pitsch [41] used large eddy simulation (LES) to study turbulence – chemistry interactions and found that small-scale interactions between turbulence, gas phase chemistry, and soot have a significant impact. Yoo and Im [42] performed a computational study of a non-premixed flame and showed that increased soot volume fractions in turbulent flames, as compared to steady laminar flames, may result from the rapid transport of soot particles out of high temperature regions rather than enhanced chemistry. Tian et al. [43] used a fully coupled transported PDF approach featuring a 78-dimensional joint-scalar space, including enthalpy, gas phase species and 62 soot sections to show that soot may be transported to fuel lean mixtures and highlighted a correlation with local extinction events.

The complexities of soot formation in turbulent flames suggests that the use of a flexible compact burner configuration with well-defined boundary conditions and precise control of flow characteristics is of significant advantage. Accordingly, a back-to-burnt opposed jet configuration [44, 45] is used to study the impact of changes in stoichiometry and rates of strain on the formation of soot in premixed turbulent ethylene–air flames crossing the soot inception limit [3]. Simultaneous elastic light scattering (ELS) and planar laser

induced fluorescence ($\text{CH}_2\text{O}/\text{PAH}$ -PLIF) is used to complement probe mea-
 surements, featuring GC-MS and GC-TCD, to provide quantitative data on
 the evolution of species concentrations in turbulent premixed flames crossing
 the soot inception limit. The parametric variations include, principally, (i)
 the stoichiometry of the upper nozzle reactant mixture ($1.8 \leq \phi_{UN} \leq 2.2$) and
 (ii) the total rate of strain ($255 \leq a_T [\text{s}^{-1}] \leq 610$). (iii) The impact of the tem-
 perature of the opposing hot combustion products ($1400 \leq T_{HCP} [\text{K}] \leq 1700$)
 on the normalised PAH and ELS signals is also investigated.

2. Experimental setup

2.1. Burner configuration and experimental conditions

An opposed jet configuration is used to advance the fundamental un-
 derstanding of particle inception, formation and oxidation in turbulent pre-
 mixed ethylene/air flames. The burner configuration facilitates the precise
 adjustment of the chemical and turbulent timescales [44, 45]. Premixed ethy-
 lene/air mixtures emerging from the upper nozzle (UN) are stabilised against
 the lower nozzle (LN) hot combustion products [46] with the distance be-
 tween the nozzles set to one diameter [47]. The UN is equipped with a
 cross fractal grid, located 50 mm upstream of the nozzle exit, that provides
 well developed multi-scale turbulence [48]. The LN provides hot combustion
 products (HCP) originating from stoichiometric H_2 flames diluted with N_2
 and stabilised on a perforated plate (PP) located 100 mm upstream of the
 LN exit [3]. The lower nozzle exit temperature (T_{HCP}) is measured using a
 50 μm R-type thermocouple [49]. Nitrogen, emerging from the concentric
 shrouds of UN and LN nozzles, is used to shield the flames. The experimental

conditions are summarised in Table 1. The reference condition (REF) is defined as a C₂H₄ flame with equivalence ratio of $\phi_{UN} = 2.0$ and a bulk rate of strain ($a_b = 2U/H$) of 120 s⁻¹ that is stabilised against a lower nozzle stream with a HCP temperature of 1500 K. The total rate of strain ($a_T = a_b + a_t$) was estimated using the approach of Kostiuk et al. [50] with $a_t = (\varepsilon_r/\nu_r)^{1/2}$, where ε_r is the rate of dissipation in the reactants, determined using the method of George and Hussein [51] as applied by Goh et al. [48], and ν_r the corresponding fluid viscosity.

Table 1: Experimental conditions used to study the impact of equivalence ratio, rate of strain and burnt gas temperature. The UN and LN fuels are C₂H₄ and H₂, respectively, and $\phi_{LN} = 1.0$ with $\alpha = X_{H_2}/X_{N_2}$, where X indicates a mole fraction, used to control T_{HCP} , U is the upper nozzle bulk velocity and u' the velocity fluctuations. The reactant temperatures are $T_r = 320$ K, $L_I = 3.9 \pm 0.2$ mm is the integral length scale of turbulence, $Re_t = u'L_I/\nu$ the turbulent Reynolds number and a_t is the turbulent, $a_b = 2U/H$ the bulk and $a_T = a_t + a_b$ the total rates of strain [50]. Values shown in brackets feature only CH₂O/PAH-PLIF and ELS measurements.

Variation	Reactants	HCP	Rate of Strain
ϕ_{UN} [-]	(1.7), 1.8, 2.0, 2.2	2.0	2.0
a_b [s ⁻¹]	120	120	80, (105), 120, (135), 160
a_t [s ⁻¹]	300	300	175, (253), 300, (357), 450
a_T [s ⁻¹]	420	420	255, (358), 420, (492), 610
Re_t [-]	72	72	50, (64), 72, (81), 94
U [m s ⁻¹]	1.8	1.8	1.2, (1.6), 1.8, (2.0), 2.4
u' [m s ⁻¹]	0.30	0.30	0.21, (0.26), 0.30, (0.33), 0.39
T_{HCP} [K]	1500	1400, 1500, 1600, 1700	1500
α [-]	0.51	0.43, 0.51, 0.64, 0.75	0.51

Figure 1 shows photographs illustrating the experimental conditions used to study the transition from lightly to heavily sooting flames at different rates of strain and equivalence ratios. The flame conditions, listed in Table 1, were selected to cover a range of scales affecting the formation of soot and soot precursors. The flame with a stoichiometry of $\phi_{UN} = 1.7$ and $a_T = 420$ s⁻¹

Figure 1: Sample photographs illustrating the experimental conditions used in the current study. Top row: ϕ_{UN} variation at a constant total rate of strain of $a_T = 420 \text{ s}^{-1}$ at (a) $\phi_{UN} = 1.7$, (b) $\phi_{UN} = 1.8$ and (c) $\phi_{UN} = 2.2$; Bottom row: a variation of the rate of strain at a constant $\phi_{UN} = 2.0$ at (d) $a_T = 610 \text{ s}^{-1}$, (e) $a_T = 420 \text{ s}^{-1}$ (Reference flame) and (f) $a_T = 255 \text{ s}^{-1}$.

111 is the lightest sooting condition shown and features strongly intermittent
 112 appearance of soot. The soot layer thickness increases significantly with a
 113 decreasing rate of strain and increasing equivalence ratio with the flames
 114 becoming bright yellow/orange at $\phi_{UN} = 2.2$ and $a_T = 255 \text{ s}^{-1}$. Hampp
 115 and Lindstedt [52] have shown that the impact of the HCP temperature is
 116 comparatively modest for fuel-lean self-sustained flames that detach from the
 117 stagnation plane. The influence on soot formation is investigated below.

