The Evolution of Soot Morphology in an Atmospheric Laminar Coflow Diffusion Flame of a Surrogate for Jet A-1

Mohammadreza Kholghy¹, Meghadad Saffaripour¹, Christopher Yip², Murray J. Thomson¹,*

¹ Department of Mechanical and Industrial Engineering, University of Toronto,
5 King’s College Road, Toronto, Ontario, M5S 3G8, Canada

² Department of Chemical Engineering and Applied Chemistry, University of Toronto,
160 College Street, Toronto, Ontario, M5S 3E1, Canada

* Corresponding author: Email: thomson@mie.utoronto.ca
Tel: 1-416-580-3391
Fax: 1-416-978-7753
Abstract

An experimental study is performed to investigate the evolution of soot morphology in an atmospheric laminar coflow diffusion flame of a three-component surrogate for Jet A-1. The Laser extinction measurement method and the rapid thermocouple insertion are used to obtain soot volume fraction profiles and temperature profiles respectively; thermophoretic sampling followed by transmission electron microscopy and atomic force microscopy is used to study the morphology of soot particles at different locations inside the flame. Soot formation on the centerline appears to be different from conventional models. Large liquid-like particles which are transparent at the wavelength of 623 nm are formed and grow up to a volume equivalent diameter of $d_p = 60$ nm at temperatures below $T = 1500$ K. When the temperature exceeds $1500$ K, carbonization or the transition from transparent phase to the mature agglomerated particles happens very fast, i.e. in less than 12 ms. The volume of the liquid-like particles just before the start of the carbonization process is about 5 times larger than the volume of mature soot primary particles. This significant size difference suggests that a large liquid-like particle does not transform into a single small soot primary particle. In addition, multiple dark nuclei can be observed in the liquid-like particles prior to carbonization. The significant size discrepancy and the presence of multiple dark nuclei may indicate that primary particle formation and agglomeration happen inside the liquid-like particles on the centerline. In contrast to the centerline, on another streamline with significantly different temperature history, soot particles form from relatively small liquid-like particles. These particles have the same size as mature soot primary particles. Carbonization happens early on the streamline. A single dark nucleus grows inside each liquid-like particle and primary particles agglomerate after carbonization is finished. Most of the currently used computational soot models assume a single evolution process for all of the streamlines inside the flame which may not be an accurate assumption. This study shows that soot evolution processes can be different across the flame and may be a function of the temperature history of the particles.

Keyword: Soot morphology, PAH, Jet A-1 Surrogate, Kerosene, Laminar coflow diffusion flame
1. Introduction

Soot is often an undesirable combustion product with harmful environmental and health effects [1] that impedes the efficient use of hydrocarbon fuels in transportation engines [2, 3, 4]. Soot formation and evolution consist of complex and concurrent physical and chemical processes, including fuel pyrolysis, polycyclic aromatic hydrocarbon (PAH) formation, particle inception, coagulation, particle coalescence, surface growth, carbonization, agglomeration and oxidation which all occur over a few milliseconds [1, 5, 6, 7, 8]. Knowledge of the size and the morphology of soot precursors and mature soot particles and the transformation of fuel molecules to fully developed solid soot aggregates is extremely important for the understanding of the process of soot evolution and developing accurate computational models [1, 9, 10]. The particle evolution process is not yet completely understood [6]. Solid soot particle inception [8, 10, 11, 12] and the transition from spherules to fractal soot aggregates [13] are the least understood steps. These two steps have significant influence on the final soot particle nanostructure, size distribution and soot aggregate structure which have recently became the main focus of several studies [14].

While there are several studies performed with different combustion configurations such as shock tubes, flow reactors, and premixed flames [8, 15, 16], the study of soot evolution in a steady laminar coflow diffusion flame is of special interest [4] because such a type of multi-dimensional flame represents a simpler version of complex practical flames [17], has all of the physical and chemical processes that affect soot [18], and is relatively simple to model numerically [18, 19].

The thermophoretic sampling technique was used by Dobbins and Megaridis [3] to study soot morphology in a laminar coflow ethane diffusion flame. Transmission Electron Microscope (TEM) analysis of the collected soot samples from different locations inside the flame revealed highly rigid soot aggregates composed of partially merged primary particles, with relatively uniform sizes. The primary particle size increases as the particles move toward higher heights in the flame before the oxidation process starts. Intense particle inception and coagulation in low heights of the flame were suggested to broaden the size distribution and decrease the number concentration of the aggregates, respectively. At intermediate heights of the flame, surface growth becomes dominant and results in material deposition on the exposed surfaces of the primary particles.

