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# Soot formation characteristics of *n*-heptane/toluene mixtures in laminar premixed burner-stabilized stagnation flames



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#### ABSTRACT

The soot formation characteristics in laminar premixed flames of pure *n*-heptane and binary mixtures of toluene and *n*-heptane with liquid volume ratios ranging from 0.2 to 1 were studied with the C/O ratio and unburned gas-mixture velocity being kept the same for all tested flames. The particle size distribution functions (PSDFs) at several selected burner-to-stagnation surface separation distances ( $H_p$ ) were measured by using the burner-stabilized stagnation probe/scanning mobility particle sizer (SMPS) technique. In addition, the morphology of soot particles sampled from the probe was examined using transmission electron microscopy (TEM). From the PSDFs at different  $H_p$  and TEM images, it was observed that with the addition of toluene, soot inception occurred at lower flame heights and the primary particle size of soot aggregates was significantly reduced. A combustion kinetics model for toluene and *n*-heptane was used to explore the precursor chemistry. The modeling results were found to be consistent with the observations of the measured PSDFs.

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## 1. Introduction

Increasingly stringent regulations in many countries on soot emission for on-road vehicles are driving the need for higher accurate computational soot models for internal combustion engine design. The commercial transportation fuels we use such as gasoline, diesel, and jet fuel are mixtures of hundreds of hydrocarbons. The high complexity of fuels has encouraged the search for limited fuel formulation (surrogate fuels) to emulate the physical and chemical properties of a real fuel. Among various surrogate fuel formulations [1,2], *n*-alkanes and aromatics are essential, in that *n*-heptane and toluene are often used to optimize both the fuel formulation and engine design [3,4].

The studies on surrogate fuels have been widely conducted with a focus on auto-ignition, flame propagation, and extinction characteristics [5–12]; they are indispensable for the understanding of combustion properties of various fuel formulations. By contrast, the soot formation characteristics of surrogate fuels remain less understood, especially the synergistic effects of multicomponent mixtures. It has been reported that in a spherical

droplet flame in an optically accessible sealed chamber, adding toluene significantly enhanced sooting propensities of *n*-heptane [13]. Mathieu et al. [14] studied the soot tendency of a diesel fuel surrogate composed of n-propylcyclohexane, n-butylbenzene, and 2,2,4,4,6,8,8-heptamethylnonane in a heated shock tube and found that the soot induction delay time and soot yield depend strongly on the structure of the hydrocarbon and the concentration of oxygen, and the soot inception process was initiated by the fuel molecule that produces soot fastest. A similar observation was also made in a premixed *n*-heptane flame study [15], where the *n*-propylbenzene addition gave rise to a faster soot inception at lower heights above burner, yet the ultimate soot loading was similar to those flames without aromatics addition due to slightly lower temperature and lower acetylene formation. Choi et al. [16] investigated the binary fuels of toluene/n-heptane and toluene/iso-octane in the counterflow diffusion flames, a synergistic effect was observed to have caused an initial increase and then decline in PAH concentration with toluene addition. The soot amount, however, was marginally changed with the addition of small amount of toluene. Another study of *n*-heptane/toluene mixtures in a wick-fed diffusion flame [17] showed that the dependence of soot particle size distributions on height changed to resembling an aromatic fuel from resembling a paraffinic with an increased ratio of toluene in the binary mixtures with *n*-heptane.

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| Flame  | Volume ratio of $C_6H_5CH_3$ to $C_7H_{16}$ | Mole fraction                                 |                                | Equivalence ratio | $T_{max}(\mathbf{K})^{\mathbf{b}}$ |
|--------|---|---|--------------------------------|-------------------|------------------------------------|
|        |   | C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> | C <sub>7</sub> H <sub>16</sub> |                   |                                    |
| H10    | 0   | 0.0000  | 0.0512                         | 1.89              | $1764 \pm 84$                      |
| H10T2  | 0.2   | 0.0111  | 0.0401                         | 1.81              | $1780\pm88$                        |
| H10T4  | 0.4   | 0.0183  | 0.0329                         | 1.76              | $1822\pm94$                        |
| H10T10 | 1   | 0.0298  | 0.0214                         | 1.69              | $1913~\pm~108$                     |

 Table 1

 Summary of flame conditions.<sup>a</sup>

 $^{\rm a}$  Unburned gas composition: 0.0512 fuel-0.2988 O\_2- 0.65Ar; cold gas velocity:4 cm/s (298 K, 1 atm); C/O: 0.6.