118 2.2. Optical diagnostics setup

119 The laser diagnostic setup has been presented in prior studies [3, 53]
 120 and is schematically depicted in Fig. 2. The measurements feature simul-

121 taneous $\text{CH}_2\text{O}/\text{PAH}$ -PLIF and elastic light scattering (ELS). A frequency
 122 tripled (355 nm) Spectra-Physics Quanta-Ray Lab-150 Nd:YAG laser is used
 123 for $\text{CH}_2\text{O}/\text{PAH}$ -PLIF and a frequency doubled (532 nm) Litron Nano LG
 124 175-10 Nd:YAG laser for the ELS measurements. The laser pulse energy is
 125 approximately 150 mJ at 355 nm and 30 mJ at 532 nm. The two spatially
 126 overlapped light sheets, with a height of 18 and 27 mm and thickness of 100
 127 μm (determined using burn marks), are located symmetrically around the
 128 theoretical stagnation plane. The top and bottom of the laser light sheets
 129 are clipped to minimise the spatial energy distribution across the sheet height.
 130 Excitation at 355 nm offers simultaneous detection of CH_2O and PAH via
 131 LIF. The former can be used to identify the preheat zone and thus reaction
 132 onset. At the present turbulence conditions, the CH_2O layer is continuous
 133 and upstream of any PAH appearance. Consequently, the CH_2O layer can
 134 be spatially segregated from the PAH signal by means of a computer vision
 135 based image segregation technique [46, 53]. It is worth pointing out that the
 136 segregated CH_2O data is only used to indicate the flame front in the current
 137 study. On the other hand, excitation via the 3rd harmonic (at 355 nm) only
 138 facilitates probing of PAHs with three or more rings thus omitting prevalent
 139 smaller aromatics such as naphthalene. The latter can be included by using
 140 an excitation wavelength of 266 nm as shown by Geigle et al. [39, 40]. Bejaoui
 141 et al. [54] measured PAH concentrations in laminar flames using excitation
 142 at 266 and 355 nm. A 50 nm shift towards 450 nm, compared to 500 nm,
 143 was noted with the latter excitation wavelength and attributed to different
 144 efficiencies. However, only modest differences in the resulting spatial distri-
 145 butions were shown, with both wavelengths indicating a rather homogeneous

146 PAH pool under premixed conditions. The current probe measurements in
 147 Section 4.3 further supports this. Nonetheless, it is worth mentioning that
 148 the LIF measured PAH pool may be shifted towards the soot region [55, 56].
 149 However, excitation at 355 nm is adequate for the present purpose of delin-
 150 eating qualitative differences in the spatial PAH distribution. The relative
 151 high laser fluence at 355 nm suggests that incandescence is induced from the
 152 soot particles and superimposed onto the PAH - LIF signal [57]. For abso-
 153 lute soot volume fraction measurements it is preferable to use wavelengths
 154 ≥ 670 nm due to possible contamination by PAH signals [58]. However, in
 155 the present work only relative soot concentrations are measured and the data
 156 obtained by Simonsson et al. [58] at 532 nm showed the correct qualitative
 157 trend with comparatively modest absolute errors. In order to eliminate elas-
 158 tic scattering in the LIF detection systems, ELS is recorded 200 ns prior to
 159 LIF. Dichroic filters are used to spatially and spectrally segregate the signals.
 160 The ELS camera (LaVision LX 8M) is equipped with a 180 mm f/2.8 Sigma
 161 lens and a narrow bandpass filter (3 nm) centred at 532 nm. A LaVision
 162 intensifier relay optic unit and imager intense camera are used to record the
 163 PAH-PLIF. The latter is equipped with a 85 mm (f/1.2) lens and a 400 nm
 164 long-pass filter (Edmund Optics #84-754). An intensifier gate time of 70 ns
 165 and a low gain level of 60% minimises flame luminescence and noise. The
 166 detection systems are calibrated and their coordinate systems superimposed
 167 using a multi-frequency target (Thorlabs #R3L3S4P1). The spatial resolu-
 168 tion of the detection system is determined to approximately 100 μm using a
 169 NBS 1963A target. However, spatial filtering and superposition of the images
 170 degrade the effective spatial resolution to 250 μm [53].

Figure 2: Laser diagnostics schematic: 1) Quanta-Ray laser; 2) Nano PIV; 3) Camera; 4) Beam dump; UN – Upper Nozzle; LN – Lower Nozzle.

171 2.3. Sampling Probe

172 The sampling system has been outlined by Shariatmadar et al. [3] and
 173 features a quartz probe (manufactured by Hilgenberg GmbH) and dual ni-
 174 trogen dilution ports. In order to minimise flame disturbances, a tip orifice
 175 diameter of $286 \mu\text{m}$ and an opening angle of 20 degrees were used [59, 60].
 176 Two large vacuum chambers with a combined volume of 36.8 litres are used
 177 to eliminate any pressure fluctuations or gradual shifts in the sampling pres-
 178 sure. A vacuum regulator is used to set a pressure differential of 20 mbar
 179 between the sampling line and the flame. This results in a constant sample
 180 flow rate of $3.125 \times 10^{-6} \text{ kg/s}$. The transfer line is equipped with a pressure
 181 transducer (UNIK 5000; GE Measurement and Control) and frequent leak
 182 tests were performed to preclude sample contamination. A sampling time of
 183 about 10,000 integral time-scales of turbulence is used (120 s) to ensure sta-

184 tistical independence and collection is terminated by disconnecting the probe
 185 from the vacuum system. The sampling line assembly can be traversed in all
 186 directions using linear translation stages and the location is calibrated using
 187 the optical setup. The ELS camera determines the X and Y position (i.e.
 188 $X/L_I = 0.5$, $Y/L_I = 0$) and the laser light sheet determines the alignment
 189 of the probe tip with the theoretical stagnation point streamline ($Z/L_I = 0$).
 190 The origin (0, 0, 0) is the theoretical stagnation point. The positioning of
 191 the sampling system (i.e. probe tip) on laboratory jacks and sliders enables
 192 a fine adjustment within an accuracy of ~ 0.1 mm. The sampling process is
 193 discussed further below.

194 *2.3.1. Probe effects*

195 To determine the quantitative impact of probe effects is challenging as
 196 the combined influence of the probe configuration and sampling conditions
 197 (i.e. the applied suction pressure ΔP) need to be taken into account in the
 198 evaluation of flame perturbations [61]. Shariatmadar et al. [3] performed
 199 an uncertainty analysis to quantify probe effects for the current sampling
 200 system with PAH—PLIF and ELS used to determine the flow perturbations
 201 at different suction pressures. The analysis shows that the mean PAH and
 202 ELS profile peak and location are not affected by the presence of the probe
 203 at suction pressures of 20 mbar as used here. At higher suction pressures,
 204 measurements progressively deviate from the undisturbed profiles.

205 *2.3.2. Probe clogging*

206 Clogging at the probe tip is a potential source of errors. The static pres-
 207 sure of the sampling line (pressure transducer) is recorded regularly for each

208 data set. In a case of a pressure fluctuation or sudden pressure change in the
 209 sampling line, the experiment is stopped to check for any signs of probe clog-
 210 ging. Wang and co-workers [62], and Roberts and co-workers [36] used a fine
 211 needle/wire to resolve orifice clogging issues between experiments. Camacho
 212 et al. [62] reduced the sampling time (50 s) to avoid clogging at the probe
 213 tip. The sampling time was chosen to provide a compromise between size
 214 distribution smearing at short times and orifice clogging at long scan times.
 215 In the current study, a different approach was used to avoid experimental
 216 errors and potential probe cracking. The probe was disconnected from the
 217 vacuum suction and a reverse nitrogen flow used to direct soot particulates to
 218 the outside of the probe tip. The sampling line assembly was then traversed
 219 in the X-direction towards the burnt gas state using the linear translation
 220 stage. This leads to the combustion of particles at the probe tip and any
 221 particles remaining in the sampling line were pushed out with the assistance
 222 of the nitrogen flow.