Interaction of precursors prior to the formation of the first primary particle were studied by Dobbins in [20] and Graham [15]. It was concluded that nanometer size precursor particles, consisting of polycyclic aromatic hydrocarbons (PAHs), undergo coalescence collisions forming larger singlet particles
rather than chained aggregates irrespective of their liquid-like or solid nature. Meanwhile, it was noted in other studies that high reactivity of young solid particles results in continued surface growth that eliminates asymmetries caused by noncoalescent collisions [21]. As a result of this argument, no aggregates will form during the early stage of soot formation because all collisions are either coalescence or result in single spherical particles because the surface reactions ultimately eliminate asymmetries caused by noncoalescent collisions. This mechanism is shown in Figure 1.

Figure 1. The evolution of young soot particles as suggested by [15] and [20].

Transparent particles with nonuniform sizes were reported by Koylu et al. [2] in a laminar coflow ethylene diffusion flame. Two types of soot with different appearances were observed in the coflow flame: (1) Single translucent precursors with nonuniform sizes at lower flame heights, and (2) carbonaceous aggregates with mono-dispersed spherical particles joined together at higher flame heights. It was suggested that agglomeration starts before precursor particles are fully carbonized. As a result, the coagulation of precursor particles leads to the formation of clusters instead of complete coalescence. In other words, aggregate formation starts in early stages of soot formation. This mechanism, as depicted in Figure 2, is different from Dobbin’s suggested mechanism because first it does not consider complete coalescence of premature particles and second, surface reactions do not eliminate asymmetries caused by partial coalescence in this mechanism. As a result of Koylu’s mechanism, soot aggregates are expected to appear much sooner than in Dobbin’s suggested mechanism.

Figure 2. The evolution of young soot particles as suggested by [2].

Agglomeration of premature particles before their complete carbonization was also suggested by Vander Wal [22]. The chainlike structure of the premature soot aggregates (tarlike substance) in inverse diffusion flames (IDF) was considered as a sign of early agglomeration. As shown in Figure 2, IDF studies showed that young soot particles do not coalesce to form a single large particle. However, TEM
analysis of normal diffusion flame (NDF) samples revealed a different soot evolution process from those of IDF and [2]. In NDF, coalescence of PAHs was observed to form highly crystalline soot precursor particles that agglomerate later. Consequently, in NDF experiments, aggregate formation started after solid soot primary particles were formed (Figure 3).

Agglomeration after complete carbonization was also suggested by Lahaye [10]. In high temperature regions of the flame, i.e. \( T > 1300 \text{ K} \), PAHs change continuously by dehydrogenation and gradually form mature soot particle from the “transparent” particles [23]. As a result of this argument, the internal rearrangement of a partially aromatic polymeric structure, rather than continued formation of very large PAH structures, is considered as a mechanism for soot inception [23]. First, a multitude of particles is produced. Then, larger spherical particles appear by the collision or growth of small particles. Finally, aggregates are formed by the agglomeration of the spherical particles. A schematic of this evolution process is provided in Figure 3.

![Figure 3](image)

Figure 3. Representation of the evolution of soot particles as suggested by Lahaye [10].

A completely different mechanism for solid soot inception and agglomeration was proposed by Reilly et al. [6]. Aggregate formation within the large PAH-containing particles was observed to better describe the evolution of particle morphology in diffusion flames. Agglomeration of individual mature spherules after carbonization was rejected because large PAH-containing particles should break down into small particles before carbonization and agglomeration. Very fast transformation from PAH-containing soot to mature soot aggregates and the insolubility of individual soot spherules in the PAH-containing media enables the carbonization of mature soot particles within the PAH-containing transparent particles. As a result, a large number of spheroidal soot particles form inside the transparent medium. Consequently, large PAH-containing transparent particles transform to mature soot aggregates with the same size. See Figure 4.
The goal of the present work is to provide insight into the evolution of soot morphology at the particle level on different streamlines of a laminar, atmospheric pressure, coflow, diffusion flame of a Jet A-1 surrogate. Mature soot inception and the transformation of liquid-like transparent particles to fully aggregated solid soot particles were studied in the flame. Morphology of soot particles were tracked along two streamlines with significantly different temperature profiles in the flame and were compared to Figure 3 and Figure 4 to evaluate the validity of the two suggested mechanisms. The two main goals of the present study are: (1) to investigate the transformation process of precursor liquid-like particles to fully carbonized solid soot aggregates along the flame centerline at the particle level, and (2) compare the centerline soot evolution process with those of other streamlines within the flame.