<sup>b</sup>  $T_{max}$  is the measured maximum flame temperature with radiation correction at  $H_p = 1.2$  cm.

All these studies show that fuel structures indeed play a very important role in soot formation process, and a few reaction pathways have been proposed to explain the experimental observations. For aliphatic fuels, such as *n*-alkanes, the formation of the first ring is regarded as the rate-limiting step in the reaction sequence to large aromatics and is generally described by the reactions involving radicals such as CH<sub>3</sub>, *i*-C<sub>4</sub>H<sub>5</sub>, *i*-C<sub>4</sub>H<sub>3</sub>, C<sub>3</sub>H<sub>3</sub>, C<sub>5</sub>H<sub>5</sub> [18–21]. As for aromatic hydrocarbons such as toluene, research results show that the second aromatic ring instead of the first controls the rate of soot formation through the pathway of C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub> + C<sub>3</sub>H<sub>3</sub> = A<sub>2</sub> (C<sub>10</sub>H<sub>8</sub>) + 2H [22,23]. Once small aromatic rings are formed, the subsequent growths are similar through the hydrogen-abstraction-C<sub>2</sub>H<sub>2</sub>-addition (HACA) and the PAH condensation pathways [19,20,24].

Despite the significant gains in understanding of combustion characteristics and soot formation of surrogate fuels, more quantitative experimental data from well-defined configurations are still needed for model validation and for a better understanding of the mechanism of soot formation, such as the measured soot particle size distribution functions at different heights above burner using burner-stabilized stagnation flame (BSSF). BSSF does not only have the advantages of well-defined boundary conditions but also well-understood probe effects [25,26]. On top of that, the detailed characteristics of soot formation, including nucleation and mass growth can be captured from the evolution of soot particle size distribution functions. In the present study, we investigate the evolution of soot particle size distribution functions and particle morphology in BSSF of pure *n*-heptane and binary mixture fuels of *n*-heptane/toluene. Since *n*-heptane/toluene mixtures are regarded as representative components in gasoline fuel and their combustion characteristics have been widely studied in the literature [3,15,16,27-29], we expect our study on their sooting behaviors would deepen our understanding of the particulate emission characteristics.

# 2. Experimental setup

The laminar premixed fuel-rich flames on a stainless steel McKenna burner at atmospheric pressure were studied with four different compositions (Table 1): pure *n*-heptane (H10), and binary mixtures of toluene and *n*-heptane with liquid volume ratios of 0.2 (H10T2), 0.4 (H10T4), and 1 (H10T10), respectively. The C/O ratio (0.6) and unburned gas-mixture velocity (4 cm/s, 298 K & 1 atm) were kept the same for all conditions. The flames were stable and isolated from the air by a shroud of nitrogen flowing at 30 cm/s through a concentric porous ring.

Details of the BSSF setup (Fig. 1) and the experimental procedure were introduced in our previous works [25,30,31]. Briefly, the sample probe was made of a stainless steel tube with a 160 µm orifice in the middle and embedded in a flat aluminum plate. Soot particles were sampled in the axial centerline at several selected burner-to-stagnation surface separation distances ( $H_p$ ) with a positional accuracy of  $\pm$  0.04 cm, and were diluted immediately by a



Fig. 1. The schematic diagram of experiment.

30 L/min nitrogen flow to quench chemical reactions, prevent particles from coagulation, and reduce wall diffusion loss in the sampling line. The flow rate of the unburned gas was controlled by sonic nozzle calibrated by a soap-film flow-meter. The orifice temperature was about 450  $\pm$  30 K, which was measured by a type-K thermocouple embedded inside the stagnation aluminum plate. The procedure introduced in [25] for determining the optimal dilution ratio was used. Since soot PSDFs are insensitive to the dilution ratios ranging from 1500 to 5000 for the present experimental setup, we took a dilution ratio of ~3000 when taking samples. The detailed procedure for data inversion of the absolute number density (*N*) in the flame related to the number density (*N*<sub>s</sub>) measured by SMPS can be found in [25,31].