223 **3. Data analysis**

224 *3.1. Optical diagnostic*

225 Laser diagnostic images are shown in Fig. 3 for lightly and heavily sooting
 226 flames. The introduced image labelling is based on defined terminologies [3]
 227 with primary particles and aggregates referred to by the term "soot" as
 228 presented in the ELS and PAH-PLIF images. Due to the high laser fluence
 229 at 355 nm, soot incandescence is likely to contribute to the LIF images [57].
 230 A direct comparison of the PAH and ELS image pairs further supports this.
 231 The flame with an equivalence ratio of $\phi_{UN} = 1.7$ corresponds to a lightly

Figure 3: Laser diagnostic images obtained for $\text{CH}_2\text{O}/\text{PAH}$ -PLIF (top) and ELS (bottom). The relatively high laser fluence at 355 nm suggests that soot particle incandescence contributes to the PAH - LIF signal [57]. Thus, this data is likely to include contributions from PAHs infused on soot particles as well as gaseous species. 1st column : $\phi_{UN} = 1.7$, $a_T = 420 \text{ s}^{-1}$ and $T_{HCP} = 1500 \text{ K}$; 2nd column : $\phi_{UN} = 2.0$, $a_T = 420 \text{ s}^{-1}$ and $T_{HCP} = 1500 \text{ K}$; 3rd column : $\phi_{UN} = 2.0$, $a_T = 492 \text{ s}^{-1}$ and $T_{HCP} = 1500 \text{ K}$; 4th column : $\phi_{UN} = 2.0$, $a_T = 420 \text{ s}^{-1}$ and $T_{HCP} = 1700 \text{ K}$. Dark red indicates a high signal count and blue a low signal count in a.u.

sooting condition with a sporadic appearance of soot layers. By contrast, the REF flame ($\phi_{UN} = 2.0$) represents a flame with relatively thick soot layers. Soot nucleation, mass growth and PAH adsorption are enhanced considerably in the low-temperature region in the proximity of the stagnation plane ($X/L_I = 0.5$) of the richer flame [63]. A comparatively higher intensity, shown in PAH-PLIF and ELS images, reinforces the evolution of the balance between formation and consumption over the reaction zone layer.

239 3.2. Sampling process

240 3.2.1. Major gaseous species

241 The sampling process for gaseous species, schematically depicted in Fig. 4,
242 is performed without using nitrogen dilution [64, 65]. Tedlar bags are placed
243 in the vacuum chamber to collect gaseous species [66] and a gas-tight syringe
244 (purchased from ESSLAB) is used to inject the sample into the GC-TCD [67].
245 Measurements of gaseous species can be affected if the sample contains ex-
246 cess water vapour [68] and a filter unit consistent of quartz wool and sodium
247 sulphate is used to remove water [69]. To avoid trapping of gas residues and
248 eliminate cross-sample contamination, the sampling system is flushed at the
249 end of each sampling process with nitrogen (5 L/min) for 120 s. The flushing
250 gas is injected in a 1:1 split ratio into the sampling system using two dilution
251 ports, i.e. at the probe tip and along the sampling line.

252 The chemical analysis is performed using a gas chromatograph (Agilent
253 7890A) equipped with a thermal conductivity detector (TCD). A HP-PLOT
254 Q and a HP-Moleseieve column (helium carrier gas) are used to quantify the
255 concentrations of selected C₁–C₄ hydrocarbons along with CO, CO₂, N₂
256 and O₂. The GC-TCD was calibrated regularly with Scotty gas mixtures
257 (purchased from Agilent Technologies LTD) containing these species [70].
258 The accuracy of the GC/TCD analysis and the reproducibility of the data
259 was evaluated by repeating the sampling at constant flame and measurement
260 positions. A standardised operational procedure was used to improve the re-
261 producibility with each measurement point repeated at least five times. It
262 was found that the repeatability was significantly enhanced by removing wa-
263 ter vapour from gaseous sample and by repeating routine calibration steps

Figure 4: Sampling collection system used to measure gaseous species over $-2.5 \leq X/L_I \leq +2.5$. 1) Pressure transducer; 2) Quartz wool; 3) Sodium sulphate; 4) Vacuum chamber; 5) Tedlar bag; 6) Vacuum regulator; 7) Vacuum volume; 8) Vacuum pump.

before the sample injection. The maximum cumulative error in the measured concentrations (based on the standard deviation) is estimated at $\pm 2.1\%$ for major gaseous samples.

3.2.2. PAH species

The details of the PAH sampling and extraction process including a comprehensive uncertainty analyses were discussed by Shariatmadar et al. [3]. The sampling system, shown in Fig. 5, features dual-port dilution with preheated N_2 at 523 K and PID controlled heated walls to minimise thermal gradients between the sample and probe walls, and therefore reduce PAH losses e.g. [71]. A temperature of 523 K was found optimal to minimise soot agglomeration as well as thermophoretic, adsorption and condensation losses within the system [72–74]. The probe-tip dilution ratio corresponds to the limit of minimum species losses during the collection process [3]. The sampling process suggests that transmission losses are relatively small using the respective optimum dilution ratio for each experimental condition as presented in the Supplemental Material.

The experimental repeatability, also presented in the Supplemental Material, is evaluated based on the standardised operational procedure that comprises

282 analyses of the individual repeatability of sample collection, extraction and
 283 preparation. Figure 6(a) shows the evaluation of filter units assessed in pre-
 284 liminary studies. Filter unit-1 includes a quartz fiber filter ahead of quartz
 285 wool and a XAD adsorbent resin (Sigma Aldrich). Filter unit-2 consists a
 286 series of quartz wool and XAD resin. Direct analysis of the species con-
 287 centration recorded with the quartz fibre filter in place leads to incorrect
 288 conclusions as it eliminates a significant fraction of the total signal measured
 289 using the mass spectrometer. For example, direct analysis of the species con-
 290 centration shows a loss of 17% of the benzo(a)pyrene after a 120 h sonication
 291 time. The losses can stem either from a loss of particles or PAHs in the quartz
 292 fibre filter. The effect of centrifuging samples [75] is illustrated in Fig. 6(b)
 293 by B(a)P concentrations obtained at different experimental conditions. The
 294 composition of soot particles includes aromatic structures featuring stacked
 295 PAHs bound via (weak) van der Waals forces [76]. Resonance-stabilised rad-
 296 icals can deposit/infuse on soot particles either during sample collection or in
 297 the flame [14]. The infusion of PAHs onto particles is significantly increased
 298 at more highly sooting conditions as illustrated in Fig. 6(b) by the increase
 299 of B(a)P when reducing $a_T = 420 \text{ s}^{-1}$ to $a_T = 255 \text{ s}^{-1}$.

300 External and internal standard (reference) solutions are used to calibrate
 301 non-unit ion counts [77]. The former includes 17 different PAH compounds
 302 (Accustandard [DRH-006S]) and 29 refinery gas aromatics (Accustandard
 303 [M-GRA-CAL-R/IS-R-01]). The latter contains deuterated PAH standards
 304 (Accustandard [Z-014J-0.5X]). The internal standard solution is added to
 305 the liquid samples to account for routine variations in the response of the
 306 chromatographic system [78]. A Select-PAH column (CP7462) is used to

Figure 5: Sampling collection system used to measure PAH species over $-1.0 \leq X/L_I \leq +1.5$. 1) Nitrogen dilution; 2) Heater; 3) PID controller; 4) Thermocouple; 5) Pressure transducer; 6) KF vacuum fitting; 7) Quartz wool; 8) XAD resin; 9) Vacuum chamber; 10) Vacuum regulator; 11) Vacuum volume; 12) Vacuum pump.