A three component surrogate for Jet A-1 which is a kerosene-type jet fuel commonly used in civilian turbine-engine powered aviation was used to perform the experiments. The thermophoretic sampling technique followed by Transmission Electron Microscope (TEM) analysis and Atomic Force Microscopy (AFM) were used to study the morphology of soot particles at various locations inside the flame. TEM images show a two dimensional representation of soot particles and can reveal some three dimensional morphology characteristics of the aggregates [9]. However TEM images are not useful to analyse liquid-like particles sampled from fuel rich locations inside the flame. Consequently, in the current study, the AFM method is used to obtain the 3D topological maps of the particles while statistical analysis of TEM pictures is used to yield important 2D morphological characteristics of mature and liquid-like soot particles. The ability of AFM technique to reveal the 3D particle morphology was proved in several studies before [24, 25, 26]. Laser extinction measurement and rapid thermocouple insertion techniques are also used to obtain soot volume fraction and temperature profiles, respectively, inside the flame. Temperature and soot volume fraction profiles in combination with TEM pictures are used to find the temperature and location corresponding to the onset of the carbonization (solidification) of precursor liquid-like particles. Detailed soot modeling [27] is used to provide information on the fluid streamlines and particle temperature history within the flame.
2. Experimental Methods

2.1. Burner Setup, Flame Description and Surrogates

A coannular burner is used to experimentally study an atmospheric pressure laminar diffusion flame of Jet A-1 surrogate. The burner consists of a 10.90 mm inner diameter (ID) fuel tube and a concentric 90 mm ID air annular. The flame is protected from lab drafts by a clear acrylic chimney with 152.4 mm ID which has access holes for the thermophoretic sampling probe, the thermocouple and the laser beams. The burner can be traversed in horizontal and vertical directions to accurately adjust the sampling location. Additional details and a schematic of the burner setup can be found in [28].

In order to vaporize the surrogate fuel, a W-102A Bronkhorst vapor delivery system is used. To lower the required temperature for vaporization, fuels are highly diluted with nitrogen. The fuel is mixed with the diluent and vaporized at 463 K. To reduce flame lift-off, the coflow air is heated to 423 K using an inline air flow heater and additional oxygen with a flow rate of 0.19 kg/h is added to the air stream to enable high dilution of the fuel stream without increasing the flame lift-off. Heated tubes maintained at 500 K are used to transfer the vaporized fuel to the burner without condensation. Moreover the last two inches of the fuel tube are heated to 473 K using thin flexible Minco heaters to avoid fuel condensation at the fuel tube exit. The fuel and carrier gas (N₂) flow rates are 0.0143 kg/hr (±2%) and 0.81 l/min (± 5%, at 293 K), respectively, set by Bronkhorst digital flow controllers. To prevent potential inaccuracies of the fuel flow meter, the fuel flow rate is monitored continuously by measuring the weight of the fuel container using a high precision scale connected to a computer for data acquisition. The flow rate of the coflow air is 55 l/min at 294 K. The temperature of the fuel at the burner tip is 450 k (± 3%)

A three component surrogate mixture is used in the current study for Jet A-1. The surrogate blend composition is shown in Table 1. The surrogate mixture is proposed by Dagaut and coworkers [29] and has been used previously for numerical modeling studies in this laboratory [27, 30]

Table 1. Composition of the Jet A-1 surrogate.

<table>
<thead>
<tr>
<th>Component</th>
<th>MW</th>
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<th>Mass%</th>
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<td>Propylcyclohexane</td>
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2.2. Thermophoretic Sampling

Thermophoretic Sampling (TS) technique is used to extract representative soot samples for subsequent Transmission Electron Microscopy (TEM) [2] and Atomic Force Microscopy (AFM) analyses. The sampling instrumentation consists of a 50 mm stroke double-acting pneumatic cylinder
controlled by two two-way high flow rate solenoid valves, and a programmable logic controller (PLC). The sampling grid is held by the TS probe which has two strips of stainless steel with the dimensions of 0.3x5x40 mm and 0.3x5x37 mm. The probe is aligned parallel to the flow field and is kept far from the flame before insertion to prevent heating. Transit and exposure times are measured with a 30 mW He-Ne laser and two detectors. Two laser beams five millimetre apart pass through the flame. The TS probe blocks the beams as it traverses radially through the flame. Transit times were less than 5 ms while grid exposure times varied between 30 ms and 100 ms to have less than 20% of grid coverage [3]. Sampling grids are carbon-supported 3.05 mm diameter TEM grids (CANEMCO-MAVIRAC, 200 mesh Carbon coated standard square copper girds, Cat # 182, and 200 mesh Carbon coated thin bar hexagonal copper girds, Cat # CFTH200-CU). Hexagonal mesh grids were used to have the maximum area of specimen available for viewing under the microscope [31] and also to easily adjust the orientation of the grids relative to flow field for subsequent TEM analysis. Sampling locations were on the centerline of the flame at different heights and on a streamline passing through the radial position of peak soot volume fraction at \( Z = 50 \) mm. Streamline coordinates were calculated using a computational model developed previously in our research group [27]. The goal was to compare the particle morphology of the specified streamline with that of the centerline. The center of the grid was exposed to the desired location inside the flame using the procedure suggested by [2] to obtain a reasonable spatial resolution. Sampling coordinates inside the flame were chosen to cover all of the selected streamline in order to track the evolution process of soot.