The fuel vaporization system is similar to the one used in [32]. Liquid fuels were injected into a conical vaporization chamber by a syringe pump (Longer, LSP01-1A). To ensure complete liquid fuel vaporization, a nebulizer was used to atomize liquid fuels with a stable constant argon flow of 0.5 L/min (STP) at the upstream to shear liquid fuels into small droplets. Then the atomized fuel droplets were vapored immediately by a hot mixture gas flow of oxygen and argon (403  $\pm$  2 K). The conical vaporization chamber and the transfer line to the burner were maintained at a constant temperature (403 K) by strip heaters. Different from Ref. [32], the burner was cooled with hot water at 348  $\pm$  2 K to prevent both fuel condensation in the porous plug and overheat of the burner. Note the boiling temperatures of *n*-heptane and toluene are  $371.5 \pm 0.3$  and  $383.8 \pm 0.3$  K, respectively [33]. According to the Antoine equation [34], the boiling temperature of the binary mixtures of *n*-heptane and toluene will be slightly lower than 383.8 K. Hence, the temperature of 403 K is adequate to vaporize the fuel mixture.

The flame temperature was measured by an S-type thermocouple coated with a Y/Be/O mixture (12% yttrium oxide and 88% beryllium oxide [35]) to prevent surface catalytic reactions. The diameter of the thermocouple before and after coating is 125 and 142 µm, respectively. The radiation-corrected procedure defined by Shaddix [36] was adopted. The uncertainty of the emissivity of coated thermocouple ranges from 0.3 to 0.6 [37], which determines the upper and lower limits of temperature. The gas properties were calculated using a modified OPPDIF code [38,39] with a detailed mechanism of JetSurF (version 0.2) [40]. The detailed error analysis of the thermocouple measurement can be found in the supplemental material. In order to minimize the deposition of soot particles on the thermocouple, the thermocouple had been cleaned by a fuel-lean butane flame torch to remove any deposited soot particles before it was inserted very rapidly into flame for temperature measurement.

The PSDFs were measured by Scan Mobility Particle Sizer (SMPS, TSI 3936). According to Li et al. [41,42], mobility measurement can overestimate the physical size of soot particles smaller than 10 nm due to the inherent limitation of the empirical Cunningham slip correction. To correct the mobility diameter, we adopted a parameterized correlation introduced in Ref. [39]. All diameters reported hereafter are corrected diameters. In addition, a nanometer aerosol sampling instrument (NAS, TSI 3089) was applied to collect soot particles charged by a bipolar charge (TSI 3087) using the same BSSF setup. The NAS consisted of a cylindrical sampling chamber and an electrode with a flat round plate being mounted perpendicular to the aerosol flow. The flow rate through the NAS was 1 L/min and the voltage was -10 kV. Positively charged soot particles were captured on the substrate of negatively charged grids transmission electron microscope (TEM) grids (230 mesh copper grids coated with carbon film). According to Li et al. [43], the smaller the particles, the larger the collection efficiency of the NAS. As the particle size drops from 160 to 60 nm, the collection efficiency increases from  $\sim$ 39% to  $\sim$ 99.5%. To examine the soot morphology, a TEM (Tecnai G<sup>2</sup> 20) was used to image the collected particles. The diameters of those near-spherical primary particles in aggregates were determined by Image-Pro Plus software (https://www.mediacy.com/imageproplus).

# 3. Computational method

To examine the flame structure and gas-phase species profiles for all tested flames, we used a detailed combustion kinetics model, KAUST Mech 2 (KM2) [28] and the Premixed Laminar Burner-Stabilized Stagnation Flame application from the Chemkin-Pro software package [44] to simulate the experimental configurations. Considering that temperature plays an important role in soot formation processes, instead of solving the energy equation, the measured temperature profiles were set as an input. According to the study of Ref. [27], KAUST Mech predicts well the profiles of PAHs and also captures the synergistic effect between *n*-heptane and toluene in the counterflow diffusion flames. Other input parameters include the boundary temperatures at the burner surface and at the stagnation plate, which were maintained at 403 K and  $450 \pm 30$  K respectively, and the grid properties, for which the adaptive mesh resolution with a maximum number of grid points of 250 was used. Thermal diffusion and mixture-averaged transport formula were adopted. To be noted, our objective is not to model soot dynamics, but to obtain the major gas-phase species profiles, which can help understand the experimental observations qualitatively.