Table 2: GC-MS analysis conditions, where $P_{in} = 34474$ Pa and $T_{in} = 573$ K are the inlet pressure and temperature.

Instrument	MSD (Agilent 5975C)
Column	Select-PAH (CP7462)
Carrier	Helium, constant flow 0.94 mL/min
Oven	343 K for 1 min, 40 K/min to 453 K,
program	3 K/min to 503 K, 1.5 K/min to 508 K,
	10 K/min to 553 K, 553 K for 5 min,
	5 K/min to 571 K, 10 K/min to 593 K,
	593 K for 5 min.

quantify the PAH species. The GC conditions are summarised in Table 2.
A selection of major identified compounds is listed in Table 3. The NIST
Library and AMDIS software are utilised for the identification of species [79].

3.3. Laminar flame calculations

Laminar flame calculations were performed to support the interpretation
of species growth and particle inception for various flame conditions. The
inflow boundary conditions for the computational study matched the exper-
imental data with identical reactant compositions and inlet temperatures.
The computational domain also resembled that of the back-to-burnt exper-

Figure 6: (a) Benzo(a)pyrene (B(a)P) concentration over sonication intervals extracted from different filter units for the REF flame at the spatial location of $X/L_I = 0.5$. (b) B(a)P concentration with respect to centrifuge time for $a_T = 420 \text{ s}^{-1}$ (black) and $a_T = 255 \text{ s}^{-1}$ (gray) at a constant $\phi_{UN} = 2.0$ and $T_{HCP} = 1500 \text{ K}$. The results are consistent with the uncertainty analyses presented by Shariatmadar et al. [3].

316 imental setup with the exception that the flow is laminar. Hence, only the
317 impact of bulk strain (not the turbulent strain) can be accounted for accu-
318 rately in the simulations. However, approximate computations based on the
319 addition of mean turbulent rate of strain were also performed and it must
320 be noted that such computation are only indicative of the flame behaviour.
321 The computational domain was resolved by 233 distributed cells with local
322 refinement in the reaction zone providing a resolution of $36 \mu\text{m}$. The detailed
323 chemical mechanism featuring 358 species and 1789 reactions described by
324 Lindstedt and Waldheim [34] was applied. The laminar flame data is used
325 below to compare with experimental species profiles in mixture fraction space
326 to illustrate the impact of the rate of strain.

Table 3: The selection of identified species illustrated in Fig. 11. Bold texts are deuterated internal standard solutions. Gray numbers refer to species including isomers.

ID	Name	ID	Name
1	m/z = 92	d	Phenanthrene-D10
a	1,4-Dichlorobenzene	15	Phenanthrene
2	m/z = 132	16	Anthracene
3	m/z = 130	17	m/z = 192
b	Naphthalene-D8	18	m/z = 206
4	Naphthalene [A2]	19	Pyrene isomer
5	m/z = 148	20	Pyrene [A4]
6	m/z = 146	21	m/z = 216
7	2-Methylnaphthalene [2-MN]	22	Benz(a)anthracene
8	1-Methylnaphthalene [1-MN]	e	Chrysene-D12
9	1-MN isomer	23	Chrysene
10	m/z = 156	24	m/z = 240
11	m/z = 154	25	Benzo(b)fluoranthene
12	m/z = 165	26	Benzo(k)fluoranthene
c	Acenaphthene-D10	27	Benzo(a)pyrene (B(a)P)
13	Fluorene	f	Perylene-D12
14	m/z = 170	28	m/z = 276

327 4. Results and discussion

328 4.1. Results from non-intrusive measurements

329 The strain and equivalence ratio impact on the PAH-PLIF and ELS sig-
330 nals are shown in Fig. 7 along the theoretical stagnation point streamline
331 and normalised by the corresponding maximum in each subfigure. The ex-
332 tent of the turbulent reaction zone is $\sim 2.4 L_I$, consistent with Shariatmadar
333 et al. [3] and Hampp et al. [53].

334 The peak ratios of the signals compared to the reference (REF) flame
335 are presented in Table 4. The results show that the occurrence of soot and
336 PAH are strongly dependent on the properties of the flow field (e.g. the
337 equivalence ratio and rate of strain) [40, 80]. The relative increase in the
338 soot concentration ratio (7.72) is higher than for gaseous PAH species (6.31)

Figure 7: Normalised PAH-PLIF (top) and ELS (bottom) signals across the turbulent reaction zone for various equivalence ratios (left), total rates of strain (middle) and burnt gas temperature (right). The relatively high laser fluence at 355 nm suggests that soot particle incandescence contributes to the PAH - LIF signal [57]. Thus, this data is likely to include contributions from PAHs infused on soot particles as well as gaseous species. Left column : $1.8 \leq \phi_{UN} \leq 2.2$, $a_T = 420 \text{ s}^{-1}$ and $T_{HCP} = 1500 \text{ K}$; Middle column : $\phi_{UN} = 2.0$, $358 \leq a_T [\text{s}^{-1}] \leq 492$ and $T_{HCP} = 1500 \text{ K}$; Right column : $\phi_{UN} = 2.0$, $a_T = 420 \text{ s}^{-1}$, $1400 \leq T_{HCP} [\text{K}] \leq 1700$. Signals are normalised by the corresponding maximum value among the cases presented in each subfigure. The profiles are taken at the theoretical stagnation point streamline, i.e. $Y/L_I = 0$.

339 although soot incandescence is also contributing to the PAH signal as the
340 rate of strain rate is reduced from $a_T = 492 \text{ s}^{-1}$ to $a_T = 358 \text{ s}^{-1}$. Overall,
341 the results indicate that the both soot and PAH formation are exceptionally
342 sensitive to the rate of strain and by implication to the local flow field condi-
343 tions. The results further indicate that soot, in particular, can grow rapidly
344 in regions of low rates of strain [37, 81–83]. By contrast, PAH concentrations
345 are comparatively strong influenced by the equivalence ratio with an increase

346 of a factor of 4 compared to 1.92 for soot in the range $2.0 \leq \phi_{UN} \leq 2.2$. The
 347 two values are inevitably linked due to PAH adsorption on soot particles.
 348 The PAH concentrations are comparatively insensitive to the lower nozzle
 349 HCP temperature as shown in Fig. 7. There is a decrease in PAH from the
 350 reference value to 0.88 when the temperature is reduced from 1500 to 1400 K.
 351 A decrease is also noted as the temperature is raised to 1600 and 1700 K. The
 352 trend correlates with the ELS signal which implies a high level of competition
 353 between soot formation and oxidation reactions with soot oxidation starting
 354 to take precedent at temperatures higher than 1600 K. The trend is stronger
 355 for soot with a drop of the normalised peak to 0.23 compared to 0.59 for
 356 PAH-PLIF and even more so considering a soot incandescence contribution
 357 to the PAH signal. The decreased thermodynamic stability of soot precur-
 358 sors and reduced surface reactivity at higher temperatures are expected to
 359 decrease soot formation as suggested by Frenklach et al. [84] and will also
 360 promote soot oxidation. Beyond a critical value, determined by the balance
 361 between formation and oxidation reactions, an increase in the hot combustion
 362 temperature (T_{HCP}) will favour PAH and soot oxidation reactions. Based
 363 on laminar flame calculations, the peak reaction zone temperature increases
 364 from 1412 K to 1795 K with an increase of T_{HCP} from 1400 K to 1700 K
 365 at a constant $a_T = 420 \text{ s}^{-1}$ and $\phi_{UN} = 2.0$ (see Fig. 4(b) in Supplemental
 366 Material). The resulting gradual increase in temperature leads to a modest
 367 reduction in the normalised PAH-LIF peak value at an unchanged location
 368 of $X/L_I = 0.5$. At the highest HCP temperature investigated, it can be noted
 369 that the peak of the substantially reduced ELS signal shifts approximately
 370 $3/4 L_I$ towards the HCP stream suggesting that soot is more likely to prevail

