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Flame and from Polymer Combustion

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**Morphological characterization of soot from an idealized diffusion flame and
from polymer combustion**

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Thèse présentée en vue de l'obtention du diplôme de *Philosophiæ Doctor*

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Morphological characterization of soot from an idealized diffusion flame and from polymer combustion

présentée par **Stefan Cristian BOANTA**

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ABSTRACT

In this thesis, we aim to study the morphology of soot obtained from two experimental configurations, namely from a simple one-dimensional unstrained counterflow diffusion flame and a complex flame resulting from the combustion of polymers. Given the complexity of the soot formation mechanism and that conventional burners used to study it are characterized by a strong coupling between the flow field and the flame chemistry, we propose to initially investigate its morphological evolution in a flame located in a one-dimensional flow field. The data gathered in this simple configuration is primordial to the development of predictive models of soot formation because turbulent diffusion flames encountered ubiquitously in practical applications can be modeled as laminar one-dimensional diffusion flames. Moreover, the morphology of soot is also important when investigating its toxicity. We propose to extend the study of its morphology to a flame representative of accidental combustion obtained in a cone calorimeter due to its relevance to toxicity studies and fire safety.

The burner used for the one-dimensional diffusion flame is operated using methane and oxygen as reactants, diluted with carbon dioxide to control the fuel equivalence ratio. It is characterized by an oxidizer stream that diffuses against a one-dimensional bulk flow, resulting in a unidirectional flow at the flame sheet and allowing for long soot residence times on the fuel side of the flame. To acquire soot, a sampling method is developed using carbon-coated nickel transmission electron microscope grids. Aggregates are collected at various locations within the soot layer of four flames characterized by an increasing freestream fuel equivalence ratio. The samples are viewed and recorded on a transmission electron microscope. The sampling method is then extended to collect soot from burning polymers in the cone calorimeter. The material used for the polymer fire consists of a cellulose-reinforced thermoplastic polyurethane mixed with fire-retardant additives, namely melamine polyphosphate and activated carbon at various loadings according to a design of experiments methodology. In addition, aerosol sampling is performed above the polymer flame to track the evolution of the particle size throughout the duration of the combustion.

To aid the morphological analysis of the soot aggregates collected in these two configurations, a soot monomer detection algorithm is presented which uses the outer edge map of individual

aggregates as an input image. The algorithm is developed using soot from both configurations to extend its range of applicability, given the wide spectrum of morphologies expected from these flames. The performance of the detection algorithm was assessed using soot samples from increasingly rich one-dimensional flames and polymer flames. It has been able to detect a shift in the particle size distribution towards larger particles, as expected. Moreover, soot obtained from burning polymers showed considerably larger monomer diameters, as detected by the algorithm. However, the size distribution was typically underestimated by the algorithm compared to that obtained by manual measurement. By comparing the locations between manually measured soot monomers and automatically detected ones, we were able to observe that the former method is typically focused on regions that are internal to the aggregate. This observation suggests the necessity to use more complete aggregate edge maps that include edges within the region of aggregates in the input image for a better algorithm performance.

Given that the algorithm could not replicate the results obtained by manual measurement, we resorted to a manual detection and measurement of soot monomers for the morphological analysis of soot. In the one-dimensional diffusion flame, we observed the coexistence of isolated primary particles with aggregates throughout the visible soot layer. The former follow a log-normal distribution and are much smaller than the monomers found in aggregates, which follow a normal size distribution. The size of these particles is positively correlated to the freestream fuel equivalence ratio. Numerical simulations of the flame structure indicate the presence of soot growth species, namely acetylene, throughout the entire region where soot has been observed. Given the one-dimensional flow field in the vicinity of the flame sheet, the soot particles are subjected to two opposing forces, namely the drag force and the thermophoretic force, thereby increasing the residence time of particles in the soot growth region. According to a model involving spherical particles of constant size and the simulated flame temperature gradient, particles smaller than $5\text{ }\mu\text{m}$ tend to be trapped in the growth region until their size is large enough for the drag force to dominate and entrain them into the flame, resulting in their burn off. The morphological evolution of soot particles throughout the visible soot layer also indicates that irrespective of the freestream fuel equivalence ratio, monomers found in aggregates have comparable dimensions early into the visible soot layer and grow subsequently according to the equivalence ratio. The

decrease in size as they approach the flame sheet is quite limited, highlighting their maturity. With regards to the aggregates, their fractal dimension evolves mostly early into the visible soot layer followed by a convergence towards a value between 1.6-1.8 at maturity for all flames.

