

External irradiation effect on the growth and evolution of inflame soot species

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External Irradiation Effect on the Growth and

Evolution of In-Flame Soot Species

Cheng Wang

A thesis in fulfilment of the requirements for the degree of

Master by Research



School of Mechanical and Manufacturing Engineering

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External irradiation-soot species interaction is a subject that is of great interest due to its existing and future use in research and industrial sectors. An assessment of the impact of broadband radiation on the evolution of soot species within a laminar ethyleneair flame is therefore performed to improve the fundamental understanding of the interaction process. Radiation at an average flux value of 120 kW/m² is provided by a solid-state plasma light to the lower region of the flame. Soot samples, thermophoretically collected at flame positions that are close and downstream from the irradiation location, are imaged using normal-resolution and high-resolution transmission electron microscopes (TEMs). The results, derived from processing the TEM images, reveal that the application of an external irradiation is found to increase the soot loading of the flame, and have a pronounced impact on the soot morphology, and influence the in-flame soot growth processes/mechanisms. The effects are also found to persist downstream from the irradiation location, with the soot precursors, for the configuration used.

Thermophoretic sampling, coupled with TEM imaging, is used to derive the required soot morphological data. The particulates characterization, however, can be complex when the images are of low contrast, noisy and have non-uniform background, or the samples collected have large variability in shape and size and have some degree of overlapping. A processing method that permits time-efficient automated characterization of particulates from the TEM grids, is therefore developed. The parameters required to be set to facilitate the automated process are identified and assessed. The proposed method is first applied to TEM images of samples acquired from the non-irradiated flame. The automated result is then compared with that derived via manual assessment, for validation purpose. The same analysis is also applied to samples extracted from the irradiated flame, which were previously observed to have different geometrical characteristics, to assess the morphological dependence of the proposed method. Using the optimized setting, the largest discrepancies associated with the automated results of primary particle diameter, fractal dimension and prefactor value of the aggregates for the tested cases, are approximately 3, 1 and 10%, respectively, when compared with the manual assessments.

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Abstract

External irradiation-soot species interaction is a subject that is of great interest due to its existing and future use in research and industrial sectors. An assessment of the impact of broadband radiation on the evolution of soot species within a laminar ethylene-air flame is therefore performed to improve the fundamental understanding of the interaction process. Radiation at an average flux value of 120 kW/m² is provided by a solid-state plasma light to the lower region of the flame. Soot samples, thermophoretically collected at flame positions that are close and downstream from the irradiation location, are imaged using normal-resolution and high-resolution transmission electron microscopes (TEMs). The results, derived from processing the TEM images, reveal that the application of an external irradiation is found to increase the soot loading of the flame, and have a pronounced impact on the soot morphology, and influence the in-flame soot growth processes/mechanisms. The effects are also found to persist downstream from the irradiation location. The effects are mainly attributed to coupling of the broadband irradiation with the soot precursors, for the configuration used.

Thermophoretic sampling, coupled with TEM imaging, is used to derive the required soot morphological data. The particulates characterization, however, can be complex when the images are of low contrast, noisy and have non-uniform background, or the samples collected have large variability in shape and size and have some degree of overlapping. A processing method that permits time-efficient automated characterization of particulates from the TEM grids, is therefore developed. The parameters required to be set to facilitate the automated process are identified and assessed. The proposed method is first applied to TEM images of samples acquired from the non-irradiated flame. The automated result is then compared with that derived via manual assessment, for validation purpose. The same analysis is also applied to samples extracted from the irradiated flame, which were previously observed to have different geometrical characteristics, to assess the morphological dependence of the proposed method. Using the optimised setting, the largest discrepancies associated with the automated results of primary particle diameter, fractal dimension and prefactor value of the aggregates for the tested cases, are approximately 3, 1 and 10%, respectively, when compared with the manual assessments.

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Chapter 1

Introduction

In this chapter, a brief outline of the research area is presented, leading to the motivation behinds this work. This is followed by the specific aims of this work and the dissertation layout.

1.1 Motivation

The interaction of externally-introduced radiation and soot species is a subject that is of great interest due to its existing and future use for research diagnostics, nanomaterial synthesis and energy generation applications. Some notable examples of the current applications that involve the coupling of soot and radiation include the laser-heating of soot particles for soot diagnostics, *i.e.* laser-induced incandescence (LII) [1-3] and nanomaterial synthesis [4,5]. In the implementation of the LII measurement technique [6–8], the soot particles are heated with a high-power laser pulse to induce incandescence. The magnitude and decay rate of the LII signal are used to provide the corresponding soot concentration and particle size distribution information [9]. In the context of the nanomaterial synthesis application, it has been demonstrated that an acetylene flame, when irradiated with a high-power continuous wave laser, can produce shell-shaped carbon particles with unique electrical properties that are well-suited for gas-storage and battery applications [4]. The interest in the radiation-soot interaction process is also motivated by its potential use in a hybrid solar receiver-combustor (HRC) [10-12] for energy generation. In a HRC, both the solar receiver and combustor are combined into a single device to reduce infrastructure investment and to achieve potential thermodynamic synergies [12]. The direct interaction of concentrated solar radiation with flame species would therefore occur in some operating cycles of the HRC, and therefore impact on the corresponding energy generation and emission performances [10,11]. Despite its increasing use in many applications, the physical and chemical mechanisms involved in the coupling of external irradiation and inflame soot species are still not well-understood [11]. An improved fundamental understanding of the interaction and coupling between the external irradiation and the in-flame soot species can therefore help to control and optimise the aforementioned processes to achieve more accurate diagnostic information, and better control in nanomaterial and power generation applications.

The coupling of radiation and soot species is a complex process that has an impact on the ensuing combustion processes. In a highly sooty flame, the radiative heat transfer from the flame due to black-body emission can result in a reduction in the peak flame temperature [13,14]. The change in the temperature can then affect other quantities that are temperature sensitive, such as the formation of NO_x , unburned hydrocarbons and also on soot generation itself [15]. Radiation, on the other hand, can be coupled with the combustion process through soot species and gas molecular absorption. For example, it has been reported fuel molecules can be stimulated to undergo oxidative or pyrolysis reactions to promote or suppress soot formation, when sufficient radiative heating is present [11]. Whilst the importance of soot-radiation interaction is well-recognised with considerable effects undertaken towards understanding it, previous work has largely focused on the coupling of soot processes with the natural radiation from the flame itself (*e.g.*, [14,16,17]). Less effort has been made towards extending the understanding of the interaction between externally introduced irradiation and soot species [11], which is the focus of the present work.

Externally introduced irradiation can interact with a flame either through molecular excitation, direct and indirect soot species absorption, or both [11]. The strength of the interaction process is therefore dependent upon the spectral properties of both the incoming radiation and also the species that the radiation is interacting with. For example, it is known that the soot precursors

first only absorb in the ultraviolet (UV) region [18–20] and their optical absorptivity extends into the visible region as they grow and evolve [21,22]. Carbonised mature soot particles, on the other hand, behave like black-bodies and are capable of absorbing over a wide spectrum [11,18]. Previous studies have demonstrated that the attenuation of the incoming radiation can be significant when its wavelength overlaps with the absorption spectrum of the soot species that it is interacting with [18–20]. The strength of the interaction process is also affected by the concentration of the species that are present. For example, whilst gas molecules such as water, oxygen and carbon dioxide have been reported to have low absorption coefficients [23,24] in the UV to visible regions, a recent computational study has demonstrated the molecular-gas radiation effects can still impact on the local temperatures, when the gases are present in sufficient quantity [15]. When assessing the impact of external irradiation on soot species, it is therefore important that the influence of different mechanisms are effectively isolated or taken into account, as is the approach of current work.

There are a number of investigations that have been conducted to assess the external-irradiation induced changes in the soot or flame properties. It is noted that the irradiated flame height were typically varied in these studies (*e.g.*, [5,11,25]) so that specific flame or soot species, which were present in abundance at the corresponding irradiated positions can be targeted for detailed assessment. In these studies, pulsed or continuous-wave monochromatic laser were typically used as the high-power external irradiation sources, as the collimated single-wavelength laser beam outputs can be shaped and directed easily [5,11,25–27]. The locations of irradiation sources relative to their flames can therefore be varied and positioned accurately to suit the objectives of their studies. A recent study [10], which is still in its early stage of development, was performed to understand the coupling process between an externally introduced broadband high-flux irradiation and a laminar flame. In the study, a custom-built solar simulator [28,29], which comprised of an array of metal halide lamps coupled with ~ 1 m diameter elliptical reflectors, was used as the light source. It was shown that the maximum soot concentration

within the flame was enhanced when external broadband radiation was introduced. The solar simulator used, nonetheless, has a large uncollimated output beam with a diameter of ~ 50 mm and therefore cannot be conveniently used to target specific flame regions/species, for detailed assessment. It is also noted that the focus of the study was to investigate the influence of the externally introduced broadband irradiation on the structure and distribution of in-flame soot species using LII. No analysis of the morphological structure of the ensuing in-flame soot particles, which is useful to provide insights to their evolution and growth [30], was performed.

There are many techniques for soot diagnostics, both intrusive and non-intrusive, which are employed by the research community [31–33]. However, the thermophoretic sampling of soot coupled with transmission electron microscope (TEM) imaging remains the only method that permits a direct observation of soot morphological information. The soot morphological information is useful to the combustion research community as it provides important insights to the formation and evolution of soot particulates in different combustion conditions [30,34–37]. The combined thermophoretic and TEM imaging approach is therefore used for this work. The identification and the measurement of the soot particles from the TEM images, however, can be complex as the soot TEM images are typically of low contrast, noisy and have non-uniform background signal level due to the nature of the TEM imaging process [38]. Additionally, the processing of the TEM images, which mainly proceeds through direct manual assessment, can be challenging and time-consuming as the soot samples have some degree of overlapping, in addition to having large variability in shape and size, even when they are collected from the same combustion environment [35,39]. A large number of TEM images would therefore need to be processed manually for statistically meaningful quantities to be generated. There are several studies in the literature that are aimed at developing automated methods to detect and categorise objects from images [38,40–43]. Many of these automated methods, however, were not specifically developed for soot TEM image processing and therefore not directly applicable. There is therefore a strong motivation to develop an automated method to reduce manual labour,

whilst ensuring that reasonably accurate soot morphological information are still extracted from the soot TEM images, which is another aim of this work.

1.2 Aims

In light of the aforementioned gaps in knowledge, the primary aim of this work is to investigate the impact of the coupling between the external broadband (ultraviolet to visible regions) irradiation and the soot precursors on the in-flame soot growth and evolution processes, through the analysis of thermophoretically sampled soot samples that are imaged using transmission electron microscopes (TEMs). The secondary aim of this work is to develop an automated image processing method to facilitate automatic detection of soot morphological information, from the soot TEM images obtained.

1.3 Dissertation Layout

This dissertation consists of six chapters. Following this chapter, Chapter 2 presents a review of the background literature related to this work. A critical review on the subject of the coupling between external irradiation and flame is presented, whereby the literature review confirms that the current understanding of the interaction between external irradiation and soot species, in particular its impact on the growth and evolution of in-flame soot species, is inadequate and requires further investigation. The background information of the thermophoretic sampling and transmission electron microscope (TEM) imaging technique, which are used in this work to derive the soot morphological information required to understand the effects of external irradiation-soot species interaction, is also presented. The technical issues concerning the techniques are described, and the need to develop an automated method to assist with the morphology information extraction process from the soot TEM images is highlighted.

Chapter 3 describes the experimental apparatus and setup used for this work. The technical details of the data acquisition and analysis, in addition to the image processing procedures used are provided as well.

Chapter 4 addresses the first aim of this work. The uncertainties associated with the thermophoretic sampling system and process were first established to give confidence to the validity of the subsequent results obtained using the sampling system. The soot samples were then thermophoretically sampled, using the same sampling system, from different flame regions of a non-irradiated flame (NI-flame) and an externally-irradiated flame (I-flame). The soot morphological data derived from soot samples acquired from the flames were compared to provide important insights into the evolution and growth process of the soot particles, in the absence and presence of external irradiation.

Chapter 5 presents the development of a novel three-stage image processing sequence to facilitate time-efficient automated identification and detection of soot particles from soot TEM images, to address the second aim of this work. The soot samples that were acquired from the NI-flame and I-flame, which have different geometrical characteristics, were used to develop and validate the automated algorithm presented.

Chapter 6 presents the conclusion and recommendations for future work.

All work presented in this thesis has been published in archival scientific journals and conference proceedings (details provided in Appendix C).

Chapter 2

Literature Review

In this chapter, the background literature that is relevant to the understanding of the external irradiation effect on the growth and evolution of in-flame soot species is presented and discussed.

2.1 Flame-Radiation Interaction

The coupling of radiation and soot species is a complex process that has an impact on the ensuing combustion process. Radiation, when absorbed by the flame species, can be used for the overcoming of the activation energy barriers of combustion processes, which are previously inhibited due to energetics. Similarly, radiative losses from flame can result in a drop in flame temperature, and therefore retard reactions that are previously temperature-enabled. For example, in a highly sooty flame, the radiative heat transfer from the flame due to black-body emission can result in a reduction in the peak flame temperature [13]. The change in the temperature can then affect other quantities that are temperature sensitive, such as the formation of NO_x [44], and unburned hydrocarbons (UHCs) [45]. For example, the formation of thermal NO_x proceeds through the high-temperature reaction of nitrogen and air. The reaction rate of the process is primarily dependent on the temperature of the process, in addition to the residence time of the nitrogen at the temperature. A change in flame temperature would therefore significantly impact on the generation of NO_x during combustion.