Table 4: Peak PAH-PLIF and ELS values at various experimental conditions normalised relative to the reference (REF) flame ($\phi_{UN} = 2.0$, $a_T = 420 \text{ s}^{-1}$ and $T_{HCP} = 1500 \text{ K}$). The relatively high laser fluence at 355 nm suggests that soot particle incandescence contributes to the PAH - LIF signal [57]. Thus, this data is likely to include contributions from PAHs infused on soot particles as well as gaseous species.

Case	PAH-PLIF	ELS
$\phi_{UN} = 1.80$	0.36	0.21
$\phi_{UN} = 2.00$	1.00	1.00
$\phi_{UN} = 2.10$	2.80	1.38
$\phi_{UN} = 2.20$	4.00	1.92
$a_T = 358 \text{ s}^{-1}$	2.27	4.17
$a_T = 420 \text{ s}^{-1}$	1.00	1.00
$a_T = 492 \text{ s}^{-1}$	0.36	0.54
$T_{HCP} = 1400 \text{ K}$	0.88	0.90
$T_{HCP} = 1500 \text{ K}$	1.00	1.00
$T_{HCP} = 1600 \text{ K}$	0.77	0.57
$T_{HCP} = 1700 \text{ K}$	0.59	0.23

371 in the reaction products.

372 The current laser diagnostic measurements cannot (i) distinguish between
373 different PAH species or (ii) elucidate the transition from molecular to solid
374 nanostructures and soot formation. Accordingly, interactions between PAHs
375 and particles cannot be precisely distinguished [85]. ELS can also be prone
376 to errors including interference by absorbing gas-phase species [76]. A probe
377 sampling method is accordingly utilised to provide information on the flame
378 structure and the spatial distribution of PAHs contributing to adsorption
379 and primary particle formation.

380 4.2. Flame structure and major gaseous species

381 4.2.1. Sampling probe

382 The overall flame structure was investigated by obtaining major species
383 concentrations at 11 axial sample positions along the stagnation point stream-
384 line (i.e. X direction). The measurement intervals were approximately half
385 an integral length scale of turbulence ($0.5 L_I$). The measured mole fraction of
386 major gaseous species (C_2H_4 , O_2 , CO , CO_2 , CH_4 , C_2H_2 , C_3H_6 and C_3H_8)
387 are shown in Figs. 8 and 9. The experimentally determined major species
388 mole fractions for all cases are also given in tabular form in the Supplemental
389 Material.

390 The peak ratios of the measured mean concentrations of stable hydrocar-
391 bon species are presented in Table 5. For the sooting flames, the increasing
392 amount of acetylene mirrors the increase in PAH concentrations to some ex-
393 tent. The PAH-PLIF signal increases by a factor of 4 from $\phi_{UN} = 2.0$ to 2.2
394 (see Table 4), while the acetylene concentration increases by a factor of 2.25.
395 The corresponding increase in the ELS signal is a factor of 1.92, close to
396 the increase in the acetylene concentration. The same trend is observed for
397 major hydrocarbon species including CH_4 , C_2H_2 , C_3H_6 and C_3H_8 as the
398 stoichiometry is varied from $\phi_{UN} = 1.8$ to $\phi_{UN} = 2.2$. It can be noted that
399 the increase in the acetylene concentration with stoichiometry is less than
400 for the C3 species. This may be due to depletion caused by acetylene addi-
401 tion to soot via HACA type mechanisms (c.f. [86]). The current data also
402 shows that the rate of strain has a very significant impact with $a_T = 610 s^{-1}$
403 resulting in a decrease of 60% for propene and 55% for propane compared
404 to the reference flame. The reduction is due to both the flame structure

Table 5: The peak ratio of major gaseous species. The peaks are normalised relative to the reference (REF) flame ($\phi_{UN} = 2.0$, $a_T = 420 \text{ s}^{-1}$ and $T_{HCP} = 1500 \text{ K}$). The two last columns indicate the impact of a rate of strain variation for the $\phi_{UN} = 2.0$ flame.

Species	$\phi_{UN} = 1.80$	$\phi_{UN} = 2.20$	$a_T = 255$	$a_T = 610$
CH ₄	0.37	1.60	2.28	0.43
C ₂ H ₂	0.46	2.25	3.00	0.57
C ₃ H ₆	0.20	2.46	3.00	0.40
C ₃ H ₈	0.34	2.53	3.20	0.45

and turbulence effects [87] with the latter leading to a Damköhler (Da) number dependent species scattering within the reaction zone [88]. Thus, the interface thicknesses can become governed by the turbulent transport and mixing suggesting a potentially significant impact of turbulence and the rate of strain on the species distribution within the flame structure. On the other hand, the mean concentration of species rises at lower strain rates and higher equivalence rates [89]. The increase in concentrations of intermediate species at lower rates of strain ($a_T = 255 \text{ s}^{-1}$) further indicates complex turbulence–chemistry interactions.

4.2.2. Mixture fraction and chemical species correlations

The experimental determination of major carbon containing species permit the tentative evaluation of the carbon based mixture fraction (f_c). The carbon based mixture fraction is calculated from seven carbon containing species (CO, CO₂, CH₄, C₂H₂, C₂H₄, C₃H₆ and C₃H₈) for both experimental data and the laminar flame computations on a dry basis (omitting the water concentrations). The use of an equal diffusivity approximation or the inclusion of all carbon containing species (including soot sections) in the

Figure 8: The impact of equivalence ratio on mole fractions of major gaseous species at different spatial location for $a_T = 420 \text{ s}^{-1}$ and $T_{HCP} = 1500 \text{ K}$. Circle – $\phi_{UN} = 1.8$; Square – $\phi_{UN} = 2.0$; Triangle – $\phi_{UN} = 2.2$. The filter unit, containing quartz wool and sodium sulphate, is used to remove water vapour from the gaseous sample. $X/L_I > 0$ is towards reactants and $X/L_I < 0$ towards the hot combustion products.

Figure 9: The impact of strain rate on mole fractions of major gaseous species at different spatial location for $\phi_{UN} = 2.0$ and $T_{HCP} = 1500$ K. Circle – $a_T = 225 \text{ s}^{-1}$; Square – $a_T = 420 \text{ s}^{-1}$; Triangle – $a_T = 610 \text{ s}^{-1}$. The filter unit, containing quartz wool and sodium sulphate, is used to remove water vapour from the gaseous sample. $X/L_I > 0$ is towards reactants and $X/L_I < 0$ towards the hot combustion products.