Despite the validation of the soot sampling methodology in a configuration representative of that encountered in the cone calorimeter, soot samples could not be observed in the scanning electron microscope for the various material combinations of cellulose-reinforced and fire-retarded thermoplastic polyurethane. We have thus resorted to soot samples from phenolic and epoxy carbon-fiber reinforced composites, obtained in the cone calorimeter, for the development of the image processing algorithm. Nevertheless, the aerosol spectrometer was able to track the evolution of particulate matter throughout the duration of these tests, providing insights as to the effects of the additives on the formation of soot and its size. We have observed that the addition of cellulose into thermoplastic polyurethane enhances the production of smoke. However, a synergistic reaction between cellulose and melamine polyphosphate reduces it compared to its non-cellulose counterpart. In addition, further smoke reduction can be achieved by incorporating activated carbon into this material combination. In fact, the presence of activated carbon reduces the size and the concentration of particulate matter.

RÉSUMÉ

Dans cette thèse, nous visons à étudier la morphologie de la suie obtenue à partir de deux configurations expérimentales, notamment à partir d'une simple flamme de diffusion unidimensionnelle à contre-courant et d'une flamme complexe résultant de la combustion de polymères. Étant donné la complexité du mécanisme de formation de la suie et les brûleurs conventionnels utilisés pour l'étudier caractérisés par un fort couplage entre le champ d'écoulement et la chimie de la flamme, nous proposons d'étudier dans un premier temps son évolution morphologique dans une flamme située dans un champ d'écoulement unidimensionnel. Les données recueillies dans cette configuration simple sont primordiales pour le développement de modèles prédictifs de formation de suie car les flammes de diffusion turbulentes rencontrées de manière omniprésente dans les applications pratiques peuvent être modélisées comme des flammes de diffusion unidimensionnelles laminaires. De plus, la morphologie de la suie est également importante lors de l'étude de sa toxicité. Nous proposons d'étendre l'étude de sa morphologie à une flamme représentative d'une combustion accidentelle obtenue dans un calorimètre à cône en raison de son intérêt pour les études de toxicité et de sécurité incendie.

Le brûleur utilisé pour la flamme de diffusion unidimensionnelle fonctionne avec du méthane et de l'oxygène comme réactifs, dilués avec du dioxyde de carbone pour contrôler la richesse de mélange. Il se caractérise par un flux de comburant qui diffuse à contre-courant d'un écoulement unidimensionnel, résultant en un écoulement unidirectionnel au niveau de la nappe de flamme et permettant de longs temps de résidence de la suie du côté combustible de la flamme. Pour acquérir la suie, une méthode d'échantillonnage est développée à l'aide de grilles de microscope électronique à transmission en nickel revêtues de carbone. Les agrégats sont collectés à divers endroits dans la couche de suie de quatre flammes caractérisées par une richesse de mélange croissante. Les échantillons sont visualisés et enregistrés sur un microscope électronique à transmission. La méthode d'échantillonnage est ensuite étendue pour collecter la suie des polymères en combustion dans le calorimètre à cône. Le matériau utilisé pour la flamme de polymère est constitué d'un polyuréthane thermoplastique renforcé de cellulose mélangé à des additifs ignifuges, à savoir du polyphosphate de mélamine et du charbon actif à différentes charges

selon une méthodologie de conception d'expériences. De plus, un prélèvement d'aérosol est effectué au-dessus de la flamme de polymère pour suivre l'évolution de la taille des particules tout au long de la durée de la combustion.

Pour faciliter l'analyse morphologique des agrégats de suie collectés dans ces deux configurations, un algorithme de détection des monomères de suie est présenté qui utilise les bords externes des agrégats individuels comme image d'entrée. L'algorithme est développé en utilisant la suie des deux configurations pour étendre son domaine d'application, compte tenu du large spectre de morphologies attendues de ces flammes. Les performances de l'algorithme de détection ont été évaluées à l'aide d'échantillons de suie provenant de flammes unidimensionnelles et de flammes polymères de plus en plus riches. Il a été en mesure de détecter un déplacement de la distribution de taille vers des particules plus grosses, comme prévu. De plus, la suie obtenue à partir de polymères en combustion a montré des diamètres de monomères considérablement plus grands, tels que détectés par l'algorithme. Cependant, la distribution de taille était généralement sous-estimée par l'algorithme par rapport à celle obtenue par mesure manuelle. En comparant les emplacements entre les monomères de suie mesurés manuellement et ceux détectés automatiquement, nous avons pu observer que la première méthode se concentre généralement sur les régions internes à l'agrégat. Cette observation suggère la nécessité d'utiliser une image d'entrée plus complète contenant aussi des bords dans la région interne des agrégats pour une meilleure performance de l'algorithme.