The in-flame soot processes such as nucleation, coalescence, surface growth and agglomeration are also temperature dependent [46]. For example, in a previous study that was conducted by

Vander Wal *et al.* [47], it was reported that the formation of growth of polycyclic aromatic hydrocarbons (PAHs) are favoured at low flame temperature of 1250°C. The manner in which the PAHs can be added onto the potential sites on the soot surface, however, is restricted as many of the sites are inactive at such low temperature. This results in the formation of very amorphous soot with randomly orientated, discontinued inner-structure. The decomposition of PAHs into smaller species, such as C_2H_2 , however is reported to be favoured at a higher flame temperature ~ 1650 °C. The mass growth process through the addition of smaller molecular species, coupled with the availability of more surface sites, therefore result in the formation of more structurally ordered soot.

Whilst the importance of the coupling between flame and radiation is well-recognised with considerable efforts undertaken towards understanding it [16,17], previous studies have mainly focused on the interaction between the combustion processes and natural radiation generated from the flame itself. To date, few studies have extended the understanding towards the interaction between the externally introduced radiation and in-flame soot species, despite its increasing use in many research and industrial applications [11].

2.2 External Irradiation and Soot Species Interaction

The interaction of externally introduced radiation and soot species is a subject that is of great interest due to its existing and future use for research diagnostics [1–3], nanomaterial synthesis [4,5] and energy generation applications [10–12]. Some notable examples of the current applications that involve the coupling of soot and radiation include the laser-heating of soot particles for soot diagnostics, *i.e.* laser-induced incandescence (LII) and nanomaterial synthesis. In the implementation of the LII technique, the soot species are heated by a high-power laser pulse from the local ambient temperature to the soot sublimation temperature (~ 4000 K) [6–8]. The incandescence from the soot particles, resulting from the laser heating, subsequently is

measured using collection optics and photodetectors. With appropriate calibration, the corresponding information on soot volume fraction and particle size distribution can be derived from the magnitude and the decay rate of the LII signal [9]. In the context of nanomaterial synthesis, previous studies have shown that the direct application of high-power continuous wave laser to acetylene can result in the formation of hollow carbon materials with high crystallinity. Such crystallined materials possess unique electrical properties that are well-suited for applications such as intercalation materials for Li batteries, gas-storage media, cold-electron field emitters [4].

The interest in the radiation-soot interaction process is also motivated by its potential use in a hybrid solar receiver-combustor (HRC) for energy generation application [10–12]. The HRC concept has seen significant interest due to its potential to offer significant economic benefit through reduced infrastructure investment and thermodynamic synergies. In a HRC, both the solar receiver and combustor are integrated into a single device, that is, the flame burns within the same cavity used to collect concentrated solar radiation from the solar receiver [12]. The simultaneous introduction of both the concentrated solar radiation (CSR) and combustion into the same device permits the use of solar-generated heat to either (1) facilitate stand-along power generation without combustion; (2) increase the power output relative to the base-load output from the combustor; (3) displace some of the fuel that is fed into the combustor to maintain a constant output from the hybrid facility [12]. The introduction of CSR and combustion into the same receiver cavity, however would also result in the complex and coupled heat transfer and reaction processes during the mode of simultaneous operation, and therefore impact on the corresponding energy generation and emission performances [11,29].

Despite its increasing use in different applications, many of the physical and chemical mechanisms involved in the coupling of the external irradiation and in-flame soot species are still not well-understood [11]. An improved fundamental understanding of the interaction

between external irradiation and soot processes can help to optimise the control and the implementation of the aforementioned applications.

2.3 Interaction Species and Light Source

Of the limited studies that have been performed to date to understand the coupling of externallyintroduced radiation with flame, the interaction species [4,11,25] and the light source used [4,5,11,25,26,48] have been demonstrated to have a significant impact on the coupling process.

2.3.1 Interaction Species

When external irradiation is introduced, the light would propagate through a variety of medium before reaching its intended destination. Some examples of the species that the externally introduced irradiation can interact with, along its propagation direction, include the shield gas (in certain burner configurations), the fuel-air mixture and also the in-flame soot species [4,11,25,48]. Previous studies have demonstrated the strength of the interaction process is affected by the species that the radiation interacted with. For example, Choi *et al.* [4,48] have reported that shell-shaped carbon nanoparticles (SCNPs) with high level of crystallinity were formed only when a continuous-wave laser was directed at the acetylene gas in the lower flame region of an acetylene-air flame. Such structural change in the soot particles, however, was not observed when the irradiation was directed at the upper flame region of the same flame, where mature soot was prevalent. It is therefore critical for the interaction species to be taken into account, when assessing the impact of the externally introduced irradiation.

In-flame soot species, *i.e.* soot precursor and mature soot, and their propensity to absorb radiation is a subject of great interests to different research communities [18,19,49–52]. Previous studies have shown that when soot begins to form in a flame, liquid-like precursor

particles are first developed. Such precursor particles are found to have limited absorptivity only in the ultraviolet (UV) region of the incoming spectrum [18–20,22]. However, as the precursor particle develop in size with increasing flame residence time, lesser energy is required to stimulate the electrons into excited state and therefore the optical absorptivity extends into visible region, and ultimately into infrared (IR) [18,20,22]. In other words, at this point, the mature soot behaves like black-body, and absorbs light in all wavelength[11,49–52]. It should be noted that the amount of energy that is required to overcome the energy barrier to initiate the subsequent chemical reaction, would differ in accordance to the soot species involved [53]. It is therefore important that both the absorptivity and the energetics of the species are taken into account, when assessing the coupling the external irradiation with the soot species. The dependence of the interaction process on the soot species involved in has been reported in a number of previous studies investigating the coupling between the externally introduced laser and soot [4,25,48]. For example, Lee et al. [25] have demonstrated that the transition of a nonsooting flame (no soot release from flame) to a sooting flame (soot escapes from flame) is dependent on the irradiation location of their laser light. In their study, it was shown that when the laser light was irradiated at the soot formation region (lower region) of the flame, the temperature of the soot was raised through the effective absorption of laser energy introduced. The increased temperature was observed to enhance the soot formation and hence, the local soot loading of the flame, which lead to the transition. The same transition, however was not found when the laser was irradiated at the upper region of the flame, where mature soot was more prevalent. The results demonstrate the importance of the laser irradiation location (irradiated soot species) on the external irradiation-soot coupling process.

The externally introduced radiation can also interact with a flame through molecular absorption, whereby the molecular excitation process can occur directly, or indirectly [11]. The direct excitation process is an efficient process, but can only be facilitated if there is a direct overlapping of the molecular excitation spectrum with the wavelength of the incoming

irradiation. The indirect process, on the other hand, is the process whereby incoming radiation is absorbed by gas molecules of high concentration to make them vibrationally hot. In the indirect process, the absorbed energy could also be transferred to other gases through inter-molecular energy transfer process. The relative strength of these interaction process is largely dependent on the spectral characteristics of the gases. Nevertheless, whichever the mechanisms, when sufficient heating of the fuel molecules occurs, the reactions, which may be oxidative or pyrolysis nature, depending on the composition of the gases present, can be stimulated. The effects of the overlapping of the spectrum and the incoming ray is best exemplified by the findings of the study of Medwell et al. [11]. In their study, the in-flame soot distribution and structure of an ethylene-air flame, when interacting with a high intensity CO_2 laser was examined. It was found that, the in-flame soot volume fraction was enhanced by up to 250%, with the introduction of the external irradiation. In their work, it was also found that, the mechanism exerting the greatest impact on the soot concentration of the flame is that of the direct excitation of ethylene fuel, which has a strong ro-vibrational transition overlapping the oscillating lines of a CO_2 laser at around 10.6 um [54]. The strength of the interaction process is also affected by the concentration of the species that are present. For example, whilst gas molecules such as water, oxygen and carbon dioxide have been reported to have low absorption in the UV to visible regions [24,55], some recent computational studies have demonstrated the molecular-gas radiation effects can still impact on the local temperatures, when the gases are present in sufficient high quantity [15].

2.3.2 Light Source

A number of irradiation light sources have been used in the previous soot species-radiation interaction studies [4,5,11,25,26,48], whereby the irradiation light sources to be used were selected based on their intensity and wavelength.

The combustion reactions in flame, such as soot formation, are energy dependent, and can therefore only proceed at reasonable rate when sufficient energy is available to overcome the activation energy barriers. For example, in the previous study that was conducted by Medwell et al. [11], a significant enhancement of in-flame soot concentration was only observed when the flux of the radiation introduced exceeded a threshold value of 3.4×10^2 W/cm². The energy flux of the light source required to induce the changes, however can vary depending on the type of laser used, the species that the laser interacted with, and also the condition in which the interaction took place. For example, in the previous studies that were conducted by Vander Wal et al. [26,56], it was found that, a laser pulse generated by pulsed Q-switched Nd:YAG laser at 1064 nm with high intensity energy flux of ~ 5×10^7 W/cm², was required to enable the generation of nanocarbon materials with highly ordered long fringes from the soot particle that was extracted from a rich premixed C₂H₂ flame, in a nitrogen environment. However in a separate study that was conducted by Hu et al. [5], it was found that similar nanoparticles can be attained when a continuous wave InGaAs/GaAs/AlGaAs laser diode, operating at 980 nm with a lower energy flux value between ~ $10^3 - 10^6$ W/cm², was used to heat treat their soot samples under vacuum.

There are light sources with different wavelengths that were used in the literatures, and in their studies, pulsed and continuous wave lasers were typically used as the external irradiation sources, as the collimated single-wavelength laser beam outputs can be shaped and directed relatively easily. The locations of the irradiation sources relative to their flames can therefore be varied and positioned accurately to suit the objectives of their studies. For example, Nd:YAG laser at 1064 nm [26] and InGaAs/GaAs/AlGaAs laser diode at 980nm [5], were used to conduct ex-situ laser heating of extracted soot samples for nanoparticle synthesis. There are also many previous studies that have employed CO_2 laser at 10.6 um in their investigations of the impact of external irradiation on flame structure [25], soot formation process [11], as well as nanocarbon material synthesis [4,48]. Nonetheless, a recent study, which is still in its early stage

of development [10,28], used a custom-build solar simulator that comprised of an array of metal halide lamps with ~ 1 m diameter elliptical reflectors, to understand the coupling progress between an externally introduced broadband high-flux irradiation and a laminar flame. The solar simulator, nevertheless, has a large uncollimated output beam with a diameter of ~ 50 mm, and can therefore not be used to conveniently target specific flame region/species. The light source selection is inevitably dependent on the availability of the irradiation source itself, the spectrum characteristics of the targeted species, but more importantly, the objective of the studies.

In summary, when assessing the impact of external irradiation on the flame, it is important that the influence of different mechanisms, such as the interaction species, and the wavelength and the intensity of the light source, to be effectively isolated or taken into consideration.

2.4 Soot Formation in Diffusion Flame

Over the past three decades, a large number of investigations on the soot formation, growth and oxidation have been reported. A wide range of combustion situations, ranging from laboratory-scale burners to full-scale combustion systems, have been used, depending on the objectives of the investigations. Nevertheless, many of the fundamental insights into the soot formation and growth processes have resulted from the studies of structurally-simple premixed and diffusion flames [37,57–61]. This section provides a brief overview of the characteristics and also the soot processes within a laminar diffusion sooty flame, which is the flame medium of choice of this work.

2.4.1 Diffusion Flame

In a diffusion flame, the reactants, *i.e.* fuel and oxidiser, are not combined prior to combustion. The fuel and oxidiser reach the reaction front by diffusion and the flame occurs at the interface of the reactants. In contrast, the premixed flames have the reactants mixed before combustion. The use of laboratory-scale laminar diffusion flames offers the advantage of avoiding the complexities of turbulence, and are of greater relevance to the turbulent diffusion flames, which are more commonly used in industrial applications than premixed flames [37,57–62].

Laminar diffusion flame has a relatively simple flow field: the fuel exits burner nozzle and flows along the flame axis, and diffuses radially outward, whilst the oxidiser diffuses radially inwards [62]. Laminar diffusion flames have distinct regions with different chemical reactions taking place [22], as illustrated in Figure 2.1.



Figure 2.1: Structure of a laminar diffusion flame, adapted from [22].
2.4.2 Soot Formation

The soot formation in diffusion flame commences with the fuel pyrolysis process, whereby the hydrocarbons fuel molecules are heated and decompose into fragments [63]. Some of the fuel fragments combine to form larger molecules, which are also termed as basic structural units (BSUs) in the literature [4]. In the soot inception region, the larger molecules would polymerise and grow in size to form liquid-like precursor particles with no internal structure. These precursors then flow into the soot growth zone, where they are transformed into solid, black soot particles (nucleation) [62]. The solid-phase nuclei do not contribute significant to the total soot mass, but provide sites for the subsequent mass-addition process [64].