422 computations does not alter results appreciably.

$$f_c = \frac{\sum_{k=1}^{nsp} n_{C_k} X_k}{\sum_{k=1}^{nsp} X_k M_k} \cdot \left(\frac{n_{C_F}}{M_F}\right)^{-1} = \frac{M_F}{M} \frac{1}{n_{C_F}} \sum_{k=1}^{nsp} n_{C_k} X_k \quad (1)$$

423 where n_{C_k} denotes the number of carbon atoms in species k and n_{C_F} the
 424 number of carbon atoms in the fuel, and M is the mean molecular weight.
 425 Results from laminar flame computations with the approximately limiting
 426 rates of strain of $a_b = 120 \text{ s}^{-1}$ and $a_T = 420 \text{ s}^{-1}$ are shown in Fig. 10 for
 427 the REF flame. The latter features an approximate total rate of strain of
 428 420 s^{-1} , a stoichiometry $\phi_{UN} = 2.0$, and a counterflow $T_{HCP} = 1500 \text{ K}$. As
 429 shown, the mole fractions of major species are mostly bounded by the flamelet
 430 computations. However, the strong impact of the rate of strain, particularly
 431 on intermediate hydrocarbons, is clearly illustrated. The mixture fractions
 432 and chemical species are presented for all other experimental conditions in
 433 the Supplemental Material.

434 4.3. Distribution of PAHs through the flame brush

435 Direct probe sampling from the flame (online sampling) leads to PAH
 436 losses within the extraction line and the filter unit and neglects PAH adsorp-
 437 tion onto soot. Samples should also include internal standard solutions to
 438 account for routine variations in the response of the chromatographic sys-
 439 tem, which is not applicable to online sampling. Therefore, optimum sam-
 440 pling conditions were established to minimise experimental uncertainties as
 441 outlined in the SMM. The Select-PAH column is used to quantify the major

Figure 10: Species profile versus mixture fraction for $\phi_{UN} = 2.0$ at rates of strain of $a_T = 420 \text{ s}^{-1}$ (red) and $a_b = 120 \text{ s}^{-1}$ (black) and a burnt gas temperature of $T_{HCP} = 1500 \text{ K}$. Experiments indicated by circles.

PAH species (see Table 3). As shown in the mass spectrum (Fig. 11), the mass distribution of PAH species covers the interval of $92 \leq m/z [u] \leq 300$. Accordingly, the concentrations provided in Figs. 12 and 14 correspond to the mole fractions of PAH species ($92 \leq m/z [u] \leq 300$) in the analysed liquid sample including the solvent (DCM) contribution. A direct comparison of in situ techniques and probe sampling is challenging. On the one hand, laser diagnostics cannot precisely quantify the infusion level of resonance-stabilised radicals on soot particles in the flame. The quantification of PAH species using LIF is a challenging task as PAHs species contain a mixture of distinct functional groups with broad spectra. The spectra of such species can overlap with each other. On the other hand, GC-MS can present the mass spectrum of species up to $m/z = 300$ amu. The given data cannot include all PAHs.

Mass spectra (MS) extracted from the lower and upper limit rates of strain ($a_T = 225$ and $610 s^{-1}$) are shown in Fig. 11. Samples of mass spectra extracted at different spatial locations are also presented in Supplemental Material for the various experimental conditions. The results cover four intervals of the retention time (RT). The letters (a, b, c, d, e, f) refer to the internal standard solution (ISD) used to correct the MS response. The major species determined here have also been observed experimentally in other studies [13, 90, 91]. The MS results present known species where these can be identified and confirmed using external standard calibration, NIST library and AMDIS software. In other cases, the m/z ratio is presented as shown in Table 3. The presence of two peak sequences is noticeable among the species shown in the mass spectra. The first sequence appears with 24 m/z

units gap, which supports the role of C₂ addition via HACA style sequences followed by dehydrogenation. The growth of PAHs is further consistent with the addition of CH₂ (methylene) and CH₃ (followed by dehydrogenation) as shown by the 14 m/z gaps between PAH species [92]. The formation of a five-member rings can result from C₂H₂ addition, intramolecular hydrogen migration, CH₂ addition, and cyclization with H elimination [93].

The mass spectra show that concentrations of comparatively heavy PAHs (i.e. B(a)P and m/z = 276) can build up ahead of light species [14]. However, the importance of lighter molecules (e.g. 1-methyl naphthalene (1-MN) and m/z = 154) should not be neglected. For instance, 1-MN is a comparatively stable methyl-substituted two-ringed PAH. Schulz et al. [16] and Commoco et al. [17] suggest that methyl group substitutions make an important contribution to soot formation. As shown in our study, 1-MN is one of the major PAHs detected in the current turbulent flames. By contrast, 2-MN is present in smaller quantities suggesting a comparatively modest contribution to soot formation. Johansson et al. [94] suggest that it is crucial to consider the contributions made by all m/z = 154 isomers to the nucleation process. Reactions featuring PAHs also provide a route for mass growth [32] and structures involving C₅ rings can appear in quantities similar to, or exceeding, those based on C₆ rings [95].

The impact of the equivalence ratio and rate of strain on the spatial distribution of PAHs is shown in Figs. 12 and 14. The experimentally determined PAH species mole fractions for all cases are also given in tabular form in the Supplemental Material. It is important to note that the prevalence shown includes the solvent and correspond to the amounts present in the

Figure 11: Mass spectra extracted from low ($a_T = 225 \text{ s}^{-1}$ – black) and high rates of strain ($a_T = 610 \text{ s}^{-1}$ – red) showing the distribution of major PAH species. The mass spectra were extracted from a spatial location of $X/L_I = 0.5$ at a constant equivalence ratio of $\phi_{UN} = 2.0$ and burnt gas temperature of $T_{HCP} = 1500 \text{ K}$. The peak labels correspond to a list presented in Table 3.

492 treated sample collected over approximately 10,000 integral time scales of
 493 turbulence. The consumption of PAHs is aided by the elevated temperatures
 494 found in the nearly sooting flame ($\phi_{UN} = 1.80$ and $a_T = 610 \text{ s}^{-1}$) leading to
 495 increased oxidation. By contrast, flames at low rates of strain ($a_T = 225 \text{ s}^{-1}$)
 496 or high equivalence ratios ($\phi_{UN} = 2.20$) support the formation and survival
 497 of PAHs [96].

498 As shown above, through the use of PAH-PLIF and ELS, the rate of

Figure 12: The impact of equivalence ratio on the extracted distribution of PAHs along reaction zone layer at a constant $a_T = 420 \text{ s}^{-1}$ and $T_{HCP} = 1500 \text{ K}$. The concentrations correspond to the mole fractions of PAH ($92 \leq m/z [\text{u}] \leq 300$) in the analysed liquid sample including the solvent (DCM) contribution. Open circle – $\phi_{UN} = 1.8$; Square – $\phi_{UN} = 2.0$; Filled circle – $\phi_{UN} = 2.2$. $X/L_I > 0$ is towards reactants and $X/L_I < 0$ towards the hot combustion products.

Figure 12 (Cont.): The impact of equivalence ratio on the extracted distribution of PAHs along reaction zone layer at a constant $a_T = 420 \text{ s}^{-1}$ and $T_{HCP} = 1500 \text{ K}$. The concentrations correspond to the mole fractions of PAH ($92 \leq m/z [u] \leq 300$) in the analysed liquid sample including the solvent (DCM) contribution. Open circle – $\phi_{UN} = 1.8$; Square – $\phi_{UN} = 2.0$; Filled circle – $\phi_{UN} = 2.2$. $X/L_I > 0$ is towards reactants and $X/L_I < 0$ towards the hot combustion products.