Étant donné que l'algorithme ne pouvait pas reproduire les résultats obtenus par mesure manuelle, nous avons eu recours à une détection et une mesure manuelle des monomères de suie pour l'analyse morphologique de la suie. Dans la flamme de diffusion unidimensionnelle, nous avons observé la coexistence de particules primaires isolées avec des agrégats à travers la couche de suie visible. Les premiers suivent une distribution log-normale et sont beaucoup plus petits que les monomères trouvés dans les agrégats, qui suivent une distribution de taille normale. La taille de ces particules est positivement corrélée à la richesse de mélange. Des simulations numériques de la structure de la flamme indiquent la présence d'espèces propices à la croissance de la suie, à savoir l'acétylène, dans toute la région où la suie a été observée. Compte tenu du champ d'écoulement unidimensionnel au voisinage de la nappe de flamme, les particules de suie sont

soumises à deux forces opposées, à savoir la force de traînée et la force thermophorétique, augmentant ainsi le temps de résidence des particules dans la région de croissance de la suie. Selon un modèle impliquant des particules sphériques de taille constante et le gradient de température de flamme simulé, les particules inférieures à 5 μm ont tendance à être piégées dans la région de croissance jusqu'à ce que leur taille soit suffisamment grande pour que la force de traînée domine et les entraîne dans la flamme, résultant ainsi en leur combustion complète. L'évolution morphologique des particules de suie dans toute la couche de suie visible indique également qu'indépendamment de la richesse de mélange, les monomères trouvés dans les agrégats ont des dimensions comparables au début de la couche de suie visible et croissent ensuite selon le rapport d'équivalence. La diminution de taille à l'approche de la feuille de flamme est assez limitée, soulignant leur maturité. En ce qui concerne les agrégats, leur dimension fractale évolue le plus tôt dans la couche de suie visible suivie d'une convergence vers une valeur comprise entre 1,6 et 1,8 à maturité pour toutes les flammes.

Malgré la validation de la méthodologie de prélèvement de suie dans une configuration représentative de celle rencontrée au calorimètre à cône, des échantillons de suie n'ont pas pu être observés au microscope électronique à balayage pour les différentes combinaisons de matériaux de polyuréthane thermoplastique renforcé de cellulose et ignifugé. Nous avons donc eu recours à des échantillons de suie de composites phénoliques et époxy renforcés de fibres de carbone, obtenus dans le calorimètre à cône, pour le développement de l'algorithme de traitement d'image. Néanmoins, le spectromètre d'aérosol a pu suivre l'évolution de la matière particulaire pendant toute la durée de ces tests, fournissant des informations sur les effets des additifs sur la formation de suie et sa taille. Nous avons observé que l'ajout de cellulose dans le polyuréthane thermoplastique augmente la production de fumée. Cependant, une réaction synergique entre la cellulose et le polyphosphate de mélamine le réduit par rapport à son homologue non cellulosique. De plus, une réduction supplémentaire de la fumée peut être obtenue en incorporant du charbon actif dans cette combinaison de matériaux. En effet, la présence de charbon actif réduit la taille et la concentration des particules.

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LIST OF ACRONYMS

Acronym	Definition	Units
% v/v	Concentration given as a percentage calculated on a volume basis	-
%RM	Percent of initial specimen mass remaining at the end of the test	-
%THR _{smold}	Percent of the total heat released in the smoldering combustion regime	-
(C ₆ H ₁₀ O ₅) _n	Chemical formula of the cellulose polymer	-
∇T	Spatial temperature gradient	K/mm
1D	One-dimensional	-
2D	Two-dimensional	-
3D	Three-dimensional	-
a	Strain rate	s ⁻¹
A	Preliminary list of circle parameters (x _c ,y _c ,r _c ,S ₁) representing potential solution circles for input image I	-
A ₁	New version of list A where duplicates in (x _c ,y _c ,r _c) have been combined into one entry	-
A ₂	New version of list A ₁ where candidate circles located outside the aggregate area are removed	-
A ₃	New version of list A ₂ where the optimal radius r _c ' is selected and score S _C is calculated	-
A ₄	New version of list A ₃ where entries are arranged in increasing order of r _c ' and decreasing order of S _C	-
A ₅	New version of A ₄ after application of the threshold score S _{C,th}	-
A _a	Projected area of the aggregate	pixels
AC	Activated carbon	-
ANOVA	Analysis of variance	-
A _p	Projected area of the primary particle	pixels
AR	Aspect ratio of isolated primary particles	-
C ₂ H ₂	Chemical formula of acetylene	-
CFD	Computational fluid dynamics	-
CH ₄	Chemical formula of methane	-
CHT	Circular Hough transform	-