As the small soot particles proceed to flow downstream, they evolve through various soot mechanisms, such as coagulation, agglomeration and surface growth, to form larger soot cluster. Coalescence refers to the process in which the particles collide and coalescence due to Brownian motion. The coalescence process mainly occurs between a pair of large and small particles, whereby the pair then merges to form a single particle with slightly fractal-like structure, before becoming spherical, or near spherical due to surface reactions [46]. It is noted that the mass of the particles do not change during coalescence process, and therefore, the process do not contribute to an increase in the soot loading. The process, however, would impact on other quantities, such as the number of primary particles per aggregate and the local particle size distribution [65]. It is noted, however, for large enough particles, the collision process would result in aggregation instead, as there is insufficient time for complete merging to take place [66]. During the surface reaction processes, the soot mass increases either through a hydrogen abstraction carbon addition (HACA) based surface growth mechanism and/or condensation of PAHs onto the particle surfaces [4]. It should be noted that whilst the soot mass is determined by surface reactions, the final size of soot particles are mainly affected by particle-particle coagulation process [64].

Those clusters are then driven to the top of the flame, where they can be consumed by the oxidization reactions with O_2 molecules and OH radicals. In the case of a non-sooting diffusion flame, the region which the oxidation occurs is also termed as the soot-oxidation zone [62].

2.5 Thermophoretic Sampling and Transmission Electron Microscope Imaging Techniques

In this section, a brief review of the thermophoretic sampling method, coupled with transmission electron microscope (TEM) imaging is presented. The combined approach is used to extract the soot morphological information that are needed to understand the soot growth and evolution process in the presence of external irradiation in this work.

The thermophoretic sampling method is a direct sampling approach that is widely-used by various research communities to provide quantitative particle/aggregate size and morphology information [30,39,67,68]. The thermophoretic sampling method, as its name implies, relies on the thermophoresis effect to drive the deposition of particulates from a high temperature environment, such as a flame, onto a cold substrate that is inserted into the medium [30,57]. It is noted that thermophoresis is virtually independent of particle size when the particle diameters are smaller than ~ 150 mm, therefore making it a convenient yet powerful sampling method for soot diagnostic [69,70]. The sampling grid is typically coated with a thin substrate, such as a carbon or silicon oxide to support the particulates that are deposited onto the grid [57]. It is noted that the fine background structure of the carbon film permits good background contrast to be produced and is therefore typically used for high-resolution diagnostics. The sampling grid, along with the deposited particulates, are then placed underneath a transmission electron microscope (TEM), whereby energised electrons from the microscope are used to interact with the particulate [71,72]. The electrons, which have transmitted through the particulates and grid,

are subsequently directed and focused onto a photo-sensor to form an image, which can be used for morphology analysis. The spatial distribution and the pixel intensity values of the image are therefore dependent upon the interaction of the electrons with the particulates. For instance, the image would be darker in region where the electrons do not transmit, when compared with the area where the electrons are least scatted. It is noted that the TEM images generated are of high resolution (pixel resolution down to the order of nanometres), which can be used for the detailed examination of details of the imaged objects.

2.5.1 Challenges Associated with Soot TEM Image Processing

The use of energised electrons for image, however, result in a number of challenges issues in image processing, as the interaction and transmission of the electrons are inevitable affected by the composition of the object that the electrons interact with. For example, the interaction of the energised electrons with particulates that are more amorphous in nature, would result in weaker edges for the imaged objects in the produced TEM images. The transmission of the electrons through the image would also differ, depending on the local thickness differences in the film that is used to support the sampled particulates, which would then lead to the issue of non-uniform background signal level across the image [38]. All these issues imply that the detailed examination of the TEM images can be challenging to proceed other than through direct manual assessment by an operator, who has to visually distinguish the imaged objects from the background to extract the required morphological information [39]. For the cases where the imaged objects display significant variability in shapes and sizes, or experience some degree of overlapping, a large number of TEM images would need to be processed by the operator to generate statistically meaningful quantities to describe the characteristics of the imaged objects. The operator would also need to have a clear understanding of the object structures and

properties, to be able to consistently distinguish the objects from the background when analysing the images [35,39].

The manual image processing of a large number of TEM images, nevertheless is cumbersome and time-consuming [38]. For example, the detection of the primary particles within the soot aggregates, is not straight-forward as the primary particles do not have clear boundaries and often overlap with each other. The soot particulates are often associated with a wide range of shapes and characteristics, even when they are generated from similar sources or processing environments [38]. In addition, the soot particulates are typically found in aggregate form, therefore a complete description of their morphology would require a detailed analysis of their size at different scales, *i.e.* from primary particle size to aggregate size [43]. In view of all the challenges in manual processing of TEM images for soot diagnostic, there is a strong motivation to develop an automated method so that the morphological information to be derived using a set of mathematical criteria that can be applied consistently (for which manual assessment cannot) to the images. There is another need of an automated approach that is capable of providing reasonable accurate soot morphological information to reduce manual labour.

2.5.2 Development of Automated TEM Imaging Methods

There are several studies in the literature that are aimed at developing automated methods to detect and categorise objects from images. For example, Fisker *et al.* [40] have proposed the use of a deformable ellipse model to detect and determine the size distribution of nanoparticles from electron micrographs. Their proposed method, however, is only reliable when the particles are well separated and have near circular or ellipse-like shapes. There are also other automated methods that are based upon component labelling and feature computation [73] or textual methods [41]. The level of false positives detected by these proposed methods, however, can be high. Woehrle *et al.* [42] have investigated the potential use of several public domain image

processing software packages for automatic nanoparticle detection in TEM images. In their survey, it was found that the investigated software packages are only useful when they are used in conjunction with high-contrast TEM images with uniform background noise and nonoverlapping particles. Bescond et al. [43] have proposed an approach that is based upon the Euclidean distance mapping method (EDM) to automatically extract the morphological information from TEM images. Whilst the proposed automated method has the advantage of not relying on the assumption of a specific shape for object detection, the approach itself, however, is morphology dependent and can therefore generate erroneous results, if not calibrated carefully. Grishin et al. [38] have recently proposed an image processing procedure that is based upon the Circular Hough Transform (CHT) algorithm to locate and to size primary particles within soot aggregates on their TEM images. In their study, it was demonstrated that the proposed image processing procedures are capable of yielding automated data that are in good agreement with their manual results. Their automated method, however, could only use the edge information as inputs to detect truly circular primary particles within the aggregates, and have therefore resulted in low statistical volume issue in their study. In view of all these issues, there is a need for a different or an improved version of the previous automated methods. It is also noted that many of these previous studies do not provide details for the approaches used for noise suppression, background signal removal and image contrast enhancement, all of which are critical to image processing.

Chapter 3 Experimental Details

This work was undertaken at the Advanced Combustion Diagnostic Laboratory at UNSW Australia. A summary of the equipment used during the understanding of this work is presented in this chapter. The main experimental components involved comprise of a Wolfhard-Parker style burner, an external irradiation light source, a thermophoretic sampling system and a thermocouple. A schematic diagram of the experiment layout is shown in Figure 3.1.



Figure 3.1: Schematic diagram of the experiment layout.

3.1 Burner

A Wolfhard-Parker style burner that consists of three parallel 41 mm long rectangular slots, as shown in Figure 3.2, was used. The outer slots, which carried the oxidiser, are each 26 mm wide, whilst the inner fuel slot is 13 mm wide. For the present work, air co-flow and ethylene gas were supplied to the outer and central slots at 2.4 and 9 L/min, respectively. Ethylene was used as it enables comparisons of the present findings to be made with the results of the previous studies, which were mainly conducted with the same fuel (e.g., [11,37,74]). The use of ethylene, which has a high soot formation tendency, also exacerbates the external irradiation-soot interaction effects, so that they can be more readily identifiable. Nitrogen coflow was also introduced at 3 L/min to the short ends of the inner fuel slot to prevent the formation of endflames and draft [59,60]. The planar flame sheets were therefore confined to the thin regions between the inner and outer slots. It is noted that all the gas flows were metered using massflow controllers (Omega Engineering Limited, P/N: FMA-2612A). The mass-flow controller were quoted to have an accuracy of $\pm 0.4\%$ with a repeatability of $\pm 0.2\%$, both at full-scale reading [75]. A two-dimensional contraction made of two curved wire mesh screens was used to stabilise the flames and to prevent flickering [59,60,76]. It should be noted that the heating rates are lower in a two-dimensional flame due to its planar geometry, which only permits thermal conduction of heat from the flame front (as opposed to the cylindrical configuration that is present in a co-annular flame) [76]. The soot precursors can therefore persist to higher flame heights in the planar flame, as their conversion to soot is slower than in an axisymmetrical flame because of the lower heating rates. The planar flame was therefore used to facilitate better targeting of soot precursors, which is the focus of the current work.



Figure 3.2: Burner configuration.

3.2 External Irradiation Light Source and Optical Components

The configuration of the external irradiation source is illustrated in Figure 3.3. A solid-state plasma light source (Thorlabs, P/N: HPLS-30-04) with a spectrum that approximates a blackbody at 6500 K with 2800 lumens and 13.9 W of total output power, as showing in Figure 3.4, was used as the light source. The lamp is designed to emit converging light rays that focuses down to a 9 mm spot from its circular aperture. Two plano-convex lenses of 37 mm and 80 mm focal lengths were placed in front of the light source, to collimate and to focus the light rays down to a 12 mm diameter spot within the flame. The radiation was focused at the lower region of the flame, *i.e.* 15 mm height above burner (HAB), when required. The average irradiation achieved, after focusing, was measured to be ~ 120 kW/m², with a temporal flux variation of ~ 0.5% (1 standard deviation). It is noted that the irradiation was focused on the flame sheet located closest to the light source (see the top view in Figure 3.3) and all of the soot samples were acquired from the same flame sheet.



Figure 3.3: External light source configuration.



Figure 3.4: Spectra power distribution of solid-state plasma light source [7].

3.3 Thermophoretic Sampling

The soot samples were extracted at 20, 30 and 40 mm HABs using either a carbon-supported TEM grid (Agar Scientific, Agar-S160-4H) or a lacey carbon TEM film (Emgrid, LC300-CU-150) for normal-resolution and high-resolution TEM imaging studies, respectively. The grids were attached to a 3.1 mm diameter circular recess at the tip of a 4 mm wide and 2 mm thick stainless steel probe that functioned as the grid holder. The probe was designed to have an aspect ratio (thickness/width) of 0.5, as a minimum aspect ratio value of 0.2 was recommended for good bending stiffness [30]. As shown in Figure 3.5, the probe was mounted onto the end of a pneumatically driven double-acting cylinder system with damper (Bimba Manufacturing, P/N: NR-096-DXPB). The cylinder was controlled by a four-way solenoid valve (Mac Valves, P/N: 411ADOA-DM-DDA-J2JD). The inlet pressure of the actuating gas (compressed nitrogen gas) was regulated using a pressure regulator (CKD, P/N: W3000-10-W) with an operating pressure ranging from 0 to 7 bar. The grid holder was aligned parallel to the flow-field during experiments to minimise flow disturbances. The sampling pneumatic system was operated at an actuating pressure of 4 bar for all experiments. The sampling process was recorded by a highspeed camera (Phantom v7.3) and was assessed to have spatial uncertainties ~ 2.2 and 2.6 mm in vertical and the lateral directions for the specified actuating pressure, as detailed in Section 4.1. The sampling system was mounted on a translational stage to permit vertical translation and therefore, soot sampling at the selected flame positions, directly above the focal point of the external irradiation source. It should be noted that the soot sampling was performed at horizontal position of 8 mm from the centre of the burner at all heights, where maximum soot deposition was consistently observed during initial testing. The sampling process at each location was also repeated six times. This approach was adopted to obtain sufficient sample size for reasonable statistics, as the soot loadings were found to be low at all flame regions for the flames, as demonstrated in the subsequent Section 4.2. For the experiments, the characteristic insertion and retraction times of the sampling system were adjusted to 12 ms each, and the sampling/exposure time in the flame was set to 100 ms. The exposure time was selected to ensure that the TEM grid surface coverage by the sampled soot particles was sufficiently small (< 20%) [57]. Such restriction is recommended by previous studies to prevent excessive overlapping of the soot samples acquired, which can lead to changes in the particle sizes or degree of agglomeration information. The short sampling time was also necessary to minimise probe heating [57,68]. The carbon-supported TEM grids collected at the different sampling locations were imaged using a normal-resolution TEM (JEOL 1400, see Figure 3.6(a)) at University of New South Wales (UNSW Australia) operated at an electron acceleration voltage of 120 keV. The TEM images were digitised using a CCD camera with a resolution of 11 megapixels. It is noted that an image magnification of 100,000 was used to achieve a better resolution for primary particles identification. The lacey carbon TEM films were imaged using a highresolution TEM (Phillips CM200, see Figure 3.6(b)) at UNSW Australia, operated at an electron acceleration voltage of 200 kV and an image magnification of 470,000. A CCD camera with a resolution of 7.2 mega-pixels was used to digitise the images. No thermal or chemical pretreatment was performed on the sampled soot to ensure that the original properties of the soot particles are maintained as much as possible.



Figure 3.5: Schematic diagram of sampling system.



Figure 3.6: Transmission electron microscopy for examining soot samples. (a) Normal-resolution TEM (JEOL 1400). (b) High-resolution TEM (CM 200). Adapted from [11,12].