Figure 12 (Cont.): The impact of equivalence ratio on the extracted distribution of PAHs along reaction zone layer at a constant $a_T = 420 \text{ s}^{-1}$ and $T_{HCP} = 1500 \text{ K}$. The concentrations correspond to the mole fractions of PAH ($92 \leq m/z [\text{u}] \leq 300$) in the analysed liquid sample including the solvent (DCM) contribution. Open circle – $\phi_{UN} = 1.8$; Square – $\phi_{UN} = 2.0$; Filled circle – $\phi_{UN} = 2.2$. $X/L_I > 0$ is towards reactants and $X/L_I < 0$ towards the hot combustion products.

Figure 12 (Cont.): The impact of equivalence ratio on the extracted distribution of PAHs along reaction zone layer at a constant $a_T = 420 \text{ s}^{-1}$ and $T_{HCP} = 1500 \text{ K}$. The concentrations correspond to the mole fractions of PAH ($92 \leq m/z [\text{u}] \leq 300$) in the analysed liquid sample including the solvent (DCM) contribution. Open circle – $\phi_{UN} = 1.8$; Square – $\phi_{UN} = 2.0$; Filled circle – $\phi_{UN} = 2.2$. $X/L_I > 0$ is towards reactants and $X/L_I < 0$ towards the hot combustion products.

Figure 13: Normalised total PAH concentrations from probe measurements (circle) and PAH-PLIF signals (black line) along the centreline for different equivalence ratios of $\phi_{UN} = 1.8$ (left), 2.0 (middle) and 2.2 (right). Each case is normalised by the corresponding peak. The burnt gas temperature $T_{HCP} = 1500$ K and total rate of strain $a_T = 420 \text{ s}^{-1}$. The relatively high laser fluence at 355 nm suggests that soot particle incandescence contributes to the PAH - LIF signal [57]. Thus, this data is likely to include contributions from PAHs infused on soot particles as well as gaseous species. The probe results correspond to the analysis of liquid samples, including the solvent (DCM) contribution, for three different conditions: Red circle – the fraction of PAHs in the range of $92 \leq m/z [u] \leq 300$; Blue triangle – PAHs with three or more rings ($154 \leq m/z [u] \leq 300$); Grey circle – PAHs with five rings ($m/z = 252$ and 276).

499 strain has a significant impact on the formation of PAHs and soot. Fur-
500 thermore, the peak ratio of total PAH species in the measured mass spectra
501 increases by a factor of 3.05 when the total rate of strain is reduced from
502 $a_T = 420 \text{ s}^{-1}$ to $a_T = 225 \text{ s}^{-1}$ and an increase from $a_T = 420 \text{ s}^{-1}$ to
503 $a_T = 610 \text{ s}^{-1}$ results in a reduction in the peak ratio by a factor of 0.48. The
504 clear implication is that soot formation is a low Da number process due to
505 long chemical time scales. The probe measurements are consistent with the
506 non-intrusive laser diagnostics and show a peak in PAH concentrations close
507 to $X/L_I = 0.5$ as a result of the balance between formation and oxidation.
508 As shown in Fig. 13, there is a reasonable correspondence throughout the
509 flame brush between the relative PAH concentrations obtained from PAH-

510 PLIF and probe measurements. The PAH-LIF data is normalised by the
 511 corresponding maximum value for each case. The total PAH fractions ob-
 512 tained from the probe measurements are normalised by the full mass range
 513 covering $92 \leq m/z [u] \leq 300$. The fraction of PAHs, shown in Fig. 13, is
 514 provided for (i) the full range ($92 \leq m/z [u] \leq 300$) (red), (ii) the fraction
 515 with three and more rings ($154 \leq m/z [u] \leq 300$) (blue) and (iii) the fraction
 516 of five ring PAHs ($m/z = 252$ and 276) (grey). It should be emphasised that
 517 the current PAH-LIF signal stems (predominantly) from PAHs with three or
 518 more rings and thus omits prevalent smaller aromatics such as naphthalene.
 519 As shown in Fig. 13, the analysis indicates that the probe measurements and
 520 PAH-LIF data show peaks in the PAH concentrations at $X/L_I = 0.5$. The
 521 differences between the PAH-LIF data and probe measurements may partly
 522 arise from a more efficient extraction of heavier PAHs from the probe sample
 523 and the omission of smaller aromatics from the PAH-LIF data. However,
 524 it should be emphasised that a complete comparison is impossible as the
 525 GC/MS (probe measurements) provides species concentrations up to $m/z =$
 526 300 , while PAHs identified using PAH-PLIF contain a mixture of distinct
 527 functional groups with broad spectra. The used excitation wavelength and
 528 laser fluence at 355 nm are likely to cause some level of crosstalk between
 529 PAH-LIF and ELS detection system. Thus, the applied laser induced fluo-
 530 rescence method cannot distinguish PAHs present in the gas phase or infused
 531 on soot particles.

532 Mean concentration profiles of major PAHs (e.g. 1-MN, $m/z = 154$, m/z
 533 $= 276$ and B(a)P) indicate potential contributions to the formation of partic-
 534 ulates with B(a)P present in relatively large quantities irrespective of lightly

535 or heavily sooting conditions. It is important to note that PAH concentra-
 536 tions are comparatively low before applying the centrifuge process as shown
 537 in Fig. 6(b). This illustrates the importance of PAH adsorption on soot
 538 particles. The concentrations of acenaphthylene and acenaphthene are con-
 539 sistently low from lightly to heavily sooting conditions indicating a differ-
 540 ence balance between formation and consumption. For example, the reac-
 541 tion flux through these species leading to soot particles may be significant.
 542 Benzo(b)fluoranthene also reaches to a maximum at $X/L_I = 0.5$, yet de-
 543 creases significantly faster towards both boundaries of the reaction layer. The
 544 detected concentration of pyrene is much lower than that of benzo(a)pyrene
 545 and the amount determines the collision probability (e.g. with a soot parti-
 546 cle). However, while pyrene and benzo(a)pyrene appear closely related from
 547 a chemical point of view, structural differences may result in differences in
 548 the reaction flux leading to soot particle growth via PAH adsorption due to
 549 different sticking probabilities.

550 The coupling between gas-phase and surface reactions [97] is an impor-
 551 tant factor and, as shown above, PAH adsorption onto soot particles assumes
 552 a distinct role. Soot nucleation is proportional to PAH concentrations [98]
 553 with higher concentrations leading to a higher collision frequency. However,
 554 the probability of stabilisation depends on a number of other factors such as
 555 PAH size and orientation. Figures 15 and 16 show the evolution of the rela-
 556 tive concentrations of the main PAHs in the size range $92 \leq m/z \leq 300$ amu
 557 over the entire reaction zone. The mole fractions of species in the analysed
 558 liquid sample include the solvent (DCM) contribution and the PAHs infused
 559 on soot particles that can be separated as outlined above.