CNF	Cellulose nanofibers	-
CO ₂	Chemical formular of carbon dioxide	-
C _{ov}	Actual overlap coefficient	-
C _{ov,proj}	Observed overlap coefficient between two partially overlapping primary particles	-
D ₅₀	Median of a distribution	-
d _{cc}	Distance between the centroid of the aggregate projection and a soot monomer	pixels
d _{ce}	Distance between the centroid of the aggregate and the edge along the line defined by d _{cc}	pixels
DEHS	Di-ethyl-hexyl-sebacate oil	-
D _f	Fractal dimension when calculated using R _g	-
D _{fL}	Fractal dimension when calculated using L _{max}	-
D _{ij}	Length of the region common to two overlapping particles along an axis joining their center points	pixels
d _m or d _p	Diameter of particles as measured by SMPS or GRIMM	nm
DMA	Differential mobility analyzer	-
D _{max}	Distance constraint between two points p ₁ and p ₂ for inclusion into V _{pairs}	nm
d _{min}	Length of line l ₃	pixels
d _{ms}	Distance below the oxidizer inlet plane for mass spectrometer sampling	mm
D _p	Diameter of primary particles found in aggregates	nm
D _{p,max}	Upper bound of the permissible primary particle diameter range of the circle detection algorithm	nm
d _{p,max,flm} *	Diameter at the mode of the particle size distribution when peak smoke production occurs in the flaming regime	nm
d _{p,max,smold} *	Diameter at the mode of the particle size distribution when peak smoke production occurs in the smoldering regime	nm
D _{p,min}	Lower bound of the permissible primary particle diameter range of the circle detection algorithm	nm

EDM-SBS	Euclidean distance mapping surface-based scale	-
FAA	Federal Aviation Administration	-
f_{agg}	Fraction of the aggregate's projected area covered by solution circles	-
f_c	Sub-unitary quality parameter capturing the fraction of a candidate circles' pixels matching edge map pixels	-
f_{dist}	Non-dimensional distance parameter quantifying the location of a soot monomer with respect to the centroid and the edge of the aggregate's projection	-
f_{frag}	Sub-unitary parameter capturing the level of fragmentation between the edge map and a candidate circle	-
FFT	Fast Fourier transform	-
f_i	Flame ID where i takes values from 1 to 4	-
f_{ov}	Sub-unitary coefficient controlling the extent of the region around r_c' around (x_c, y_c) to eliminate solution candidates	-
GT	Gas turbine	-
H^+	Chemical formula of hydrogen radical	-
H_2	Chemical formula of dihydrogen	-
H_2O	Chemical formula of water	-
H_c/A	Heat of combustion per unit area of specimen's exposed surface	MJ/(kg·m ²)
HRR	Heat release rate	kW/m ²
HT	Hough transform	-
I	Original gray-level image (i.e. micrograph) of soot aggregate	-
I_{binary}	Binary image obtained by conserving only the aggregate area from $I_{binary,1}$	-
$I_{binary,1}$	Binary image obtained following a thresholding operation	-
ICE	Internal combustion engine	-
I_{circle}	Binary image of a solution circle	-
I_{edge}	Binary image of the aggregate edge map	-
$I_{edge,normal}$	Gray-level image of the gradient direction of the aggregate map	-