3.4 Thermocouple

The temperature measurements were performed using an R-type thermocouple (Omega Engineering, P/N: P13R-005-10) with wire and junction diameter values of 0.125 and 0.300 mm, respectively. The thermocouple junction used was not coated as the catalytic effects were not expected to be significant in the non-premixed flame, which has low radical concentration [37]. As illustrated in Figure 3.7, the thermocouple setup used consisted of two high-temperature ceramic tubes attached to rotatable supports, which were mounted 30 mm apart. The thermocouple was stretched between the two ceramic tubes, whereby the wires were threaded through the tubes, before being connected to a thermocouple connectors. A spring was attached to the end of the thermocouple tubes to pull the tubes together. The spring was used to keep the wire taut to prevent the junction from sagging downwards when the thermocouple was inserted into the flame, due to thermal expansion. The mount was attached onto a carriage that can slide backward and forward on an optical rail. When performing the temperature measurements, the carriage was slid along the rail manually until the thermocouple reached its intended measurement location. A proximity sensor was used to trigger the data acquisition system once the thermocouple reached its final position, and the temperature measurements continued over

50 s. The thermocouple reading was sampled at a fixed rate of 300 samples per second by a personal-computerbased data acquisition system (Measurement Computing, USB2408). It is noted that after each measurement, the thermocouple was cleaned of soot deposits by moving it to the oxidizing region of the flame. It is also noted that for the present study, the thermocouple was aligned parallel to the burner slots to minimise thermal gradient along the axis of the wire to improve the accuracy of the thermocouple measurements [37].



Figure 3.7: Thermocouple configuration.

3.5 Data Processing

3.5.1 TEM Image Processing

The raw TEM images mainly were manually processed, to derive the morphological information of soot species such as the projected area of the soot aggregate, and the diameter of the primary particles within the soot aggregates.

As is noted in Section 3.3, the sampling grid, along with the deposited particulates, were first placed underneath a TEM, whereby energised electrons from the microscope were used to interact with the particulates. The electrons, which transmitted through the particulates and grid, were then directed and focused onto a camera sensor to form a digitised image. The digitised raw TEM images acquired were then manually processed with the aid of an in-house developed Matlab code [67,77]. As described in Figure 3.1, the TEM images were first converted into binary images, using an operator-specified threshold value that was determined through visual inspection. Boundary detection was subsequently performed to the binarised images so that soot particles detected (including aggregates and single-primaries) can be identified and labelled as separate entities. The boundaries of these soot particles were then examined in detail by the operator, whereby minor adjustment operations, such as manual pixel filling and trimming, may be performed. The intention of the minor adjustment operation is to counter the effect of the previous binarisation process, so that the major features of the soot particles can be preserved.



Figure 3.8: TEM image processing procedure for aggregate size determination: (a) Raw TEM image. Highlighted is an aggregate of example for demonstration purpose. (b) Binarised image of the example aggregate after applying a user specified threshold. (c) Binarised image of the example aggregate after minor adjustment operations, such as manual pixel filling and trimming. (d) Binarised TEM image after manually processing all aggregates (aggregate in the bottom-left are intentionally excluded as it is partially overlapping with the scale bar).

The projected areas of the soot particles were subsequently determined automatically from the adjusted binarised images, using a box-counting algorithm that is embedded within the in-house Matlab code used [72]. The diameters of the primary particles for the aggregates, on the other hand, were determined visually from the original raw TEM images. The diameters of the

primary particles were manually determined by fitting the longest chords through the centres of the primary particles (see Figure 3.9). It should be noted that the primary particles within the aggregates are typically not perfectly circular due to overlapping or interconnection issues. The fitting of the longest chord process would therefore be subjective to the operator's understanding of the object structures and properties when analysing the images. Nevertheless, a previous study [39] demonstrated that the fluctuations in the selection process can be limited to $\pm 3.5\%$ if the analysis were to be conducted by experienced operators. It should be noted that both the projected area and diameter values were first determined in terms of pixels, which were then subsequently converted to length unit, by importing a length-per-pixel scaling factor into the Matlab code.

Using the manually derived sizing information of the soot primary particles and the aggregates, alongside with numerical expressions that are widely used by the soot morphology research community, other soot morphological information that is useful to provide important insights to the in-flame soot formation and evolution can therefore be derived (see Section 4.2.3).



Figure 3.9: Manual primary particles selection: (a) Raw TEM image of the aggregate of example (see highlight area in Figure 3.8) (b) The TEM image of the example aggregate after manual primary particles selection. The diameters of the selected primary particles are indicated using green arrow bars.

3.5.2 Image Processing

Image processing comprises of two basic stages: corrections, where the images acquired are corrected for the various imperfections due to the experimental system used; and quantification, which involves the conversion of the values within the image into identifiable data. A block diagram of the general steps involve is presented in Figure 3.10.

For each data set, a CCD dark-charge image was first acquired by recording an image with a lens cap placed in front of the camera lens. A background image of the experimental setting was also recorded without the object of interest, such as flame or probe. There images were then subtracted from all the raw data images acquired to ensure that signals collected are independent of extraneous signals that can either arise from the dark-charge of the CCD array and/or the background signal. Vignetting effect of the detector optics can reduce the brightness of the image at the peripheral, as compared with the centre of the image acquired. To correct for this artificial effect, a uniformly illuminated target image was therefore imaged for each data set, whereby the data images were subsequently normalised by the uniform target image recorded. Finally, the corrected data images were used to derive useful information such as the spatial positioning information of the sampling probe and also the flame luminosity information (see Section 4.1).



Figure 3.10: Image processing steps.

Chapter 4

Effect of External Irradiation on the Growth and Evolution of In-Flame Soot Species

The aim of this study is to investigate the impact of the coupling between the external broadband (ultraviolet to visible regions) irradiation and the soot precursors on the in-flame soot growth and evolution processes. The current work is performed with a solid-state plasma light as the source of irradiation and a Wolfhard-Parker style burner (engineering drawing of the burner is provided in Appendix A) firing a laminar ethylene-air flame. The output of the light source is focused at a lower flame region, where greater quantity of soot precursors is expected to be present than in the higher flame regions. The investigation is performed using a thermophoretic soot sampling system to acquire soot samples at flame positions that are closed to, and downstream from the irradiation location. Soot samples from a similar flame, but with no external irradiation, are also obtained for comparison purposes. The soot samples acquired are imaged using both normal-resolution and high-resolution transmission electron microscopes (TEMs), and the soot morphological information is used to provide insights to the soot formation and growth processes. Parameters such as soot volume fraction, soot aggregate projected area, primary particle diameter, number of particles per aggregate and fractal dimension are assessed to determine the effects of external irradiation on the soot species. It is acknowledged that the configuration selected for this work represent a great simplification over the extremely complex processes that would arise in applications involving external irradiationsoot species interaction, such as in a HRC. Such simplifications are nevertheless essential to permit the isolation of the different mechanisms that can be at present, to provide a convenient yet important starting point for the fundamental investigation focusing on the external radiationsoot precursors interactions, a subject that is still not well-understood to date.

The details of the experimental arrangement (burner, external irradiation light source, thermophoretic soot sampling system and thermocouple) used for this study have been provided in Section 3.

4.1 High-Speed Imaging of the Sampling Process

Despite the substantial research work that has been performed using the thermophoretic soot sampling technique [37,57,74,78], the spatial uncertainties and the degree of flame perturbation associated with the sampling devices used in the previous studies were rarely assessed nor reported. The knowledge of such uncertainties is important to enable the sampling device to be used with higher confidence [30,68], as these positional and flame perturbation uncertainties can significantly impact the validity of the sampling results acquired. In order to assess the positional uncertainty associated with the motion of the sampling probe and its impact on the spatial accuracy of the sampling technique, a series of instantaneous images of the probe during operation were captured using a high-speed camera against a bright background, following the approach proposed by Lee et al. [30,68]. Figures 4.1(a) and (b) present the typical instantaneous images of the same sampling probe, when inserted with horizontal and vertical orientation, at the moment of maximum deflection from the centreline. The horizontal and vertical displacements of the probe, from the instance when it reached its final position, are then plotted as a function of time at three selected piston actuating pressure settings, as shown in Figure 4.2. The imaging of the probe motion was performed three times and the uncertainties associated with each data point, which are not presented in the figures for clarity, are found to be generally small (< 0.26 mm). From Figure 4.2, it can be seen that the maximum horizontal and vertical displacements from the centreline caused by the impact vary from 2.2 to 2.8 mm, depending on the actuating pressure and the orientation of the sampling probe. The deviation is found to increase with the actuating pressure used, and is generally observed to be greater in the horizontal, or lateral direction. The effect of the piston actuating pressure of the sampling piston on the probe motion is also further assessed by plotting the insertion velocity of the sampling probe, as a function of time after the start of triggering, as shown in Figure 4.3, for the three selected piston actuating pressures. From the plot, it can be seen the lowest maximum velocity value (3.4 m/s) and therefore the longest the transition period is attained when an actuating pressure of 2 bar was applied, which is to be expected. From the figure, it can also be seen that whilst the maximum velocity value of the probe increases when higher piston actuating pressures of 4 and 6 bar were applied, the average speed attained during the transition period is similar for both. These results imply that for the present system, even though a shorter probe transition period can be attained with higher actuating pressure, the reduction is not significant once the pressure exceeds 4 bar. In view of the need to minimise the probe transition period whilst maintaining a reasonably low spatial uncertainty for accurate soot particle sampling, a piston actuating pressure of 4 bar was therefore specified for all experiments. The spatial uncertainties associated with the sampling system were therefore ~ 2.2 and 2.6 mm in the vertical and lateral directions, respectively, when operated with an actuating pressure of 4 bar.



Figure 4.1: Typical images of the (a) horizontally and (b) vertically inserted sampling probe at the moment of maximum deviation from the centreline (red-dashed line).



Figure 4.2: (a) Horizontal and (b) vertical vibration motions of the sampling probe at its final position, as a function of time, at three selected piston actuating pressure settings.



Figure 4.3: Velocity of the sampling probe as a function of time after start of triggering, at three selected piston actuating pressure settings.

In order to examine the effect of the probe penetrating the flame, a series of raw flame luminosity images were captured using a high-speed camera, as shown in Figure 4.4, following the work of Leschowski *et al.* [78]. Figure 4.4 presents the typical raw flame luminosity images of the flame that were observed, when the sampling probe was (a) 10 ms and (b) 5 ms from reaching its intended sampling position, and (c) when the probe was at its final location. The sampling probe was positioned at 20 mm HAB, in a vertical orientation, for these set of images.

The measured signal profiles acquired at the three different timings are then examined more quantitatively by averaging the signal intensities horizontally in the white-dashed regions indicated in the flame luminosity images in Figure 4.4, to generate the vertical profiles in Figure 4.5. The white-dashed region was selected so that its horizontal position coincided with the position where the TEM grid was located on the probe, when the sampling probe was at its final position. From Figure 4.5, it can be seen that there are some discrepancies in the vertical profile shapes. As is noted in the earlier Section 3.3, the sampling probe used was 4 mm wide, and was therefore positioned from 18 to 22 mm HAB when fully inserted into the flame at a HAB of 20 mm. The drop in the signal intensity observed between 18 and 22 mm HAB in the vertical profile for the second image is therefore attributed to the blocking of the flame luminosity signal by the sampling probe. Nonetheless, the measured signal intensity in the regions from 2 mm below to 3 mm above the specified region is also found to be different from the vertical profile of the first image. The differences in profiles observed demonstrate that the flame is inevitably perturbed by the sampling probe interacting with the flame sheet. It is, however, important to note that the measured intensity profiles are still similar in the upstream region (HAB< 16 mm), and are observed to overlap again at the downstream region (HAB> 25 mm) after the probe. The finding indicates that the intrusion of the sampling probe does not significantly affect the upstream region of the diffusion flame, and that the combustion gases can flow smoothly across the probe without experiencing significant instability or turbulence [78], therefore giving confidence to the validity of the results obtained using the sampling system.



Figure 4.4: Raw flame luminosity images of the ethylene/air flame captured with the grid holder penetrating through the sooting area of the flame. The images were captured when the vertically orientated sampling probe was (a) 10 ms, (b) 5 ms before reaching its intended sampling location, and (c) when the probe is at its final position. The white-dashed region is the image area that was horizontally integrated to assess the impact of the probe intrusion on the flame region.



Figure 4.5: Vertical profiles for the flame luminosity images in Figure 4.4. The red-dashed region indicates the height above flame region occupied by the probe.