## 4. Results and discussion

The maximum flame temperature  $(T_{max})$  as a function of burner-to-stagnation surface separation distance  $(H_p)$  is shown in Fig. 2. The detailed temperature distribution profiles at each  $H_p$  can be found in Figs. S1–S4 in the supplemental material. The

vertical error bars are due to the emissivity uncertainty of the coated thermocouple. For example, the temperature uncertainties at  $H_p = 1.2$  cm for flames H10, H10T2, H10T4 and H10T10 are  $\pm$  84,  $\pm$  88,  $\pm$  94, and  $\pm$  108 K, respectively. As illustrated, for each flame,  $T_{max}$  increases slowly with  $H_p$ . At the same  $H_p$ , under the same carbon/oxygen ratio and carbon mass flow, increasing the ratio of toluene to n-heptane in the binary mixtures enhanced  $T_{max}$  progressively. For example, at  $H_p = 1.2$  cm,  $T_{max}$  of flames H10, H10T2, H10T4 and H10T10 are 1764, 1780, 1822, and 1913 K, respectively. Please note that the temperature differences of these flames are due to different fuel compositions. It is known that soot formation can be affected by many factors, such as fuel structure, temperature, and residence time, etc. These factors are often coupled and difficult to separate. It is clear that different fuel structures lead to different flame structures (e.g. flame temperature and species concentration profiles), which determine the soot formation characteristics. In this study, we focus on the fuel structure effect by fixing the C/O ratio and the flow rate (i.e. similar residence time at the same  $H_p$ ). As a result, the flame temperatures vary by up to 150 K, which might be controlled by changing the diluent concentrations. However, the temperature adjustment is rather limited (~50 K) even if all argon is replaced by nitrogen in the current flame configuration. Hence, to separate the temperature effects, other strategies should be taken in future work.

Next we shall examine the measured PSDFs. Each data point shown in Fig. 3 is an average of at least 3 repeated measurements. Note that data are absent for flames H10 and H10T2 at  $H_p = 0.55$  cm because flame extinguishes under these conditions. The overall evolution characteristics of PSDFs for all tested flames show a power-law type distribution for small particles and a lognormal distribution for larger particles, which is similar to those lightly sooting ethylene-oxygen-argon flames [45]. At low separation distances ( $H_p \leq 0.6$  cm), where soot particle nucleation dominates, higher concentrations of small particles can be observed for flames H10T2 and H10T4, which indicates that the nucleation rate increases significantly with the small amount of toluene addition. However, for flame H10T10 with an even higher volume ratio of toluene in the fuel mixture, its PSDFs are slightly different from the other three flames, exhibiting a relatively earlier stage of mass growth leading to more big particles and notably fewer small particles. At higher separation distances ( $H_p \ge 0.7$  cm), flame H10 exhibits very different particle growth behavior from the tolueneadded flames. It is obvious that with the increase of  $H_n$ , the number density of small particles in flame H10 increases dramatically, and the particle size at the lognormal peak is larger than that in other flames ( $H_p = 1.0 \& 1.2 \text{ cm}$ ), which suggests both faster nucleation and mass growth rates than those aromatic-doped flames at  $H_p = 0.7$ -1.2 cm. The phenomena become more evident at  $H_p$ = 1.0 and 1.2 cm, where a remarkable reduction of number density of both small and large particles is observed with the addition of toluene. The continuous nucleation at a bigger separation distance  $(H_p = 1.5 \text{ cm})$  has also been observed for a premixed *n*-heptane flame at  $T_{max} = 1760$  K in [46].

Besides the detailed size distribution, we may also examine the absolute number density (*N*) and soot volume fraction ( $F_v$ ) measured as a function of  $H_p$  as depicted in Fig. 4. *N* and  $F_v$  were determined by integrating the number density and volume fraction at each point of PSDFs over all particle sizes measured (>2.5 nm). It clearly demonstrates that for all tested flames with the increase of  $H_p$ , the absolute number density increases first due to enhanced particle nucleation and then decreases due to coagulation and surface growth. In flame H10, the peak absolute number density ( $N_{max}$ ) occurs at a higher  $H_p$  than other toluene-doped flames, indicating a delayed nucleation process. As the amount of toluene increases,  $N_{max}$  becomes smaller but occurs at lower  $H_p$ . As to the soot volume fraction,  $F_v$  of flame H10 is obviously smaller than that



Fig. 2. Radiation-corrected maximum flame temperature at axial centerline at different burner-to-stagnation surface separation distances. Symbols represent the experimental data and lines are drawn to show the trend.