2.3. TEM and Image processing

Samples were examined using a Hitachi H-7000 TEM operating at an accelerating voltage of 100 kV. The images are analyzed using the ImageJ software. Primary particle diameters were obtained by measuring the diameter of at least 300 of them manually in high-magnification images (30,000 times). An ellipse was fitted to the primary particle by detecting apparent outlines near the edges [32], and the measured area was converted to diameter using the area equation of an equivalent circle [33]. The calculated diameters were averaged. To determine the number of primary particles per aggregate, \( N \), 8000 to 10000 aggregates were analyzed in low-magnification images (5,000 and 7,000 times). The grayscale TEM images were filtered to reduce noise and then thresholding was applied to obtain a binary image [33]. In this study, the filtering and thresholding of each TEM picture was done manually based on operator’s judgment. \( N \) was determined using the empirical relation suggested in [2] which involves aggregate projected area \( A_a \) and spherical primary particle cross-sectional area \( A_p = \pi d_p^2/4 \).

\[ N = k_a \left( \frac{A_a}{A_p} \right)^\alpha \]

Equation 1

where \( k_a = 1.15 \) and \( \alpha = 1.09 \) [34].

Manual thresholding was also used to determine the boundaries of the transparent and dark regions. The right panel of Figure 5 shows a TEM image of liquid-like soot particles sampled from the flame centerline. On the left panel of Figure 5, manual thresholding was applied to the original picture to determine the ratio of dark to transparent areas.

![Figure 5. Detection of liquid and solid boundaries using ImageJ.](image)

2.4. Atomic Force Microscopy

Atomic Force Microscopy (AFM) is an imaging technique to obtain the 3-D topological maps of particles, with a similar resolution as that of TEM [24]. AFM can reveal the height and the base diameter of flattened liquid-like particles, but as illustrated in Figure 6, the needle’s tip cannot follow the outer edge of spherical solid particles. As a result, AFM should be used with another imaging technique such as TEM to estimate the volume of solid soot primary particles. On the other hand, the AFM technique can be used to estimate the volume of flattened liquid-like soot particles with good accuracy.

![Figure 6. Differences between the AFM section analysis of liquid-like and solid soot particles.](image)
In this experiment, all images were acquired by intermittent-contact mode in air using TESP diving board cantilevers with integral pyramidal tips on a Digital Instruments Multimode AFM equipped with an E-scanner, a Nanoscope IIIA controller and using version 5.12a of the Nanoscope software. The cantilevers were oscillated at a drive frequency of ~ 361 kHz. Images were acquired as 512 x 512 pixel data sets at a scan rate of 1 Hz. All images were post-processed with a 2nd order plane fit and zero-order flatten filters.

2.5. Soot Volume Fraction and Temperature Measurements

Radial profiles of soot volume fraction and temperature at different flame heights were experimentally obtained previously [27], using the Line of Sight Attenuation (LOSA) method and the Thermocouple Rapid Insertion method [28] respectively. In addition, the volume fractions of particles in selected locations inside the flame where liquid-like transparent particles are present were obtained using Thermophoretic Sampling Particle Diagnostic (TSPD) method [2] because LOSA is not capable of detecting transparent liquid-like particles found on the flame centerline. In this study, AFM pictures are also used with TEM images to improve the accuracy of TSPD method to measure the volume fractions of liquid-like soot precursors. The ability of AFM to measure 3D morphological character of nonspherical particles are used to estimate an equivalent spherical diameter for amorphous liquid-like particles attached to the sampling grid [25]. The soot volume fraction (in parts per million, ppm) can be calculated using Equation 2 [2]:

\[ f_v = 0.78 \xi \frac{d_p^{0.82} \sum_i A_i^{1.09}}{t_e A_{ag}} \]  

Equation 2

where \( d_p \) is the primary particle diameter, \( t_e \) is the sampling time, \( A_i \) is the unit image area and \( A_{ag} \) is the aggregate projected area. \( \xi \) is calculated using equation 3:

\[ \xi = 1.95 \times 10^5 \left( \frac{(T_g + T_w)/(u_g x)}{T_g} \right)^{1.65} x \left[ 1 - \frac{T_w}{T_g} \right]^2 \]  