4.2 Thermophoretic Sampling

4.2.1 Normal-Resolution TEM Images

Figures 4.6(a) and (b) present typical normal-resolution TEM images of the soot particulates that were sampled from 20, 30 and 40 mm HABs of the laminar diffusion ethylene-air flame, with and without the introduction of external irradiation. The non-externally irradiated and the externally irradiated flames are herein referred to as NI-flame and I-flame, respectively. Throughout the current work, a comparison of the two flames is made in terms of their thermophoretic observations. For the NI-flame, the soot particulates collected at 20 mm HAB, as seen in Figure 4.6(a) possess liquid-like appearances that are poly-dispersed in size and are partially transparent to the electron beam. The boundaries of the translucent liquid-like structures are difficult to define due to their diffuseness. In the image, it can be seen that some of the larger structures have black nucleus or nuclei immersed inside them. The presence of the liquid-like structures, with and without the black nucleus or nuclei, is a strong indication that soot inception and coagulation take place at the sampling location (20 mm HAB). It is noted that the liquid-like structures, which are typically termed as soot precursors in the literature, were also sampled from low flame regions in other burner configurations, where intense particle inception and coagulation were expected to occur [30]. The absence of the aggregated/more mature particles implies the contamination of the sampling grid by soot material originating from locations other than its intended sampling position is not significant, which further demonstrates that the device can be used to sample soot reliably.

The soot particulates sampled at 30 and 40 mm HABs of the NI-flame, however, are comprised of highly opaque carbonaceous aggregates with distinct boundaries. The aggregates are observed to contain primary particles that are joined together, whereby the profiles of the particles can be identified from their spherical-like outlines. From the images, it can be observed that the number and the size of aggregates detected generally increase with height. Nonetheless, small aggregates and even single solid primary particles can still be detected. From Figure 4.6(a), it can also be seen that the translucent substances detected at 20 mm HAB, are less prevalent at 30 mm HAB, and are not observed at 40 mm HAB. Together, the observations imply that precursors detected at the lower flame height, *i.e.* 20 mm HAB, experience a greater level of graphitization with increased flame residence time and that the soot inception process is less prevalent at the higher flame region, *i.e.* 40 mm HAB. The current findings are consistent with the trends observed in previous studies [30].



Figure 4.6: Typical normal-resolution TEM images of the soot samples acquired from the (a) non-irradiated (NI-flame) and (b) irradiated (I-flame) flames, at 20, 30 and 40 mm heights above burner (HABs). The scale is the same for all images.

Figure 4.6(b) presents the TEM photographs of the soot samples that were extracted from the I-flame. From the images, the soot samples from the I-flame have a more mature appearance, when compared with the soot particulates sampled at comparative heights from the NI-flame. The soot samples from the I-flame are observed to consist of solid soot particles that are fused together to form aggregates with clear boundaries, even at 20 mm HAB. The number and the size of the soot aggregates are found to increase with flame height in the flame, as is observed in the NI-flame. It is noted that the translucent structures that were observed at 20 mm HAB in the NI-flame, are not detected in the TEM images obtained from all heights of the I-flame. From the images, it can be seen that the size of the primary particles, the morphology and the degree of

agglomeration of the soot aggregates are strongly dependent upon their positions within the flame, and also by the presence or absence of the external irradiation. The changes in the soot morphological information observed when comparing the soot TEM images obtained from the flames imply that the introduction of external irradiation can accelerate the soot processes such that the soot generation evolves more quickly, leading to soot forming earlier in the flame. The effect of the enhanced soot formation process is also observed to persist downstream, after the irradiation location, as the size and number of the soot aggregates collected at 30 and 40 mm HABs are found to be generally larger for the I-flame.

4.2.2 High-Resolution TEM Images

To further examine the internal nanostructure of the soot samples, high-resolution TEM images of the soot at 20 mm HAB for the NI-flame and I-flame were sampled and analysed. Figures 4.7(a) and (b) present the high-resolution TEM photographs of soot samples that were acquired from the flames. In Figure 4.7(a), it can be seen that the soot primary particles from the NI-flame comprise of randomly-orientated, discernible striations, with lengths that are generally not continuous for more than a few nanometres. There are also regions of carbon layers with less defined structures observed along the outer edges of the primary particles. Together, the observations indicate that the soot sample acquired do not have a significant long range order. In addition, in the central regions of the primary particle, as annotated by arrows, the structures of the underlying particles can be vaguely discerned. The detection of the underlying structures, despite the presence of the overlaying particles, implies that the observed particles are not highly graphitised. This is because carbonaceous material, when present, would interfere with the electron beam path from the microscope and therefore, obscure the underlying particles from view. The absence of long range order, in addition to the translucent nature of the soot samples in Figure 4.7(a), suggests that the soot sample acquired from the NI-flame are relatively young.

Figure 4.7(b), on the other hand, presents the high-resolution TEM image of soot particulates sampled from the I-flame. In the figure, highly concentrically orientated graphitic layers (GLs) are observed within and along the outer periphery of the soot primary particles. Typically, 6 to 10 layers of GLs are found to stack orderly on the periphery of inner cores, as indicated using crosses in Figure 4.7(b), to form shell-like nanostructures. Although still not continuous, the length of the GLs observed are generally longer than that of the striations detected in Figure 4.7(a). Further inspection of the image reveals that the primary particles are still embedded in amorphous coalesced material, although such layers are thinner. Together, the presence of longer range order, in addition to the more carbonaceous nature of the sample imply that soot presented in Figure 4.7(b) are more mature than the soot sample in Figure 4.7(a). The more mature internal nanostructure observed in the high-resolution TEM images of the soot primary particles obtained from the I-flame, when compared with the sample collected form the NI-flame, again supports the earlier assertion that the introduction of external irradiation can accelerate the soot formation processes.



Figure 4.7: Typical high-resolution TEM images of the soot samples acquired from the (a) non-irradiated (NI-flame) and (b) irradiated (I-flame) flames, at 20 mm height above burner (HAB). The arrows are used to indicate regions within the primary particles where the underlying structure are discernible. The crosses are used to indicate the inner cores detected within the soot sample. The scale is the same for both images.

4.2.3 Soot Volume Fraction

In the current work, the soot loadings of the NI-flame and I-flame were also estimated using the thermophoretic sampling particle diagnostic (TSPD) method [37] on the normal-resolution soot TEM images acquired from the flames. In brief, the local soot volume fraction value (f_v) was estimated using:

$$f_{v} = 0.78\xi \frac{d_{p}^{0.82}}{t_{e}} \frac{\sum_{l} A_{a_{l}}^{1.09}}{A_{i}},$$
 Equation 1

whereby d_p , A_a and A_i refer to the values of the primary particle diameter, aggregate projected area and the unit image area, respectively. The t_e refers to the exposure time of the sampling probe, which was set as 100 ms for the experiments. The proportionality factor (ξ) in Equation 1 was determined using:

$$\xi = \frac{2}{D_T} \frac{x}{Nu_x} \left[1 - \left(\frac{T_w}{T_g}\right)^2 \right]^{-1},$$
 Equation 2

whereby the Nu_x and D_T in Equation 2 refer to the local Nusselt number for heat transfer at the vertical position (x) on the sampling probe from the lower edge and the thermophoretic diffusivity of the soot particulates. The values of the parameters in the equation were calculated using theoretically-based empirical correlations from the literature [37,59]. The probe surface temperature (T_w) was taken as 350 K, following the recommendation of a previous study [57], and the local gas temperature (T_g) was derived from the thermocouple measurements performed. The calculated f_v at different HABs in the NI-flame and I-flame are listed in Table 4-1. From the table, it can be seen that the soot yield increases with height above burner for both flames. The f_v values are computed to be 0.12, 0.45 and 0.84 ppm at 20, 30 and 40 mm HABs, respectively, in the NI-flame. The f_v values, however, are found to increase to 0.68, 0.71 and 1.36 ppm, at the corresponding flame heights of the I-flame. In both flames, the observed increasing f_v values with flame height indicates that the soot formation/growth processes are prevalent in both flames. The higher soot loading values observed for the I-flame, however,

implies that the amount of soot produced at any given investigated height above the burner increases with the introduction of external irradiation. It is noted that the enhancement in soot concentration with external irradiation is also noted in previous studies, (*e.g.*, [4,11,25]), albeit with different flame configurations and light sources.

The increase in the soot loading of the flame can proceed via the local incipient of soot species, or the mass addition to the soot originating from the upstream region [57]. The different processes would give rise to soot particulates of varying soot morphological characteristics, such as soot aggregate projected area, primary particle diameter and number of particles per aggregate, when compared with the soot particulates in the upstream flame region. The combined knowledge of the soot morphological characteristics and their trends would therefore permit the formulation of the predominant soot processes, which would then provide information for the soot formation progress at the investigated flame heights. It should be noted, however, that the soot processes that have occurred up to flame region of interest [79]. The motivation of the analysis is therefore not to deconvolute the contributions of the various processes, but to highlight the different predominant processes that were at play at various flame heights.

HAB(mm)	NI-flame				I-flame			
	$f_{v}(ppm)$	$A_a(nm^2)$	п	$d_p(mm)$	$f_v(ppm)$	$A_a(nm^2)$	п	$d_p(mm)$
20	0.12	8610 (1190)	88 (15)	14.2 (0.2)	0.68	11520 (2930)	72 (20)	17.8 (0.1)
30	0.45	7660 (720)	52 (5)	16.8 (0.1)	0.71	18430 (6980)	99 (40)	19.9 (0.2)
40	0.84	14720 (1620)	76 (9)	19.9 (0.1)	1.36	29640 (6440)	124 (30)	22.2 (0.1)

Table 4-1: Soot aggregate statistics at different heights above burner for the non-irradiated (NI-flame) and irradiated (I-flame) flames. The standard errors of the parameters are provided in the brackets.

The soot aggregate projected area (A_a) and primary particle diameter (d_p) were first obtained manually using an in-house Matlab-based image processing code [67]. The number of particles per aggregate (n), which is generally considered to be proportional to its projection area [38], was calculated with A_a and d_p as inputs:

$$n = k_a \left(\frac{A_a}{A_a}\right)^{\alpha}$$
. Equation 3

The $A_p = \pi(\overline{d_p})^2$ in Equation 3 refers to the average projection area of the primary particles within the aggregate. The values of the empirical constant (k_a) and exponent (α) of the equation are taken as 1 and 1.09, respectively, as proposed by Megaridis and Dobbins [58], given that the soot particles are observed to have low overlapping mechanisms [71] in the TEM images (Figure 4.6). A summary of the A_a , n and d_p values obtained at different heights above burner for the NI-flame and I-flame is provided in Table 4-1. From the table, it is evident that there is a clear distinction in both the trends and also the values of the soot morphological data for the soot samples that were obtained from the NI-flame and the I-flame. From the table, the A_a and nvalues of the soot samples are found to decrease, whilst the average d_p of the soot particulates is observed to increase in the region between 20 and 30 mm HAB of the NI-flame. The decrease in A_a value implies that the soot incipient process is prevalent at the sampled flame regions, given that the soot particulates created locally would naturally have smaller sizes, when compared with the soot originating from the lower flame region. This would result in the rapid broadening in the size distribution and therefore, a decrease in the average A_a value [57]. The observed increase and decrease in the values of d_p and n, respectively, imply that the merging *i.e.* coalescence of soot primary particles to form multicore particles are also taking place. The findings therefore indicate that soot incipient and soot coalescence processes, which are typically associated with soot species in the earlier soot formation stages, are important soot growth mechanisms in the lower flame region.

The average values of the A_a , n and d_p of the soot particulates, on the other hand, are all observed to increase in the flame region between HAB 30 and 40 mm of the NI-flame. The increase in both the A_a and n values implies that soot aggregate growth through collisional aggregation, *i.e.* agglomeration, is significant as there is an increased presence of larger soot aggregates with higher number of constituent primary particles. Agglomeration by itself, however, does not lead to an increase in the f_v over the flame height [59]. The increase in the soot loading of the flame must, therefore, be mainly ascribed to surface growth as also supported by the increase in the d_p values over the same flame region. Together, the trends imply that the soot aggregate growth in the upper portion of the NI-flame is under the simultaneous actions of agglomeration and surface growth reactions. It is noted that these soot growth mechanisms are typically associated with soot in the later formation stages. The soot samples that were acquired from the I-flame, on the other hand, are observed to display an increasing trend for all of the parameters $(A_a, n \text{ and } d_p)$ with flame height. The magnitude of the parameters are also found to be higher for the soot samples from the I-flame, than that acquired from the NI-flame. The trend therefore implies that soot surface growth and agglomeration processes are in excess of the possible creation and fusion of new soot particles, and therefore the soot samples acquired are predominantly in the later soot growth stages at all of the investigated flame positions within the I-flame, when compared with the NI-flame. The changes in the soot morphological data trends in the I-flame in relation to the NI-flame indicate that the introduction of external irradiation can have an impact on the soot processes and therefore, the soot loading of the flame.