Fig. 3. Evolution of PSDFs for all tested fuels at several selected burner-to-stagnation surface separation distances.

in toluene-added flames at lower  $H_p$  because of slower soot nucleation. However it reaches the maximum value among the four flames at  $H_p = 1.0$  and 1.2 cm due to a rapid mass growth.

In order to better understand the effect of toluene addition on PSDFs, *N* and  $F_v$ , it is helpful to examine the flame structure including temperature and gas-phase species concentrations in these flames. We thus carried out numerical simulations to obtain the concentrations of species that may play an important role in soot formation, including acetylene, benzene, naphthalene, pyrene, etc. Figure 5 presents the computed mole fractions of two major aromatic species benzene and pyrene at  $H_p = 0.6$  and 1.2 cm, respectively. At  $H_p = 0.6$  cm, the concentrations of benzene (Fig. 5a) and

pyrene (Fig. 5c) both increase with the amount of toluene addition. For example, in flame H10T10, the pyrene concentration is over two orders of magnitude larger than that in flame H10. When comparing the concentrations of benzene (Fig. 5b) and pyrene (Fig. 5d) at  $H_p = 1.2$  cm, we have found the results to be quite different from those at  $H_p = 0.6$  cm. With increased amount of toluene, the concentration of benzene increases more at lower flame heights, but drops faster at higher flame heights, showing a similar trend as for the number of small particles discussed above. The difference in soot precursor concentrations of the four flames can be attributed to their different flame structures. To find out the dominant reaction paths, we performed rate of production analyses for



**Fig. 4.** Particle absolute number density and soot volume fraction measured as a function of burner-to-stagnation surface separation distances. Symbols represent experimental data. Lines are drawn to indicate trends.

the aromatic species; the results of benzene for flames H10 and H10T10 at  $H_p = 0.6$ , 1.2 cm are depicted in Fig. S5 in the supplemental material. It is clear that the net production rate of benzene is about two orders of magnitude higher in H10T10 than in H10. The reaction contributing the most to the production of benzene in H10 is the recombination of propargyl radicals, while in flame H10T10 it is R596 ( $C_6H_5CH_3 + H = A1 + CH_3$ ). At  $H_p = 1.2$  cm, the faster drop of benzene concentration at higher flame heights in flame H10T10 is because higher temperature in flame H10T10 increases the concentrations of H and CH<sub>3</sub>, promoting the consumption of benzene through R371 (A1 + H = A1- + H<sub>2</sub>) and R1159 (A1 + CH<sub>3</sub> $\rightarrow$ A1- + CH<sub>4</sub>). It can be inferred that benzene and pyrene play a very important role in the nucleation process of toluene-added flames. Besides the concentrations of aromatics, the flame temperature is also correlated with the soot formation processes but in a more complicated way. According to Abid et al. [47], in lower temperature flames, particle growth is limited by nucleation rate and mass growth, while in higher temperature flames particle size growth is limited by the thermal decomposition of chemical precursors. Compared to the toluene-added flames, in the pure heptane flame H10, at lower separation distances, soot nucleation is much slower as the flame temperature is lower  $(T_{max})$ = 1683 K) and there are not enough aromatic compounds such as benzene and pyrene available; however at higher separation distances, the coupling effect of more aromatics and a slightly higher temperature ( $T_{max} = 1764$  K) promote soot nucleation.

It is well known that acetylene plays a critical role in soot mass growth and its concentration is positively related to the soot mass growth rate. Therefore, we compared the mole fractions of acetylene at  $H_p = 0.6$  and 1.2 cm of the four flames in Fig. 6. It seems obvious that the acetylene concentration in the post-flame region decreases with the addition of toluene at a fixed  $H_p$ , but increases



Fig. 5. Mole fraction of benzene (top panel) and pyrene (bottom panel) computed at  $H_p = 0.6$  and 1.2 cm burner-to-stagnation surface separation distances for all tested fuels.