Equation 3

where \( T_g \) is the gas temperature, \( T_w \) is the sampling probe wall temperature and is roughly equal to 350K [2], \( u_g \) is local gas velocity estimated using a detailed numerical model developed in our group [27] and \( x \) is the distance between the center of the sampling grid and the lower edge of the sampling probe which was 3 mm in this experiment. The required information for TSPD method is listed in table 2.
Table 2. Information used for TSPD calculations

<table>
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<th>Radial position (mm)</th>
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<th>$d_p$(nm)</th>
<th>$t_e$(ms)</th>
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3. Results and Discussion

3.1. Soot evolution on the centerline of the flame

Formation of large liquid-like particles with several dark nuclei inside them can be observed on the centerline. Figure 7 shows TEM images of soot particles sampled thermophoretically at $Z = 30$ mm to $70$ mm on the centerline of the coflowing laminar diffusion flame of the Jet A-1 surrogate. Particles sampled below $Z = 60$ mm, have liquid-like appearances and are partially transparent to the electron beam. Liquid-like structure for soot particles were previously observed in other flame configurations as well [35]. Initially, there are poly-dispersed, single, transparent, spherical particles present in low regions of the flame, i.e. at $Z = 30$ mm. At $Z = 40$ mm, larger transparent particles can be observed. While some of the particles have a small black nucleus immersed inside them, most of them do not have the nucleus at this height. However, the particles gradually become more opaque to the electron beam. At $Z = 50$ mm, very large tarlike particles with several black nuclei are observed. The presence of single small transparent particles at $Z = 50$ mm implies that the inception of young soot is still occurring. At $Z = 50$ mm on the centerline very large particles can be seen which suggest high particle size growth. The size growth may be the result of either PAH condensation, HACA growth or coagulation followed by coalescence.

Contamination from the annular region is not expected to significantly affect the centreline images. Transit times of the sampling grids were much shorter than the exposure times. Also the flame of this study was not a heavily sooting one. Consequently, the number of particles/aggregates collected from the annular regions at low flame heights are limited [2] when the sampling is performed on the flame centerline. The small black nucleus immersed in the liquid-like particles are unlikely to be contamination from the annular region of the flame because their diameter is significantly smaller than the fully developed soot particles in the annular region.
Aggregates of mature soot particles appear from $Z = 60$ mm on the centerline. At these heights, there is no sign of liquid-like particles anymore. Most of the particles are in large clusters with uniform diameters. Small aggregates and even single solid primary particles can still be found.

![Figure 7. TEM images of soot particles sampled along the flame centerline. The dimensions of the schematic are not real.](image)

The location of mature soot formation can also be determined by measuring the centerline temperatures. Mature soot formation causes an increase in the radiated heat from the flame and can
change the local temperature significantly. As previously mentioned, black mature soot start to form from liquid-like particles near \( Z = 50 \) mm on the centerline (see Figure 7) and fully carbonize up to \( Z = 60 \) mm. Figure 8 shows that the centerline temperature constantly increases up to \( Z = 50 \) mm. Between \( Z = 50 \) mm and \( Z = 60 \) mm the temperature reaches a plateau and remains almost constant. The reason is the higher emissivity of mature soot particles at \( Z = 60 \) mm compared to the transparent liquid-like particles at lower flame heights. The higher emissivity significantly increases radiated heat from the particles. Radiated heat continues to increases after \( Z = 60 \) mm as soot volume fraction goes up. However, based on model predictions [27], the CO concentration decreases significantly at \( Z = 60 \) mm which results in substantial heat release that overcomes the increasing radiated heat from the soot aggregates.

![Figure 8. Centerline temperatures at different axial locations of the flame.](image)

Carbonization of transparent liquid-like particles happens very fast once initiated. While the transparent phase is dominant before \( Z = 60 \) mm where \( T < 1500 \) K on the centerline, all of the particles are fully carbonized at \( Z = 60 \) mm. Figure 9 shows more detailed TEM images of soot sampled on different grids along the centerline between \( Z = 48 \) mm and \( Z = 60 \) mm with 2 mm height differences. Liquid-like transparent particles with detached nuclei immersed inside them are present up to \( Z = 54 \) mm. By moving two millimeters higher, at \( Z = 56 \) mm, all of the transparent particles disappear and aggregates with similar dimensions as previous liquid-like particles can be seen. However primary particles are not circular, do not have clear boundaries and are semi opaque. The transformation from transparent phase to mature soot happens within a residence time of about 0.12 ms on the centerline when temperature exceeds 1500 K.
Based on Figures 7 to 8, the three important zones of soot formation on the centerline are: (1) liquid-like particle inception zone where the temperature is between 1100 K and 1400 K and particles are usually transparent and single; (2) solid soot inception zone where the temperature is around 1500 K and small solid nuclei immersed in the liquid-like phase can be observed; and (3) fully carbonized mature soot aggregate zone where the temperature is higher than 1500 K and only solid carbon particles are present.