Soot aggregates are comprised of primary particles forming irregular clusters and the irregularity of the aggregates is typically quantified with their fractal dimension (d_f) values [80]. In general, soot aggregates with higher degree of compactness would have larger d_f values, whilst aggregates that have more linear, open-branched structures, are characterised by lower d_f

values (values of d_f range from 1 for linear chains, to 2 for compact spherical structures on a two-dimensional projected image [74,81]). The d_f values of the soot aggregates can therefore be useful to provide useful insights to the geometrical characteristics of the soot clusters. The mean d_f value of the agglomerates are usually determined in literature by least-square regression fittings to the power law relationship:

$$n = k_f \left(\frac{r_g}{d_n}\right)^{d_f},$$
 Equation 4

whereby the radius of gyration of the soot aggregates, r_g was determined using:

$$r_g = \sqrt{\frac{\sum r_i}{m}}.$$
 Equation 5

The r_i refers to the distance from the centroid of the aggregate to individual pixels and m is the number of pixels within the projection image of an aggregate. The slopes of the least-square linear fits of log(n) and $log(r_q/d_p)$ were subsequently used to yield the d_f values. Only aggregates with more than three primaries are considered for fractal analysis, as aggregates with less than three primary particles (e.g., monomers and dimers) do not have fractal structures [71]. A summary of the mean d_f values of the soot aggregates at different HABs in NI-flame and Iflame is given in Table 4-2. From the table, the d_f values are observed to range between 1.7 and 1.9 for both flames, which are within the asymptotic values that are typically reported in the literature (*i.e.*, [35,57]). In the NI-flame, the soot aggregates are found to have d_f values of 1.73, 1.76 and 1.84 at 20, 30 and 40 mm HABs, respectively. It is noted that the trend of a slight increase in the d_f value with flame height is analogous to the d_f characteristic observed at the lower flame regions for a laminar co-annular ethylene-air flame [37]. It is also noted that the present range of the d_f values observed for the NI-flame is also in good agreement with the past investigations in laminar ethylene-air flames [58,82]. The soot aggregates of the I-flame, on the other hand, are found to have d_f values of 1.86, 1.87 and 1.82 at 20, 30 and 40 mm HABs, respectively, which are higher than the d_f values recorded for the NI-flame. The comparatively

higher values suggest that the population of the soot aggregates from the I-flame are slightly more compact than the soot clusters from the NI-flame over the flame. The discrepancy in the d_f values in both flames implies that different soot structures/appearances are developed when external irradiation is introduced. A complete explanation for the noted difference is not warranted at this time, one plausible explanation, however, is that in the I-flame, more surface sites may be activated and more thermodynamically favoured orientations may be made accessible when additional energy is introduced by the external light source [79]. The combination of the less inhibited manner and the surface sites in which soot particle can merge with another soot aggregate may therefore enable the resulting soot to assume a more compact structure when growing. The d_f value is observed to decrease slightly to 1.82 at the highest flame region *i.e.* 40 mm HAB, which is attributed to the formation of more linear, openbranched soot structures. This is consistent with the expectation that the external irradiation effect would be less pronounced in flame region that is farther away from the irradiation location. Further work, however, is still required to fully establish the variation of the fractal dimensions of the soot aggregates in both flames.

Given the difference in the light source, the burner configuration and the diagnostic technique used, it is therefore difficult to propose a strong hypothesis based upon the direct comparison of the results from the present work with that of the previous studies. Nonetheless, some useful comparisons can still be made. In an earlier study [11], a continuous-wave CO₂ laser was used to irradiate the lower flame region of a laminar ethylene-air co-annular flame. In the study, it was found that a lower-limit of radiation intensity of 3.4 MW/m² was necessary before a significant change in the soot distribution of the flame could be detected. In the current work, however, a change in the soot morphological structure is still detected even though an external irradiation source with a comparatively lower average heat flux value (~ 120 kW/m²) was used. Previous studies have established that the soot precursors and the PAHs only absorb in the UV and visible spectrum [18,20]. The solid-state light used in the current study, which emits

radiation predominantly across the UV-visible spectrum (see Figure 3.4), can therefore be expected to be a more effective tool in providing direct energy transfer to the soot precursors and PAHs that have optical absorptivity in the same spectral region [18–20]. This could lead to the observed lowering of the irradiation threshold level needed to induce changes in the soot.

HAB(mm)	d _f (NI-flame)	d_f (I-flame)
20	1.73	1.86
30	1.76	1.87
40	1.84	1.82

Table 4-2: Soot aggregate mean fractal dimension values at different heights above burner for the non-irradiated (NI-flame) and irradiated (I-flame) flames.

4.3 Temperature Measurements

The molecular gas-radiation effect is not expected to be significant as there is no significant overlapping between absorption spectrum of reactant, oxidant and the combustion gases (*i.e.*, O_2 , N_2 , $C_2 H_4$) [23,24] with the wavelength of the incoming radiation at the irradiated flame location. It is also noted that since the experiments were conducted at atmospheric pressure, the concentration/optical thickness of the gases at the irradiation location is not expected to be sufficient to impact on the local radiative heat transfer process. To verify this assertion, the flame temperature distributions in the vertical plane normal to the burner slots for the NI-flame and the I-flame were measured using the thermocouple setup described in Section 3.4, and are presented as a function of the distance from burner centre in Figure 4.8. It is noted that the relative temperatures rather than their absolute values are of interest to the current work. The thermocouple results in the figures were therefore not corrected for radiative losses. In Figure 4.8(a), it can be seen that the flame front temperatures (at ~ 9-10 mm from the burner centre) remain constant with height in part of the NI-flame investigated. The temperature is observed to decrease both in the direction towards the fuel and also the air slots, as one moves away from the flame front. The temperature trend is consistent with the measurements reported in the

literature, for a similar flame setup [59]. From Figure 4.8(b), it is apparent that temperature values and distribution characteristics of the I-flame are comparable to that measured in the NI-flame, with the differences falling within the margin of error (± 60 K [61]) of the technique. The lack of discrepancies between the temperature profiles of the flames therefore supports the earlier assertion that the molecular-gas radiation effect is not significant, and that the observed changes in soot are predominantly driven by the coupling between the broadband radiation and the soot precursors at the irradiation location. The measurements also indicate that the energy absorption by the small soot concentrations (in the order of parts-per-million, as shown in Table 4-1), are not sufficient to impact on the local temperatures.



Figure 4.8: Flame temperatures versus distance from burner centre at different heights above the burner, (a) without and (b) with external irradiation. The red-dashed line indicates the position of the wall that separates the fuel and air slots.

4.4 Summary

In summary, the effects of an externally introduced, broadband (ultraviolet to infrared regions) irradiation on the evolution of soot species within a laminar ethylene-air flame, generated using a Wolfhard-Parker style burner, have been presented. The irradiation provided from a solid-state plasma light and has an average flux value of 120 kW/m². A pneumatically-driven soot sampling system, with spatial uncertainties of ~ 2.2 and 2.6 mm in the vertical and lateral directions, was used to thermophoretically sample soot from an irradiated flame (I-flame) at flame positions that are close to and downstream from the irradiation location, and the results obtained have been compared with that obtained from a non-irradiated flame (NI-flame) at corresponding heights. No indications of significant instabilities and perturbations were observed when the soot sampling probe was inserted into the flame. The soot samples acquired were imaged using both normal-resolution and high-resolution transmission electron microscopes (TEMs) and images generated were compared and analysed in detail. The results reveal that with the external broadband irradiation was directed at lower flame region that mainly consists where soot precursors were found to be prevalent (1) the soot were found to be of more mature appearances and the effects were observed to persist downstream beyond the point of irradiation; (2) the soot yield of the flame was found to increase; and (3) changes in the predominant soot growth processes/mechanisms and the geometrical characteristics of the soot aggregates were also observed. The absorption of the external irradiation by the soot precursors that have absorption spectrum that overlaps with the wavelength of the incoming irradiation is likely to account for the observed effects, in the configurations used for the present study. This work has highlighted a number of soot morphological changes relating to the soot evolution processes under external irradiation. Future work, including detailed computational studies and soot temperature measurements, such as using the multi-colour method [4], is required to elucidate and extend the results presented in this paper.
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Chapter 5

Automated Determination of Soot Size and Morphology Information

At present, the most commonly used approach to characterise the soot particulates is to manually assess a significantly large number of TEM images-a process that can be both cumbersome and time-consuming [38]. As noted in Section 2.5.2, the automated methods to detect and categorised objects from images developed to date, however have some extent of limitation. Therefore, there is a need for a different or an improved version of the previous automated methods.

In this work, a three-stage image processing sequence, namely image preparation, automatic detection of primary particles and characterization of aggregates, is proposed to facilitate timeefficient automatic detection and sizing of the primary particles and aggregates. The objective of the first stage of the proposed image processing sequence is to reduce the image noise, whilst maintaining the edge information of the aggregates. This is to be achieved through the use of median filtering and self-subtraction [35]. In the second stage of the proposed image processing sequence, an edge detection method (Canny Edge Detection algorithm) is applied to identify the contours that are present at both the external and internal regions of the soot aggregates. A modified CHT algorithm is then applied to detect the primary particles, using the input generated from the edge detection method. The modified CHT algorithm is used as it is computationally-efficient, and when coupled with the outputs from the previous proposed image processing sequence, the output from the previous image processing sequences, are used in conjunction with a morphological closing operation [1,3], to facilitate the characterization of the aggregates. The morphological closing operation is used to ensure that each of the aggregates can be identified as a single entity, rather than an array of objects, prior to the automated aggregate characterization process. Finally, the morphology dependence of the automated method is assessed by testing the proposed procedure with aggregates of different morphology. It is noted that, throughout this work, the automated results are compared with that obtained using manual processing procedure as detailed in Section 3.5.1, to assess the feasibility of the proposed image processing methods. The Matlab code used to facilitate the proposed automated method is provided in Appendix B.

5.1 Computational Details

The image parameter values that are needed to be specified for the image processing steps are listed in Table 5-1. The values of the image scale and the maximum image intensity of the TEM images, which are dependent on the operation settings and the hardware used, are 1.02 nm/pixel and 255 arbitrary unit (a.u.), respectively. There are five image processing parameters that aff ect the automated detection of primary particles, as shown in Table 5-1. These include (1) the number of the neighbouring pixels to be specified for median filtering, (2) the self-subtraction level to be set for the self-subtraction procedure, (3) the diameter range and (4) the sensitivity factor to be used for the modified CHT algorithm, in addition to (5) the shape and size of the structural element to be used for the morphological closing operation. The effects of these parameter values on the outputs of the automated method are evaluated systematically in the subsequent sections. It is noted that when a parameter value is varied for assessment, the other parameters are fixed at the values specified in Table 5-1.

Stage 1: Preparation

Algorithms	Median filtering
	Image inversion
	Self-subtraction
TEM scale	1.02 nm/pixel
Max. pixel intensity value	255 a.u.
Median filtering	3×3 pixels
Self-subtraction level	0.7

Stage 2: Automatic detection of primary particles

Algorithms	Circular Hough Transform (CHT)
CHT min. primary particle diameter	10.2 nm
CHT max. primary particle diameter	24.4 nm
CHT sensitivity factor	0.8

Stage 3: Automated characterization of aggregates

Algorithms	Morphological closing operator
Structural element, diameter	Circular, 24.4 nm

Table 5-1: Image processing parameters.

5.1.1 Median Filtering

The image preparation stage, which involves median filtering, image inversion and selfsubtraction, are demonstrated in Figure 5.1 with a soot TEM image that was sampled at 30 mm HAB from the NI-flame. Median filtering approach is an image processing method that is widely used for digital processing as it is effective in preserving edge information in images whilst reducing impulsive noises, both of which are important for accurate morphology study. The median filtering approach is therefore selected as the filtering method of choice to reduce the noise that are observed to be present in the TEM images, which are present due to the nature of the TEM imaging process. The median filtering approach operates by generating output pixels with pixel intensity values that contain the median values of the neighbouring pixels surrounding the corresponding pixels in the input image. The shape and size of the neighbouring pixels, which is also termed as median filter elements, to be considered would therefore have a direct impact on the level of noise reduction and edge information preservation in the filtered image.



Figure 5.1: The soot TEM image preparation steps: (a) A typical soot TEM image acquired at 30 mm height above burner in the non-irradiated flame (NI-flame). (b) The image was median filtered to reduce noise. (c) Image inversion and (d) self-subtraction operations were applied the median filtered image to remove background. The soot aggregate in the red-dashed box is used to demonstrate the subsequent image processing methods.



Figure 5.2: Pixel intensity value histograms for the median filtered images when three different median filter element sizes were used. The histogram of the original image is also plotted for comparison.

For this work, the shape and number of the neighbouring pixels to be used for median filtering is selected after inspecting the effect of different box size on the ensuing pixel intensity value histogram of the filtered image. The pixel intensity value histograms of the filtered soot TEM images, when 2×2 , 3×3 and 4×4 neighbouring pixels are considered for median filtering, are computed and presented in Figure 5.2. The histogram for the original, unfiltered image is also presented in the figure for comparison purpose. From the figure, it can be seen that when 2×2 neighbouring pixels are considered, the magnitude and shape of the histogram of the filtered image are found to change insignificantly, when compared with what of the original image. This implies that an insufficient number of neighbouring pixels are taken into consideration for effective image noise suppression. The magnitude and shape of the distribution, however, are found to vary when 3×3 pixels are used for filtering, whilst a further increase in the median filter element size (*i.e.* 4×4 pixels) is not observed to yield any further changes to the ensuing distribution. From the figure, it can be observed that a peak distribution at a pixel intensity value of 180 a.u. is obtained when 3×3 neighbouring pixels are used for filtering, which still coincides with the location of the peak in the pixel intensity histogram for the original image. The finding implies that the shape of the neighbouring pixels (*i.e.* box) used is appropriate as it does not distort the original information. The width of the histogram for the filtered image, on the other

hand, is found to be narrower, which indicates that the pixel intensity values are less distributed as the image noise is suppressed by the median filtering approach. A 3×3 pixels box is therefore selected as the median filter element size of the choice for this work. Figure 5.1(b) shows a typical output image from the median filter operation. It is important to note that the peak distribution at approximately 175 a.u. corresponds to the average signal value that is detected on the photo-sensor, when the electron beams are able to transmit through the carbon grid region, without interacting with the soot deposits. The transmittance of the electrons through the grid area with soot, on the other hand, is lower and would therefore contribute data to the frequency in the lower pixel intensity range of the histogram. Given that the TEM grid surface coverage by soot was intentionally kept spare, as detailed in Section 3.3, the frequency of the pixels that is detected from the soot-covered area is therefore comparatively smaller, when compared with that from the soot-free region. The histograms are therefore found to be symmetrical, with negligible skewing.