560 The data indicates the evolution of the balance between formation and
 561 consumption over the reaction zone layer. The appearance of high concentra-
 562 tions of PAHs at $X/L_I = 0.5$ indicates the location of soot nucleation. The
 563 stoichiometry of the reactant mixture (ϕ_{UN}) and the total rate of strain (a_T)
 564 have a remarkable impact on evolution of PAH concentrations in the reaction
 565 zone layer. While B(a)P shows persistently high concentrations over the en-
 566 tire reaction zone irrespective of the conditions, the evolution of other species
 567 are strongly dependent on both the spatial location and sooting conditions.
 568 For example, the relative concentration of $m/z = 154$ (second highest peak)
 569 overtakes $m/z = 276$ at $X/L_I = +0.5$ and $+1.0$ at $\phi_{UN} = 2.2$ although the
 570 concentrations are close at the boundaries of $X/L_I = -1.0$ and $+1.5$. The
 571 concentrations of $m/z = 228$ and $m/z = 240$ appear to be higher than m/z
 572 $= 276$ in the region of soot inception at $X/L_I = +0.5$. This indicates a dif-
 573 ferent balance of formation and loss mechanisms for these PAHs. At a lower
 574 rate of strain, B(a)P still shows the highest concentration with $m/z = 154$
 575 the secondary species. However, the concentration of $m/z = 142$ (methyl-
 576 naphthalene isomers) is particularly high with competition between $m/z =$
 577 132 , $m/z = 142$ and $m/z = 146$ as the third highest species. The impact of
 578 $m/z = 276$ is less pronounced in contrast to $\phi_{UN} = 2.2$. It is expected that
 579 such detailed information on the relative abundance of different PAHs associ-
 580 ated with soot nucleation will provide a validation target for comprehensive
 581 models describing soot inception in turbulent flows.

Figure 14: The impact of the rate of strain on the extracted distribution of PAHs along reaction zone layer for $\phi_{UN} = 2.0$ and $T_{HCP} = 1500$ K. The concentrations correspond to the mole fractions of PAH ($92 \leq m/z [u] \leq 300$) in the analysed liquid sample including the solvent (DCM) contribution. Open circle – $a_T = 225 \text{ s}^{-1}$; Square – $a_T = 420 \text{ s}^{-1}$; Filled circle – $a_T = 610 \text{ s}^{-1}$. $X/L_I > 0$ is towards reactants and $X/L_I < 0$ towards the hot combustion products.

Figure 14 (Cont.): The impact of the rate of strain on the extracted distribution of PAHs along reaction zone layer for $\phi_{UN} = 2.0$ and $T_{HCP} = 1500$ K. The concentrations correspond to the mole fractions of PAH ($92 \leq m/z [u] \leq 300$) in the analysed liquid sample including the solvent (DCM) contribution. Open circle – $a_T = 225 \text{ s}^{-1}$; Square – $a_T = 420 \text{ s}^{-1}$; Filled circle – $a_T = 610 \text{ s}^{-1}$. $X/L_I > 0$ is towards reactants and $X/L_I < 0$ towards the hot combustion products.

Figure 14 (Cont.): The impact of the rate of strain on the extracted distribution of PAHs along reaction zone layer for $\phi_{UN} = 2.0$ and $T_{HCP} = 1500 \text{ K}$. The concentrations correspond to the mole fractions of PAH ($92 \leq m/z [\text{u}] \leq 300$) in the analysed liquid sample including the solvent (DCM) contribution. Open circle – $a_T = 225 \text{ s}^{-1}$; Square – $a_T = 420 \text{ s}^{-1}$; Filled circle – $a_T = 610 \text{ s}^{-1}$. $X/L_I > 0$ is towards reactants and $X/L_I < 0$ towards the hot combustion products.

Figure 14 (Cont.): The impact of the rate of strain on the extracted distribution of PAHs along reaction zone layer for $\phi_{UN} = 2.0$ and $T_{HCP} = 1500$ K. The concentrations correspond to the mole fractions of PAH ($92 \leq m/z [u] \leq 300$) in the analysed liquid sample including the solvent (DCM) contribution. Open circle – $a_T = 225 \text{ s}^{-1}$; Square – $a_T = 420 \text{ s}^{-1}$; Filled circle – $a_T = 610 \text{ s}^{-1}$. $X/L_I > 0$ is towards reactants and $X/L_I < 0$ towards the hot combustion products.

Figure 15: The impact of equivalence ratio on the PAH mass distribution at different spatial locations at $a_T = 420 \text{ s}^{-1}$ and $T_{HCP} = 1500 \text{ K}$. The label corresponds to species listed in Table 3. The concentrations correspond to the mole fractions of PAH ($92 \leq m/z [u] \leq 300$) in the analysed liquid sample including the solvent (DCM) contribution. (a) $X/L_I = -1$; (b) $X/L_I = -0.5$; (c) $X/L_I = 0$; (d) $X/L_I = +0.5$; (e) $X/L_I = +1$; (f) $X/L_I = +1.5$. Triangle - $\phi_{UN} = 1.8$; Circle - $\phi_{UN} = 2.2$.

Figure 16: The impact of the rate of strain rate on the PAH mass distribution at different spatial locations for $\phi_{UN} = 2.0$ and $T_{HCP} = 1500$ K. The label corresponds to species listed in Table 3. The concentrations correspond to the mole fractions of PAH ($92 \leq m/z [u] \leq 300$) in the analysed liquid sample including the solvent (DCM) contribution. (a) $X/L_I = -1$; (b) $X/L_I = -0.5$; (c) $X/L_I = 0$; (d) $X/L_I = +0.5$; (e) $X/L_I = +1$; (f) $X/L_I = +1.5$. Triangle - $a_T = 610 \text{ s}^{-1}$; Circle - $a_T = 255 \text{ s}^{-1}$.

582 5. Conclusions

583 A back-to-burnt opposed jet configuration has been used to study the
584 overall flame structure of turbulent premixed ethylene/air flames and the
585 relative concentrations of PAHs associated with soot inception. The exper-
586 iments covered a series of sooting flame conditions with variations in the
587 equivalence ratio and the rate of strain. The conditions traverse the soot in-
588 ception limit with non-intrusive ELS and PAH-PLIF combined probe sam-
589 pling to quantify gaseous and PAH species using GC-TCD and GC-MS,
590 respectively. It is shown that the rate of strain exerts a substantial influence
591 on both PAH concentrations and soot formation. Hence, it is likely that soot
592 formation in turbulent flames becomes dominated by contributions from low
593 strain regions. It has also been shown that the stoichiometry of the mixture
594 controls the concentrations of PAHs associated with soot inception. The lat-
595 ter aspect has been further analysed by determining the PAH mass spectra
596 over the reaction zone layer. It is shown that PAH layers extend to three
597 integral length scales of turbulence. A variation of the temperature of the
598 opposing stream of hot combustion products, used to stabilise the flames,
599 indicates that a value of around 1500 K prior to mixing with the reactants
600 provides optimal conditions for PAH and soot growth.

601 The results obtained clearly show that benzo(a)pyrene is prevalent in
602 the flame structure and that relatively large amounts are condensed onto
603 soot particles. In addition to B(a)P and $m/z = 252$ u, the prevalence of
604 species with $m/z = 142$, 154 and 276 indicate a potentially significant role
605 in particle formation due to their high concentration levels. The current
606 determination of the relative distribution of PAHs across the flame structure,

607 the impact on soot inception of reactant composition and the rate of strain
608 will likely advance the fundamental understanding of the particle formation
609 and oxidation process in turbulent premixed sooting flames. It is hence
610 expected that the results will support the development of computational
611 models that account better for the influence of PAHs on soot inception and
612 growth in turbulent flames.

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616 **References**

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