3.1.1 Effect of Sampling Time on the Morphology of Liquid-like Particles

Sampling time can have a significant effect on the appearance of transparent particles on the sampling grid. If particles collide on the grid, thermophoretic sampling could be misleading. Hence, sampling was performed in the transition region, i.e. $54 \text{ mm} < Z < 56 \text{ mm}$, with an exposure time of 35 ms instead of 60 ms to investigate its effect on the shape of the particles as they appear under the microscope. Figure 10 shows more detailed TEM images taken from the bottom to the top of a single grid on the centerline. Comparison of Figure and Figure which has a longer grid exposure time (60 ms) indicates that some of the liquid-like particles attach to each other on the sampling grid. However, for sampling times of 35 ms large liquid-like particles with numerous nuclei immersed inside them are still present at $Z = 54 \text{ mm}$ in D.1. Circular particles in D.1 gradually develop aggregate shapes in the following images.

Figure 9. TEM images of soot particles sampled along the flame centerline at different height above the fuel tube exit.

![TEM images of soot particles sampled along the flame centerline at different height above the fuel tube exit](image-url)
Full aggregates can be observed in D.8. However, primary particles in the aggregates do not have clear boundaries. These pictures show that aggregate formation starts before the carbonization of single primary particles is finished. If the formation of aggregates starts after single solid soot primary particles are formed, then the primary particles should have distinct boundaries.

Figure 10. TEM images of soot particles sampled along the centerline of the flame between Z = 54 mm and Z = 56 mm on a single sampling grid. Pictures are taken from bottom to top of the carbon coated grid with a magnification of 5000x.

The rapid formation of large aggregates from the transparent phase suggests that aggregate formation may happen inside the transparent particles as Reilly et al. suggested [6]. The rapid phase change of the particles shows an increase in the carbonization rate of soot particles after Z = 50 mm. Figure 9 shows centerline soot volume fractions as measured by LOSA and TSPD at different flame heights versus the temperature. LOSA only measures solid soot volume fraction. However TSPD values include both solid and liquid-like soot volume fractions. Both techniques indicate that the rapid increase in the soot volume fraction on the flame centerline happens between Z = 40 and 50 mm where temperatures are around 1500 K, which is close to the carbonization temperatures reported in the literature [11, 20, 36].

The presence of liquid-like particles at lower flame heights on the centerline reveals that the inception of young soot particles happens much sooner than where LOSA with a wavelength of \( \lambda = 623 \) nm suggests. The onset of soot detection on the flame centerline by the TSPD method is at Z = 30 mm, where the soot volume fraction is 0.18 ppm and the temperature is around 1100 K. However, LOSA does not detect anything below Z = 50 mm. At Z = 50 mm, LOSA shows 0.5 ppm for soot volume fraction and
the temperature is about 1500 K. At this height, most of the particles are liquid-like and transparent to the laser light. However, black nuclei immersed inside the transparent phase cause light extinction. Figure 11 shows that LOSA (at $\lambda = 632$ nm) is not a good technique to measure the concentration of transparent particles. However, the TSPD is a powerful technique to estimate the concentration of these particles. On the other hand, TSPD usually underpredicts the concentration of mature soot particles [2]. This problem may be resolved by reducing the grid exposure time which decreases the coverage of the sampling grid. Lower coverage prevents possible overlaps between the soot aggregates which directly increases the value of soot volume fraction measured by the TSPD method by increasing the $\frac{\Sigma A_i d_i^9}{r_e}$ term in equation 2. While the TSPD values are more reliable where transparent soot particles are present, LOSA is more accurate to measure the volume fraction of mature soot particles.

![Figure 9. Soot volume fraction (Fv) changes along the flame centerline vs temperature as measured by LOSA and TSPD.](image)

TSPD is a powerful diagnostics technique to measure the volume fraction of the transparent particles in the flame. This technique does not need any knowledge of the optical, physical and chemical properties of the particles [2]. However, using TEM images to calculate the volume of liquid-like particles can cause overestimation of their volume because these particles do not maintain their spherical shape upon their impact to the sampling grid [8, 25]. As a result, their projected area cannot be used to calculate their volume-equivalent diameter. Consequently, AFM measurements were used to enhance the accuracy of the TSPD technique. If we assume that a liquid-like particle attached to the surface has roughly a spherical cap shape, then the volume of the particle can be calculated using its height and projected diameter obtained from AFM analysis [25].