5.1.2 Image Inversion and Self-Subtraction

In the TEM images, the soot deposits on the carbon film would interact and impede the transmission of the energised electrons from the microscope through the imaged area. The carbon film region with soot deposits would therefore display lower pixel intensity values than the soot-free area, such as shown in Figure 5.1(a). The image inversion operation, which involves the subtraction of the original TEM image pixel intensity value by its maximum pixel intensity value (which is 255 a.u. as an 8-bit camera was used for TEM imaging), is therefore performed. The image inversion operation is intended to produce higher pixel intensity value in soot particulate regions for easier threshold level determination in the subsequent image processing step. The background of the TEM images can vary significantly between images, and even across the same image, due to the factors that were presented in Section 2.5.1. A self-

subtraction operation, which is an adaptive threshold approach that involves the subtraction of the original TEM image from its inverted image, is therefore applied to account for the background signal variation [35]. The self-subtraction approach is also selected as it is effective in enhancing the image contrast, as both the brighter soot particles and the darker carbon film regions undergo different level of pixel intensity reduction during the operation.

Figure 5.3 presents the pixel intensity distribution of the TEM images of soot that are used for this work prior to the self-subtraction operation. From the figure, it can be seen that the distribution of the pixel intensity values of the inverted images mainly fall in the range between 50 and 100 a.u. It is noted after image inversion process, the average signal value detected for the soot-free grid area is approximately 75 a.u., as is indicated by the location of the peak in the histogram. Similarly, the signals from the soot-covered grid area are now distributed towards the higher pixel intensity range of the histogram, after inversion. The pixel intensity value distributions for the TEM images, when different self-subtraction factors are applied, are also presented in Figure 5.3. The self-subtraction factor here refers to the value to which the original image was multiplied with, before the subtraction operation is carried out. From the figure, it can be seen that the distribution of the pixel intensity values is skewed towards pixels with lower intensity values (less than 25 a.u.). This is attributed to the presence of the residual background signals that arise from the incomplete background subtraction process, when a low self-subtraction factor of 0.6 is specified. This is not ideal as the residual background signal could be falsely detected as soot aggregates by the subsequent image processing steps. The histogram is observed to be more evenly distributed across the whole pixel intensity range when a greater self-subtraction factor of 0.7 is applied, which implies that the residual background signals are now removed. A further increase in the self-subtraction factor (i.e. 0.8) is not found to change the magnitude and shape of the ensuing histogram significantly, which indicates that a greater self-subtraction level specification will not improve background intensity subtraction. Rather, it can result in over subtraction that would affect the derivation of accurate structural

information of the particles. An optimised self-subtraction factor value of 0.7 is therefore specified for this work. Figure 5.1(c) and Figure 5.1(d) show the typical output images of the inversion and self-subtraction operations, respectively. It is also noted that a soot aggregate, as indicated using a red-dashed box in Figure 5.1(d), is used as the example aggregate in the discussion of the subsequent image processing steps.



Figure 5.3: Pixel intensity histograms for the inverted images, after self-subtraction with three different self-subtraction factor values. The histogram of the original inverted image is also plotted for comparison.

5.1.3 Automatic Detection of Primary Particles

Canny edge detection (CED) is an image processing operation that has been shown to be effective in detecting thin and low contrast edges [35]. The CED method is a multi-stage algorithm that involve (1) Gaussian smoothing for noise reduction, (2) Gaussian calculation to detect image intensity gradients, (3) non-maximum suppression to reduce spurious response to edge detection, and finally (4) double thresholding and hysteresis to suppress the detection of edges that are weak and not-connected to the strong edges [35]. It should be noted that when implementing the selected CED method, its Gaussian smoothing operation is not invoked to avoid over-smoothing of the images, which have undergone the median filter operation. Therefore, unlike the median filtering and self-subtraction operations detailed in Sections 5.1.1 and 5.1.2, no specification is made for the control parameters of the method. The output from the previous image processing operations, such as median filtering, image inversion and self-subtraction, would therefore have a direct impact on the effectiveness of the CED method. A typical output image after the CED operation is shown in Figure 5.4(b).



Figure 5.4: The image processing steps for the automatic detection of primary particles. (a) The same soot aggregate from Figure 5.1(d) is used for illustration. (b) Canny edge detection is applied to detect thin and low contrast edges at the peripheral and from within the aggregate.

The edges that were detected using the CED method are used as inputs for the modified CHT algorithm [83]. The CHT algorithm is a circle detection approach [35,38], which implements a voting scheme that maps the inputs into a well-defined parameter space. For example, in this work, the coordinates of the edges that were detected using the CED method are designated as inputs for the modified CHT algorithm and are asked to vote into an accumulator array. The ensuing peaks in the array that arise from the voting scheme are then used to estimate the locations of the circle centres, as well as the diameter of the circles associated with the locations [38]. The modified CHT approach has been selected due its robustness in the presence of varying background and noise. It is noted that the CHT is a computationally expensive method. A widely adopted approach in modern CHT implementations the realistic diameter range that the circles (primary particles for this work) are expected to fall within to reduce the overall computation load-an approach that is also followed in the this work. For the present work, the modified CHT algorithm was implemented using the 'imfindcircles' function in Matlab. The function requires (1) the minimum and maximum diameter values for the circular objects to be detected, and (2) a sensitivity factor (a non-negative scalar value between 0 and 1 for this work), which that controls the sensitivity of the accumulator array of the algorithm, to be specified as inputs. It is noted that the specification of a higher sensitivity value (closer to 1) would result in the detection of more circles, but at a risk of greater false detection.

The output image for the example aggregate selected from Figure 5.1(d), after the CED operation, is presented in Figure 5.5(top). The primary particles that are automatically detected by the modified CHT algorithm, when different maximum primary particle diameter (d_p^{max}) sizes are specified, are overlaid on the CED images for comparison. It is noted that the minimum primary particle diameter (d_p^{min}) was initially set at 10.2 nm, as this value is visually assessed to be most representative of the smallest primary particles for the soot aggregates detected in the soot TEM images acquired. The d_p^{max} value, which can also be assessed visually from the images, is varied here to assess the sensitivity of the modified CHT algorithm output to the specified diameter range.



Figure 5.5: The effect of the specification of the maximum diameter size d_p^{max} on the primary particle detection in the TEM image. The automatically selected primary particles, for different d_p^{max} values specifications, are overlaid on the processed soot TEM image (top). Also presented is a comparison between the size distributions obtained using manual assessment and automatic methods of different d_p^{max} value specifications (bottom).

From the figure, it can be seen that a small change in the d_p^{max} value would affect the ensuing primary particle detection. When a lower d_p^{max} value of 20.3 nm is specified, the larger primary particles are not selected by the automated method due to the diameter range restriction imposed. In contrast, when a higher d_p^{max} value of 28.4 nm is used, the larger primary particles are selected by the algorithm due to larger diameter range specified. The level of false detection is therefore high. The soot TEM images that were processed using the automatic procedures, and the size distributions for the primary particles that are associated with different d_p^{max} value specifications, are also shown in Figure 5.5(bottom). The size distribution for the primary particles that was obtained using direct manual assessment is provided for comparison purpose. Also shown in the figure are the mean and error range values of the distributions. From Figure 5.5(bottom), it can be seen that the distribution is biased towards the lower d_p range when a smaller d_p^{max} value of 20.3 nm is specified. Similarly, the distribution is observed to be shifted towards the higher d_p range when a higher d_p^{max} value of 28.4 nm is specified. An optimised d_p^{max} value of 24.4 nm is therefore selected as it provides a distribution with shape and average diameter value (16.7±0.11 nm) that best agrees with the manual result (16.8±0.09 nm). The same analysis process is also repeated to determine the optimised d_p^{min} value. It was found that a lower d_p^{min} value specification would skew the distribution towards the smaller d_p range, whilst the use a higher d_p^{min} can over-restrict the viable diameter range. A d_p^{min} value of 10.2 nm is therefore found to be most suitable. It should be noted that the histograms presented herein are quantified in frequency instead of number count, as there are inevitably some differences in the statistical volume between the methods.

The implementation of CHT also requires the specification of the sensitivity factor. It is noted that whilst the implementation of the image preparation procedures, such as median filtering and self-subtraction processes, would reduce the image noises and background signals that can result in false detection, a careful selection of the sensitivity factor is still necessary. The determination of the most suitable sensitivity factor follows the same methodology that was used to assess the optimum d_p^{max} value. The primary particles that are detected by the modified CHT algorithm in the example aggregate for different sensitivity factors are shown in Figure 5.6(top). From the figure, it can be seen that the specification of a lower sensitivity value of 0.75 leads to the detection of reduced number of primary particles, whilst a higher value of 0.85 results in the expected trend of increased detection, especially in the lower d_p range. This is also reflected in average values of the size distributions that were computed with all the soot TEM

images acquired, using different sensitivity factor specifications, as shown in Figure 5.6(bottom). From the figure, it can be seen that a size distribution with a higher sensitivity factor specifications is found to be associated with a lower mean value. The size distribution trend indicates that a sensitivity factor specification of 0.80 would yield a distribution with an average primary diameter value that best agrees with the manual assessment result for this work. It is noted, however, the mean value and the shape of the distribution are found to display less sensitivity to the sensitivity factor specified, when compared with the effect of the diameter range.



Figure 5.6: The effect of specification of the CHT sensitivity factor on the primary particle detection in the TEM image. The automatically selected primary particles, for different sensitivity factor specifications, are overlaid on the processed soot TEM image (top). Also presented is a comparison of the size distributions obtained using the manual assessment, and automatic methods of different sensitivity factor specifications (bottom).

5.1.4 Aggregate Characterization

In order to facilitate the automatic characterization of the soot aggregates, it is necessary for the soot TEM images to be subjected to a further image processing stage. In this stage of image processing, the images obtained were first binarised to facilitate the subsequent logical operation. All aggregates that touch the border of the image were removed to eliminate irregularities on the image background that could potentially interfere with the aggregate recognition [38]. A morphological closing operation [1,3,84] with a circular structural element was subsequently applied to add continuity to the major features of the aggregates. The morphological closing operator applies a user-specified structural element to fill in the gaps between, and to smooth the outer edge of the non-zero elements detected in the binarised images. The morphological closing operation is required to ensure the all sections belonging to the same soot aggregate are connected so that they could be recognised as a single entity, rather than an array of smaller, separated objects, during the automatic aggregate characterization process. This image processing operation is critical to ensure like-for-like aggregate characteristic comparisons were made between the manual and the automated methods. A circular structural element was selected in conjunction with the morphological closing operation to preserve the circular nature of the primary particles. The size of the circular element was specified as 24.4 nm to match the upper diameter range of the larger primary particles within the soot aggregates. The size of the circular structural element is assessed to be sufficiently large to add continuity to the aggregates, whilst small enough to avoid significant shape distortion of the aggregates. As a result, morphological information of the aggregate, *i.e.*, projected area, radius of gyration and fractal dimension of the aggregate, as well as the number of particles per aggregate, can be evaluated in conjunction with the use of the same numerical approach stated in Section 4.2.3.

To further assess the applicability of the automated method for aggregate characterization, the least-square linear fits of the log(n) and the $log(r_g/d_p)$ value that were generated using the

manual and the automated methods are plotted and compared, as shown in Figure 5.7. The value of the slopes and intercepts of the linear fits which correspond the d_f and k_f of the soot aggregates, are also provided in the figure for comparison purpose.

From the figure, it can be seen both plots display good linearity and the values of the d_f (1.77±0.07 for manual and 1.75±0.06 for automated) and the k_f (2.09±0.06 for manual and 1.98±0.04 for automated) that are derived from the two linear fits are in good agreement, with a small discrepancies (1% and 5%) observed for the absolute d_f and k_f values, respectively.



Figure 5.7: Plots of log(n) over $log(r_g/\bar{d}_p)$ for soot aggregates sampled at 30 mm height above burner from the non-irradiated flame (NI-flame), analysed using manual and automated methods. The d_f values and their error ranges (95% confidence) are also annotated.

5.2 Morphology Dependence of Automated Image Processing Procedure

The soot aggregates from the I-flame were used to assess the morphology dependence of the proposed automated image processing procedures. The source of soot was chosen because the coupling of an external broadband irradiation source with the soot species within a flame can produce population of soot aggregates with different morphology, *i.e.* larger soot primary particles and more compact structure (*i.e.*, greater fractal dimension), when compared with the soot aggregates obtained from the NI-flame. Figure 5.8 presents a typical normal-resolution TEM image of soot aggregates that was sampled from 30 mm HAB of the I-flame.



Figure 5.8: A typical soot TEM image acquired at 30 mm height above burner, from the externally-irradiated laminar ethylene-air flame (I-flame).