$I_{\text{edge,sol}}$	Binary image where the pixels common between the solution circle and the aggregate edge are shown	-
I_{median}	Median-filtered instance of I	-
I_{S1}	Gray-level image where the non-zero pixels represent candidate circle centers, and their value is the score S_1	-
$I_{S1'}$	New version of image I_{S1} , where non-zero pixels located outside the aggregate area are removed	-
ISO	International Organization for Standardization	-
k_a	Constant used to calculate N_P	-
k_g	Fractal pre-factor when using R_g to calculate D_f	-
k_L	Fractal pre-factor when using L_{max} to calculate D_{fL}	-
l_1, l_2	Projection lines passing through p_1 and p_2 , respectively	-
l_3	Shortest line joining l_1 and l_2 if these are skew	-
LII	Laser-induced incandescence	-
$L_{\text{major,axis}}$	Major axis length of isolated primary particles	nm
L_{max}	Aggregate maximum length	nm
LOI	Limiting oxygen index	-
MPP	Melamine polyphosphate	-
MVR	Melt volume rate	$\text{cm}^3/10\text{min}$
n_1, n_2	Vectors normal to edge points at p_1 and p_2 , respectively	-
N_{agg}	Number of individual soot aggregate micrographs in the dataset	-
n_{common}	Number of pixels common to both a solution circle and the aggregate edge map	pixels
n_{conncomp}	Number of connected components in $I_{\text{edge,sol}}$	-
N_{det}	Total number of solution circles detected by the algorithm in an input dataset	-
N_{meas}	Total number of solution circles measured manually in an input dataset	-
N_P	Number of primary particles per aggregate	-
O_2	Chemical formula of oxygen	-
OD	Outer diameter	mm
p^*	Critical value of the pair correlation function	-

p_1, p_2	Edge points used to determine the center of a candidate circle	-
PAH	Polycyclic aromatic hydrocarbon	-
PCM	Pair correlation method	-
PHRR/A*	Peak heat release rate per unit area of specimen's exposed surface after Box-Cox transformation *	-
PMC	Polymer matrix composite	-
PTFE	Polytetrafluoroethylene	-
R	Radius of circle in Hough parameter space	pixels
r_c	radius of candidate circle located at (x_c, y_c)	pixels
RCD	Randomized circle detection	-
R_g	Radius of gyration	nm
r_{tol}	Tolerance on the radius of a candidate solution circle	pixels
S_1	Score capturing the likelihood that a pair of edge points is part of a circle	-
$S_{A,flm}$	Total smoke production in the flaming regime	1/s
S_C	Combined score	-
$S_{C,th}$	Threshold value of S_C for a candidate circle to be conserved	-
SD	Surface density of isolated primary particles on the sampling substrate	# particles/ μm^2
SEM	Scanning electron microscope	-
SF	Soot-formation flame configuration in experimental counterflow burners	-
SFO	Soot-formation-oxidation flame configuration in experimental counterflow burners	-
SLPM	Standard liters per minute	L/min
SMPS	Scanning mobility particle sizer	-
t	Image threshold value in a range from 0-1.0	-
TC	Thermocouple	-
TEM	Transmission electron microscope	-
t_{ext}	Time elapsed until extinction	s
$T_{f,0}$	Inlet temperature of the fuel stream	K
T_{flame}	Numerically calculated flame temperature	K
THE	Total heat evolved	MJ/m ²
t_{ign}	Time elapsed until sample ignition	s

TiRe-LII	Time-resolved laser-induced incandescence	-
$T_{o,0}$	Inlet temperature of the oxidizer stream	K
TPU	Thermoplastic polyurethane	-
$t_{S,max,flm}$	Time elapsed until peak smoke production in the flaming regime	s
$t_{S,max,smold}$	Time elapsed until peak smoke production in the smoldering regime	s
t_{soot}	Soot layer thickness	mm
VFR_F	Volumetric flow rate of the fuel stream (SLPM)	L/min
VFR_O	Volumetric flow rate of the oxidizer stream (SLPM)	L/min
V_{pairs}	List of valid point pairs used for circle detection	-
W	Aggregate width	nm
wt%	Additive loading given as a percentage calculated by on a mass basis	-
x	Cartesian x-coordinate	-
x_c	x-coordinate of candidate circle center	-
X_i	Molar fraction of species i	-
y	Cartesian y-coordinate	-
y_c	y-coordinate of candidate circle center	-
Z	Mixture fraction	-
Z_f	Non-dimensional flame location in the 1D burner where $Z=0$ at the fuel inlet	-
Z_{st}	Stoichiometric mixture fraction	-
α_a	Empirical exponent used to calculate N_p	-
ζ_1	First empirical constant used to calculate C_{ov} from $C_{ov,proj}$	-
ζ_2	Second empirical constant used to calculate C_{ov} from $C_{ov,proj}$	-
λ	Value used for Box-Cox transformation	-
μ	Mean value of a dataset	variable
σ	Standard deviation of a dataset	variable
τ_{res}	Simulated cumulative particle residence time	s
τ_{samp}	Sampling substrate residence time at the sampling location	s

ϕ	Freestream fuel equivalence ratio calculated from flow controller values of methane and oxygen	-
$\phi_{\infty,i}$	Freestream fuel equivalence ratio calculated using measured boundary conditions in the 1D burner of flame i, where i takes values from 1 to 4	-
ε	Constant controlling the rate of decay for the calculation of the sub-unitary coefficient f_{frag}	-