AFM images show that the transparent particles flatten after their impact on the sampling grid. Flattening of the particles suggests that they are liquid-like and far from being fully carbonized at the time of impact on the sampling grid [25]. Figure 10 shows AFM and TEM images of the particles on the
centerline. The presence of single large and small particles at $Z = 40$ mm implies that nascent soot formation is still happening at this height. Moreover, the sizes of the particles seem to have a bimodal distribution which suggests that the small particles rapidly coagulate and coalesce to larger particles after their formation [21]. Bimodality of particle sizes was also observed in low temperature regions of premixed flames [35]. At $Z = 50$ mm, most of the sampling grid is covered with non-circular liquid-like particles with a height range of 20 nm to 50 nm. The high coverage ($\approx 50\%$ based on TEM images) is due to two reasons: 1. Flattening of the liquid-like particles after their impact on the sampling, and 2. high grid exposure time which was calculated based on LOSA soot volume fraction. Because LOSA at $\lambda = 632$ nm underestimates soot volume fraction for transparent particles, the calculated exposure time is high. At $Z = 70$ mm, mostly mature aggregates can be observed. Primary particles with an average diameter of $d_p = 23$ nm at this height are considerably smaller than the liquid-like particles at $Z = 50$ mm with an average volume equivalent diameter of $d_p = 60$ nm. However, based on TEM images the size of primary particles at $Z = 70$ mm is comparable with that of the solid nuclei within the liquid-like particles at $Z = 50$ mm.
Figure 10. AFM and TEM images of soot particles samples along the flame centerline at different heights above the fuel tube exit. Note the different length scale of the middle TEM image. Note that the AFM and TEM images are not of the same particles but rather the same grids.

3.1.2 Accuracy of the TSPD method

The TSPD method can estimate the volume fraction of transparent particles using both TEM and AFM images. However it usually underestimates the volume fraction of mature soot particles [2]. Figure 13 shows soot volume fraction values measured by LOSA and TSPD. Separate calculations were also performed for only mature solid particles using TSPD. The trend of centerline soot volume fraction with increasing height measured by LOSA is well reproduced with the TSPD if only dark carbonized particles are considered. However, TSPD underestimates soot volume fractions at Z = 60 mm and Z = 70 mm up to
60%. If both solid and liquid-like particles are considered for the TSPD, the trend is completely different. Instead of gradually increasing to the peak value at $Z = 70$ mm (predicted by LOSA) the volume fraction increases significantly from $Z = 30$ mm, peaks at around $Z = 50$ mm, where the carbonization process starts and decreases to its final value of $F_v = 3.1$ ppm at $Z = 70$ mm. This early increase in the volume fractions measured by TSPD indicates that soot inception starts from very low heights on the centerline. However, as TEM images show in Figure 7, young soot particles are transparent to the laser light and LOSA cannot detect them. At $Z = 50$ mm, solid soot inception begins and solid particle grow very fast. However, the density ratio of liquid-like phase to solid soot is around unity and densification of liquid-like particle could not be the reason for the decrease in TSPD measured soot volume fraction after $Z = 50$ mm. In addition, relatively low temperatures ($\approx 1500$ K) eliminate the possibility of soot oxidation. As a result, the lower accuracy of TSPD in measuring the volume fraction of mature soot particles is accountable for the lower values of soot volume fraction at the upper two heights.

![Graph](image)

Figure 11. Soot volume fraction along the flame centerline versus axial position as measured by LOSA and TSPD

### 3.2. Soot evolution on an outer streamline of the flame

The centerline is a special streamline in a laminar coflow diffusion flame. Here the particles have the longest residence time and the temperature gradients are smaller than on the other streamlines. Figure 4 shows flame temperatures along different streamlines as predicted by the computational model of [27]. Although the model slightly overestimates temperatures along the flame centerline, its accuracy for temperature predictions at other flame locations is very good [27]. The solid line (C) in Figure 4 shows the temperature versus flame height along the centerline; the other three dashed lines (W30, W40, and W50) represent flame temperatures along the streamlines passing through the radial positions of maximum soot volume fraction at $Z = 30$ mm, 40 mm and 50 mm. The centerline temperature increases
gradually after \( Z = 16 \text{ mm} \). However on the other streamlines, the temperature increases sharply from \( Z = 0 \text{ mm} \). As a result, liquid-like particles on these streamlines have less time for growth because they pass the threshold temperature of carbonization (1500 K) much sooner than on the centerline. Because soot formation processes are a strong function of temperature [8], they might not be the same when the temperature histories of the particles are very different. Thus, soot particles should be studied on the different streamlines in the flame.