Figure 5.9: A comparison of the size distributions obtained using the manual and the automatic methods for the soot aggregates sampled from the externally-irradiated flame (I-flame).

Like the automated procedures that are presented for the soot aggregates that were extracted from the NI-flame, the image parameter values that are required to facilitate the automated procedures are first assessed and optimised. No significant adjustment, however, is found to be required to be made to the parameter values that were previously determined, as the soot aggregates from the I-flame were deposited onto the same grid type, imaged using the same TEM system as the soot samples from the NI-flame, in addition to being manually processed by the same operator. Higher d_p^{min} and d_p^{max} values of 12.2 nm and 30.5 nm, respectively, are needed to be specified for the modified CHT algorithm to correspond better to the diameter range of the soot aggregates from the I-flame. The primary particle size distribution for the soot aggregates is shown in Figure 5.9. From the figure, it can be seen that the mean values (3% discrepancy) and the shapes of the distributions that were determined using the manual (19.9±0.16 nm) and automated methods (20.4±0.19 nm) are in good agreement. From the figure, it can also be seen that in the I-flame, the average automated primary particle diameter value (\sim 20.4 nm) is larger than the mean primary particle diameter that is measured for the soot samples from the NI-flame (~ 16.7 nm in Figure 5.5), which is consistent with the previous findings. As is noted in the introduction section of this work, a direct benchmarking of the current results with outcomes that are obtained using other digital algorithms in the literature is not straightforward. This is because the accuracy of the final outcomes of the automated methods are inevitably affected by the image pre-processing steps used, which are very often not provided or described in detail by the previous studies. Nevertheless, the primary particle size distribution of the soot aggregates that is obtained using an unmodified CHT algorithm (no radius range and sensitivity factor specifications) on the same soot TEM images is presented in Figure 5.9 for comparison purpose. The information from the edges of the aggregates only are also used as inputs for the unmodified CHT algorithm to simulate the approach that is typically adopted in previous studies e.g., [38]. From the figure, it can be seen that whilst the mean values of the distributions are similar, the shape of the distribution that is obtained using the

unmodified CHT algorithm deviates significantly with that manual and automated method presented in this work. This further validates the viability of the proposed automated method.

The least-square linear fits of the log(n) and the $log(r_g/d_p)$ values that were generated using the manual and the automated methods are presented in Figure 5.10. From the figure, it can be seen the plots for both methods display good linearity with similar slope (*i.e.* d_f) and intercept (*i.e.* k_f) values. The slight discrepancies (1% and 10%, respectively) observed for the derived d_f and k_f values are attributable to the morphological closing operation. The differences in the numerical values are attributed to the sensitivity of the morphological closing operation to the positioning of the non-zero elements on the binarised TEM image. The degree of the filling as well as the smoothing of the outer edges would therefore be slightly dissimilar when the morphological closing operation is performed at different sections of the aggregates. Nonetheless, the magnitude of the discrepancy is not significant, which indicates that the proposed automated image processing method is useful for soot aggregate characterization. The computed fractal dimension (~ 1.86) of the soot aggregates from the I-flame is measured to be larger than that from the NI-flame (~ 1.75 in Figure 5.7). Again, the larger fractal dimension value computed for the soot aggregates from the I-flame, which has a higher degree of compactness, is consistent with previous observations.



Figure 5.10: Plots of log(n) over $log(r_g/\bar{d}_p)$ for soot aggregates sampled at 30 mm height above burner from the externally-irradiated flame (I-flame), analysed using manual and automated methods. The d_f values and their error ranges (95% confidence) are also annotated.

5.3 Summary

In this chapter, a three-stage image processing sequence to facilitate efficient automatic detection and sizing of the primary particles and aggregates has been presented in this work. The image processing sequence began with the use of median filtering, self-inversion and self-subtraction methods to reduce image noise and to account for the local variability in the background level of the transmission electron microscope (TEM) images, whilst ensuing that the details of the soot aggregates were not significantly compromised. An edge detection method was then coupled with a modified Circular Hough Transform (CHT) algorithm, to ensure that the information from both the internal and peripheral regions of the aggregates, can be used for the detection of primary particles within the aggregates. A modified CHT algorithm, which requires user's inputs to specify its diameter range and sensitivity factor, was employed as it is more efficient computationally and can provide more accurate estimation. To facilitate the automated aggregate characterization process, morphological closing operation was carried out to ensure that each of the aggregates can be identified as a single entity during automated aggregate characterization process. The parameter values that were required to be set for each of the image processing sequence were determined, and their impact on the final result was

assessed. Statistical assessments revealed that reasonable accuracy were achieved for the estimated automated values of primary particle diameter, with up to 3% discrepancy for the tested cases, when optimised parameter values were specified. The assessment also demonstrated that the fractal dimension and prefactor data trends generated using the proposed automated method displayed good qualitative and quantitative agreement with the manual result, as demonstrated by the 1 and 10% discrepancies detected in the derived values, respectively.

Chapter 6

Conclusions, and Recommendation for Future Work

This chapter presents an overview of the conclusions for the work presented in Chapters 4 and 5, followed by the recommendations for future work.

6.1 Conclusions

In this work, the impact of an externally introduced broadband irradiation on the soot evolution in a diffusion flame, has been assessed. A thermophoretic sampling system, with known uncertainties, has been employed to extract soot samples at various heights above burner from an ethylene-air diffusion flame, both with and without the external irradiation. The transmission electron microscope (TEM) images of the collected samples reveal that, when the external broadband irradiation was directed at lower flame region where soot precursors were found to be prevalent, the in-flame soot formation process was found to have enhanced to generate higher soot yield, both at the vicinity of the irradiation point and also at flame locations further downstream, when compared with that of a non-irradiated flame. The soot samples acquired from the irradiated flame were also observed to have more mature appearances, whilst changes in the predominant soot growth processes/mechanisms and the geometrical characteristics of the soot aggregates were also found. The results indicated that the absorption of the external irradiation by the soot precursors, which have absorption spectrum that overlaps with the wavelength of the incoming irradiation, is likely to account for the observed effects, in the configurations used for this work. In this work, a three-stage image processing sequence to facilitate efficient automatic detection and sizing of the primary particles and aggregates was also presented. The image processing sequence began with the use of median filtering, self-inversion and self-subtraction methods to reduce image noise and to account for the local variability in the background level of TEM images, whilst ensuing that the details of the soot aggregates were not significantly compromised. An edge detection method was then coupled with modified Circular Hough Transform (CHT) algorithm, to ensure that the information from both the internal and peripheral regions of the aggregates, can be used for the detection of primary particles within the aggregates can be identified as a single entity during automated aggregate characterization, which is important during the process. Statistical assessments revealed that reasonable accuracy were achieved for both the estimated automated values of the primary particles and also the aggregates, when optimised parameter values were specified.

6.2 Recommendations for Future Work

Some important findings towards the understanding of the coupling between external irradiation and combustion process have been presented in this dissertation. Nevertheless, there remains issues that require further investigations to elucidate the results of this work:

In this work, thermophoretic sampling technique, coupled with normal-resolution TEM imaging, was mainly used to understand the in-flame soot evolution and growth processes in the presence of external irradiation. The insights obtained using the thermophoretic sampling technique, however, are limited by its low spatial resolution. The use of other diagnostic tools, such as laser-induced incandescence (LII) technique, would provide resolved two-dimensional measurement that would complement the results of this work.

- In this work, some of the soot samples acquired were imaged using high-resolution TEM, for visual assessment and comparison purposes. A more detailed statistical analysis of the high-resolution soot TEM images would reveal important soot nanostructure information, such as fringe length, tortuosity and separation of the internal carbon layer plane segments in the presence of external irradiation. Such information is important to provide further insights into the effects of external irradiation on in-flame soot growth and evolution process, and therefore extends the current understanding of the interaction process.
- In this work, the temperature of the gas phases was measured in the presence of external irradiation and no observable measurement was found. The finding therefore implies that the primary effect of the external irradiation is in increasing the energetics of the inflame soot species. Future work, involving detailed numerical studies and soot temperature measurements using multi-colour methods, would be useful to examine if the soot particle temperature is changing as a result of the radiation. Such information is useful to elucidate and extend the current understanding.
- As is noted in literature review presented in Chapter 2, of the limited studies that have been performed to date to understand the coupling of externally introduced radiation with flame, the interaction species and the light source used have been demonstrated to have a significant impact of the coupling process. Further investigations, involving the use of different fuel types to generate soot species with different content, and light source with more controllable power output and smaller frequency band, would provide insights to this topic.

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Appendix A

Engineering Drawings of Wolfhard-Parker Style Burner

This Section presents the engineering drawing of the in-house built Wolfhard-Parker style burner, which comprises of four main components:

- 1. Slot burner
- 2. Air panel
- 3. Nitrogen panel
- 4. Mid panel














Appendix B

Matlab Code for Automated Determination of Size and Morphology Information from Soot TEM Generated Images

```
% Automatic primary particle (works on Matlab R2012b + Image
Processing Toolbox)
% The code implements pre-processing (median filtering, image
inversion and self-subtraction),
% Canny edge detection, and Circular Hough Transform.
2
% Code was last updated on 11 May 2016 by Cheng Wang
close all;
clear all;
clc;
dp matrix = [];
% -- Parameters
TEMscale = 200/197; % 200 nm per 197 pixels in the scale bar
maxImgCount = 255; % Maxium image count for 8-bit image
SelfSubt = 0.7; % Self-subtraction level
mf = 3; % Median filter box size in pixels
rmax = 12; % Maximum radius in pixel
rmin = 5; % Minimun radius in pixel
sens val = 0.8; % Sensitivity factor 0?1) for the Circular Hough
Transform algorithm
ImgFile = ['TEMimage.tif']; % Soot TEM image
%% Pre-processing
% -- Median filter to remove noise
II1 = double(imread(ImgFile));
data = II1;
data = medfilt2(data, [mf mf]);
% -- Image inversion & Self subtraction
data bg = SubtBack*data;
data = maxImgCount-data; % Inverts image
data = data-data bg; % Self subtraction
data(data<0) = 0;
% -- Morphological closing operation
BW = data; % Creates binary mask
```

```
BW(BW>0) = 1;
seclose = strel('disk', rmax*2); % Adds continuity to the objects
BWco = imclose(BW, seclose);
BWco = imfill(BWco, 'holes'); % Fills holes in the objects
% -- Removes objects at image border
BWco = imclearborder(BWco);
data = data.*BWco;
% -- Obtains coordinate information for each object
[ilabel,num] = bwlabel(BWco);
ibox = regionprops(ilabel, 'Boundingbox');
icoord = cat(1, ibox.BoundingBox);
% -- Extracts a single object for further analysis
ilabelnum = 1;
mask = zeros(size(BWco)); % Creates a rectagular mask
xrange = round(icoord(ilabelnum, 2)):round(icoord(ilabelnum,
2)+icoord(ilabelnum, 4));
yrange = round(icoord(ilabelnum, 1)):round(icoord(ilabelnum,
1)+icoord(ilabelnum, 3));
mask(xrange, yrange) = 1;
mask(nonzeros(ilabel)~=ilabelnum) = 0;
data = data.*mask;
%% Canny edge detection
dataCED = edge(data,'canny', [], 1); % Derives edge information
[centersCED, radiiCED, metricCED] = imfindcircles(dataCED, [rmin rmax],
'objectpolarity', 'bright', 'sensitivity', sens_val ,'method',
'twostage'); % Finds circles within a single aggregate
%% Checks the circle finder by overlaying the circles on the image
with the detected edges
figure, hold;
h1 = imagesc(dataCED);
h2 = viscircles(centersCED, radiiCED, 'EdgeColor', 'r', 'linewidth', 1);
%% Saves information
dp = radiiCED*TEMscale*2;
dp_matrix = [dp_matrix dp];
save(['dp.mat'], 'dp matrix'); % Saves results
```

Appendix C

Publications

Journal Publications

- Wang, C., Chan, Q.N., Zhang, R., Kook, S., Hawkes, E.R., Yeoh, G.H., Medwell, P.R. (2016), 'Automated Determination of Size and Morphology Information from Soot Transmission Electron Microscope (TEM) Generated Images', Journal of Nanoparticle Research, accepted: 27th April 2016. DOI: 10.1007/s11051-016-3434-x.
- Wang, C., Chan, Q.N., Kook, S., Hawkes, E.R., Lee, J., Medwell, P.R. (2016), 'External Irradiation Effect on the Growth and Evolution of In-Flame Soot Species', Carbon, accepted: 12th February 2016. DOI: 10.1016/j.carbon.2016.02.039.

Refereed Conference Publications

- Wang, C., Chan, Q.N., Kook, S., Hawkes, E.R., Medwell, P.R. and Lee, J. (2015), 'External irradiation effect on the evolution of in-flame soot species', Proceedings of the Australian Combustion Symposium, University of Melbourne, Melbourne, Australia, Paper 25.
- Wang, C., Chan, Q.N., Kook, S., Hawkes, E.R., Medwell, P.R. and Lee, J. (2015), 'Development of an in-flame thermophoretic soot sampling device', Proceedings of the Australian Combustion Symposium, University of Melbourne, Melbourne, Australia, Paper 24.

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