**Fig. 6.** Mole fraction of acetylene computed at burner-to-stagnation surface separation distance  $H_p = 0.6$  and 1.2 cm for all tested fuel mixtures.

slightly with  $H_p$  for a certain flame. At  $H_p = 1.2$  cm, where the mass growth process dominates, less acetylene in toluene-added flames and higher temperature ( $T_{max} = 1913$  K) lead to smaller soot volume fractions as shown in Fig. 4. This is because soot has already passed the maximum of the soot bell [23] and is not growing anymore, while soot in flame H10 ( $T_{max} = 1764$  K) is near the maximum and is continuing growing. In contrast, at  $H_p = 0.6$  cm, even though the concentration of acetylene is higher in heptane flame H10 than that in a toluene-added flame, the soot volume fraction is still smaller, because soot nucleation dominates at this  $H_p$ . Similar results have also been reported by D'Anna et al. [48] in a laminar premixed *n*-propylbenzene/*n*-heptane flame.

Having examined the PSDFs measurements, we may take a look at the soot morphology. Representative TEM images for flames H10 and H10T10 at  $H_p = 1.2$  cm are shown in Fig. 7. The images for flames H10T2 and H10T4 at the same flame height can be found in the supplemental material. Since the diameter measured by SMPS is mobility diameter, whereas that obtained from TEM images is the diameter of the projected area of soot particles, the two types of diameter cannot be compared directly. In addition, the exact size dependency of the particle capture efficiency of the NAS is unclear. Nevertheless, the smaller particle sizes apparent for H10T10 are consistent with the PSDF measurements at  $H_p = 1.2$  cm. Furthermore, we may also examine the shapes of aggregates, which have been categorized into four types: spheroidal, ellipsoidal, branched, and linear. Details about the classification method can be found in [49]. The latter two are regarded as more complicated shapes than the former two because they have bigger surface areas. More spheroidal and ellipsoidal soot aggregates can be observed in flame H10. A most likely speculation for such a trend is that the continuous newly-formed incipient soot particles collide with large soot aggregates and fill the voids. By use of Image-Pro Plus software, a total of approximately 500 primary particles in about 100 aggregates were analyzed. It is clear that the primary particle diameters  $(d_{pp})$  of soot aggregates follow a normal distribution as shown in Fig. 8, with a fitting median diameter of 17.6 and 7.54 nm



**Fig. 7.** Selected TEM images of the soot particles from H10 (top panel) and H10T10 (bottom panel) flames at  $H_p = 1.2$  cm burner-to-stagnation surface separation distance.



**Fig. 8.** Normalized primary particle size distribution of soot aggregates from H10 (top panel) and H10T10 (bottom panel) flames. Lines are Gaussian fits of the data.

for flames H10 and H10T10, respectively. Moreover, the geometric standard deviations  $\sigma$  of the normal distribution for the two flames are 3.69 and 1.72 nm respectively, indicating a broader size distribution of the primary particles for flame H10. All of these could be caused by the higher concentration of acetylene promoting particle surface growth, or the coagulation of bigger particles with newly-formed small particles from continuous nucleation in the pure *n*-heptane flame (H10).

In this study, experimental measurements of PSDFs, flame temperature, and soot morphology were performed to investigate soot formation characteristics of pure *n*-heptane and binary mixtures of toluene and *n*-heptane using BSSF setup. Detailed kinetic modeling of the BSSF using a combustion reaction model was carried out for understanding the experimental observations. Based on the experimental and numerical results, we can draw the following conclusions:

- 1. At smaller burner-to-stagnation surface separation distances, the concentrations of aromatics such as benzene and pyrene are enhanced notably due to the addition of toluene. However, the concentrations of aromatics grow continuously with the increase of  $H_p$  in the pure *n*-heptane flame. This is consistent with the rapid particle nucleation observed in the PSDFs of toluene-added flames, but stronger particle nucleation in pure *n*-heptane flame than in toluene-added flames at larger  $H_{p}$ .
- 2. The soot mass growth, indicated by soot volume fraction, is found to be very much positively related to acetylene concentration. The addition of toluene suppresses the formation of  $C_2H_2$ , which results in smaller soot volume fraction at larger  $H_{p.}$
- 3. Compared with the results of the binary mixture fuels of toluene and *n*-heptane, in the pure *n*-heptane flame, the size of the primary particles is bigger and the shape of the soot aggregates seems to be less complicated at larger  $H_p$ . This seems to be consistent with the observations of continuous particle nucleation and the faster surface growth rate induced by a larger  $C_2H_2$  concentration.

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#### Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.combustflame.2017.08. 022.

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