![Temperature along different streamlines versus axial location](image)

Figure 14. Temperature along different streamlines versus axial location

Effects of temperature history on the evolution of soot morphology are investigated by taking particle samples from the W50 streamline in Figure 14. Three important temperature regions for soot formation on the centerline were described in section 3.1.1. The same temperature regions were chosen on W50 for sampling. Particles were only extracted from \( Z = 30 \text{ mm} \) to \( Z = 50 \text{ mm} \) along the specified streamline because lower temperature regions on W50 are too close to the fuel tube for sampling. The temperatures are expected to be between 1400 K and 1750 K when \( 30 \text{ mm} < Z < 50 \text{ mm} \). This region appears to be the inception zone for solid soot particles based on temperature predictions of the model. Figure 125 shows the TEM images of soot particles sampled along the W50 streamline. Initially, transparent soot particles are present in low regions on the streamline. Solid soot nuclei grow within the liquid-like particles as they travel higher on the streamline. The first two TEM images in Figure 125 show the same evolution processes as particles on \( Z = 30 \text{ mm} \) and 40 mm on the flame centerline, shown in Figure 7. However, unlike transparent particles on the centerline which grow very fast to larger liquid-like particles, W50 streamline particles seem to carbonize first and then agglomerate. Early carbonization in low flame heights may be the reason for the different evolution processes. As Figure 125 illustrates, there are no large liquid-like particles on the W50 streamline. Instead, at \( Z = 40 \text{ mm} \) partially agglomerated particles can be observed. It seems that small nuclei in the liquid-like particle grow completely and then
particles agglomerate. At $Z = 48$ mm, fully developed aggregates composed of mature solid soot primary particles can be seen.

Figure 125. TEM images of soot particles sampled along W50 streamline

3.2.1 Primary particle and aggregate size

Comparison of the soot primary particle and aggregate sizes between the centerline and the other streamlines can also suggest different soot evolution mechanisms in the flame. Primary particle and
aggregate sizes are shown in Error! Reference source not found.. The particles were sampled at the locations of peak soot volume fraction (measured by LOSA) at different heights where only fully carbonized soot is present. Samples from $Z = 60$ and $70$ mm are on the centerline while the other three points at $Z = 30$, $40$, and $50$ mm belong to W30, W40, and W50 respectively (see Figure 14). As discussed previously, on the streamlines liquid-like particles have less time for growth and mature primary particles have more time for agglomeration (based on the conventional model suggested by Lahaye). On the other hand, on the centerline liquid-like particle have more time for growth and grow up to a volume equivalent diameter of $d_p = 60$ nm, and since carbonization happens late on the centerline, there is less time available for agglomeration of mature primary particles. Thus based on the conventional model, centerline aggregates should be smaller than those of the streamline but with larger primary particles. However, experimental results indicate that primary particle sizes on the centerline are much smaller than those on the other streamlines and centerline aggregates are significantly larger. Thus aggregates formation on the centerline cannot be only because of the coagulation of fully carbonized particles and is different from the other streamlines.

4. Conclusions

An experimental study was performed on the evolution of soot morphology in an atmospheric laminar, coflow diffusion flame of a three-component surrogate for Jet A-1. Two different soot evolution processes were observed on the flame centerline and on a streamline which passes through the radial position of peak soot volume fraction at $Z = 50$ mm in the flame. On the centerline, transparent liquid-like particles grow up to $d_p = 60$ nm. Several dark nuclei can be observed in the transparent particles before
carbonization starts. After passing through the threshold temperature for soot carbonization, i.e. 1500 K, large liquid-like particles rapidly convert to fully developed aggregates composed of mature primary particles. This evolution process appears to be similar to the mechanism suggested by Reilly et al. [6]. However large aggregates of mature soot primary particles do not completely form inside the transparent liquid-soot particles. Based on TEM images, it seems that small aggregates form inside the liquid-like phase and then attach to other aggregates to form larger ones. Moreover, formation of large aggregates inside the liquid-like phase may be impossible because if the transparent particles are liquid, the liquid surface tension and capillary forces make the aggregates compact and more squeezed [37]. However, for small aggregates these forces do not have significant effects.

It appears that soot particles have the same evolution process on the initial regions of the selected streamline (W50) and the centerline. However no large liquid-like particles were observed on the streamline. It appears that each liquid-like particle forms a single primary particles and agglomeration starts after all particles are fully carbonized. This evolution process is similar to the mechanism suggested by Lahaye [10].

Comparison of primary particles and aggregate sizes between the centerline and other streamlines also suggests that the evolution processes are different. On the centerline there is more time for primary particles growth and less time for aggregate growth. However, the conventional soot evolution model (Lahaye [10] ) cannot give a reason for the larger aggregates composed of small primary particles on the centerline.

5. Acknowledgements

Financial Support for this work was provided by the Natural Sciences and Engineering Research Council of Canada. The authors appreciate the help of Dr. Ilya Gourevich from the Center for Nanostructure Imaging at the University of Toronto for their help with TEM imaging and also helpful discussions with Professor Hai Wang from the University of Southern California.

6. References