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CHAPTER 1 INTRODUCTION

1.1 General context

Accidental fires such as forest and crop fires are an important source of particulate matter, namely soot, resulting from the uncontrolled nature of the combustion. Fires occurring in enclosed spaces such as buildings and means of transport (i.e., trains, aircrafts) also fit in this category. These are uncontrolled by definition, thereby emitting considerable amounts of soot, as highlighted by the yellow/orange flame color and the dark smoke plumes, as shown in Figure 1.1. The heat radiated by these particles greatly contributes to the spread of accidental fires [1]. In applications where visibility is critical to the survival of the occupants, the propensity of combustible materials to generate particulate matter in an uncontrolled combustion scenario must be precisely quantified and minimized to mitigate the risk for loss of life [2]. An example of such a scenario is the accidental fire occurring in an aircraft, where an excessive smoke production by burning cabin materials could delay the evacuation and intoxicate or kill the occupants.



Figure 1.1: Car fire emitting considerable amounts of particulate matter, as highlighted by the orange flame and the dark smoke plume. Author: David Henry, source: pexels.com

Soot is also produced by a wide range of household, commercial and industrial devices. Environmental protection laws require large industries to monitor their particulate matter output, essentially focusing on the mass emitted. However, most of soot properties depend on its microstructure, a critical factor often overlooked. For example, in the upper atmosphere, the radiative properties of soot enhance the condensation of water vapor leading to artificial cloud nucleation and contrails [3]. Although some applications are designed to operate in a regime where particulate matter is generated, for others, the synthesis of such particles represents a collateral effect. Practical applications requiring an efficient transfer of heat from the flame to the surrounding medium exploit the great emissive properties of these particles to channel the heat, such as powerplant boilers, ship boilers and other heating appliances. However, devices designed to convert chemical energy into mechanical energy by means of combustion suffer from nanoparticle formation, outlining a regime of inefficient combustion. Soot clumps cause the abrasion of the cylinder liner in internal combustion engines, leading to compression loss. It can also induce wear on components of the valve train [4], namely camshafts, rocker arms, valve stems, etc. The contamination of lubrication oil by soot can alter its properties, ultimately challenging the mechanical integrity of the engine [5]. In aircraft engines, soot deposits on turbine blades can modify the aerodynamic and cooling properties of these components [6].

Particulate matter emissions from the pyrolysis and/or combustion of polymeric materials also pose an increasing concern. Our society's reliance on polymers generates high volumes of combustible trash, ranging from packaging to highly advanced materials from the aerospace, construction and automotive industries [7]. Despite their high energy content, the recycling of polymers is expensive due to high sorting costs and the limited value of recycled materials [8]. Incineration remains a plausible alternative, however such a process must be optimized to reduce harmful pollutant emissions [9]. For example, in a flow reactor where the combustion is still relatively well controlled, up to a quarter of the weight of the polymer can be converted into carbon particulates [10].

1.2 What is soot?

Soot is a solid product of incomplete combustion; these particles are responsible for many adverse effects on humans [11] but also on the environment [12, 13]. Individual soot particles may be encountered either as quasi-spherical particles, termed primary particles or monomers, or as aggregates, which are clusters of primary particles. Soot monomers have a wide diameter spectrum, from a couple of nanometers to roughly 60 nm [14]. On the other hand, aggregates may be composed from a few, up to thousands of primary particles and span across orders of magnitude in size [15]. In Figure 1.2, a transmission electron micrograph of a soot aggregate is shown, highlighting a few aggregate monomers along with some isolated primary particles. Both primary particles and aggregates can be encountered at different levels of maturity, depending on the particularities of the flame in which they were generated. The quantity and spatial arrangement of primary particles in aggregates is referred to as the morphology and is quantified by parameters such as the number of primary particles per aggregate, the aggregate maximum length, the overlap coefficient between monomers and the fractal dimension [16]. The morphology is heavily correlated with operating conditions of the given flame [17], such as the type of fuel and oxidizer, the mixture strength, the flame structure, the temperature, the residence time, the flow field, the presence of gaseous additives, etc.

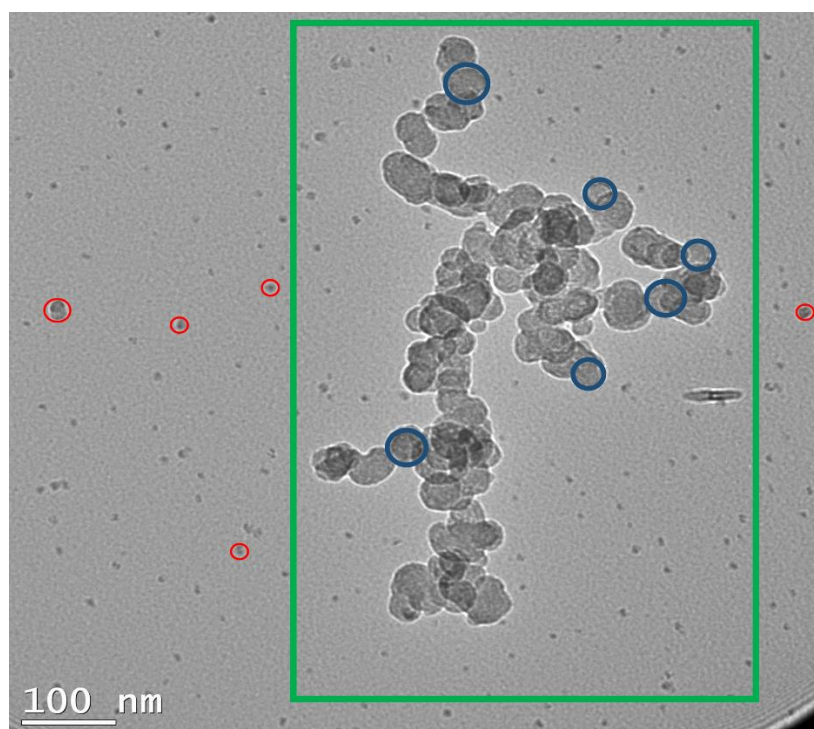


Figure 1.2: Transmission electron micrograph of a soot aggregate (green box) composed of monomers (blue circles) and surrounded by isolated primary particles (red circles)

As such, the broad domain of combustion sources outlined previously results in soot that is characterized by a wide spectrum of morphologies. Critically, non-intrusive diagnostic tools used to measure soot concentrations and particle size distributions in flames require precise knowledge of soot properties to yield accurate results. One such technique is the time-resolved laser-induced incandescence (TiRe-LII), which relies on an accurate modeling of vaporization and heat transfer of soot particles as they cool after a rapid heating event by a laser pulse to temperatures of around 4000 K. The heat transfer model, whose components depend on the particle size [18], assumes point contact between spherical primary particles in aggregates, which is seldom the case for soot. By performing a fit between the model and the time-resolved LII signal, one can determine the mean primary particle diameter in aggregates [19].

The morphology of soot is also primordial to the study of its toxicity. Indeed, soot is noted to contain a variety of poly-aromatic hydrocarbon (PAH) molecules; with some known as mutagens and human carcinogens [20]. Many PAHs can be found on the surface of soot particles, with

benzo[a]pyrene (i.e. benzopyrene) getting attention due to its carcinogenic nature. The dynamics of elution and desorption of carcinogenic PAHs into biological tissues depends on the size and maturity of the host particle [21]. Soot recovered from the lungs of deceased human subjects contained less pyrene than expected, while benzopyrene could not be detected, thus highlighting a higher elution rate into biological tissue for the carcinogenic PAH, compared to its innocuous counterpart [22]. In dogs, it was found that benzopyrene desorbed more readily in the lymph nodes than in the lungs [23]. Moreover, high levels of atmospheric pollution increase the ratio of benzopyrene-to-pyrene on the surface of particles [22], effectively making them more harmful.

As a result, a reduction in the emission of particulate matter is sought but more importantly, the morphology of soot must be accurately predicted to forecast its physical, optical, and toxicological properties.

1.3 Motivation and research goals

This research endeavour is motivated by a set of shortcomings identified in the literature with regards to soot formation. The configurations typically exploited in experimental soot formation studies often suffer from complex flow fields in the reaction zone, complicating the understanding of the phenomena leading to soot particle inception, growth, aggregation and ultimately oxidation. Indeed, it is difficult to assess the contribution of the flow field on the observed soot aggregates, and it is even more difficult to perform detailed chemical simulations while accounting for this effect. Thus, the simulated flame structure may suffer from inaccuracies and lead to erroneous conclusions regarding the role of key chemical species on the soot formation mechanism. Moreover, the various stages of the life cycle of soot (i.e. inception, growth and oxidation) and the existence of any overlap between these stages is not thoroughly understood.

In addition to the gaps in the experimental soot data from simple experimental configurations, the methods employed for the post-processing of this data are very tedious and bear some level of subjectivity. More specifically, the image processing algorithms used for the morphological quantification of soot samples are very crude and often rely on manual measurements of the primary particle diameters and the aggregate maximum lengths. Since some soot aggregates may

contain hundreds of primary particles, the manual analysis is often limited to readily distinguishable monomers on the periphery of the aggregate. The measurement of the aggregate maximum length by a human subject is also biased because an iterative procedure is required to detect the axis along which the maximum length of the 2d projection of the aggregate resides.

With respect to carbon particulates originating from unwanted or accidental combustion, little work has been done to characterize their morphology. This information is of primary relevance in scientific fields focusing on toxicological and air pollution studies. Such fires occur very often, either in open-air environments, in buildings or in the transportation sector. People exposed to the combustion effluent of such fires, whether they represent firefighting crews or occupants, must have access to adequate protective equipment to ensure their safety. The development of optimal protective equipment against a particulate effluent from uncontrolled combustion relies on the accurate characterization of this effluent. As such, we propose to incorporate soot samples acquired in an experimental configuration representative of accidental/uncontrolled combustion into the development of the image processing algorithm to ensure its robustness to a large spectrum of soot morphologies.

In this project, we study the morphology of soot in a carefully controlled experimental configuration. The soot formation mechanism being very complex, it is best studied in simple settings. The setup consists of a one-dimensional (1D) un-stretched and unstrained counter-flow diffusion flame. This configuration is a relative novelty in the field of combustion, and it uncouples the combustion chemistry from the complex three-dimensional fluid mechanics phenomena occurring in the reaction zone of typical flames used thus far in the study of soot. Moreover, we propose to extend the study to soot originating from a configuration which is representative of accidental (or unwanted) combustion as its morphology is expected to be quite different from the former case. For this purpose, polymer matrix composites (PMCs) will be manufactured, and their flammability will be assessed. During these flammability tests, soot samples will be acquired. These samples will be used in conjunction with those from the 1d diffusion flame for the development of new and implementation of existing image processing techniques for morphological quantification. This project is thus centered around contributions to the

morphological characterization of soot particles at different stages of their life cycle and from different sources, from their inception until their oxidation, if applicable.

1.4 Thesis structure

In the following chapter, the literature review is initiated by first discussing the experimental configurations used to study the formation of soot, with a special focus on their limitations for morphological characterization. Subsequently, the typical sources of soot emissions are presented, highlighting the wide morphological spectrum of these particles depending on the application from which they originate. Then, the steps involved in the morphological quantification of soot are covered, along with the pertinence of studying soot morphology from different perspectives. Generic and contextual image processing algorithms applicable for the morphological characterization of soot are also described.

Following the literature review, a critical assessment is presented, highlighting the research objectives of the present work. This is followed by a description of the methodology employed and a detailed account of the results obtained, in the form of three scientific journal articles. Finally, we present a general discussion to highlight the achievement of the research objectives and their impact and conclude the dissertation by presenting the limitations of the presented work and some recommendations for future works.

CHAPTER 2 LITERATURE REVIEW

In this chapter, the scientific literature discussing the formation and measurement of soot is reviewed. The experimental configurations used to study the pathways leading to soot formation are described, to outline their specificities pertinent to the research of the phenomenon. Next, the morphological diversity of soot originating from common research burners and practical combustion sources employed in different industries is briefly highlighted, justifying the need for simple experimental configurations to study the fundamentals of the formation process. Subsequently, the steps involved in the morphological characterization of soot are covered along with the relevance of morphological information to specific domains of particulate matter studies. The image processing tools typically employed in the morphological characterization of soot are highlighted, followed by a brief summary of the thermophoretic sampling method employed for capturing soot from flames. The reader interested in a more detailed presentation of the mechanisms governing the inception, the growth and the oxidation of soot is referred to **Erreur ! Source du renvoi introuvable.**, provided as an appendix.

2.1 Experimental configurations in soot research

In this section, burner configurations used in research settings will be discussed. Some examples of differences among burners consist of the transport mechanism of reactants, the relative flow direction of the reactants, the flame geometry and so on. The features of the main experimental burners will be covered below, but first, the main characteristic distinguishing the two categories of combustion is discussed, namely the mixing of reactants.

2.1.1 Premixed versus non-premixed combustion

Combustion of gaseous reactants is generally divided into two categories: premixed and non-premixed [24]. A spatial separation of the fuel and oxidizer prior to combustion results in a non-premixed flame (i.e. diffusion flame), whereas the combustion of a homogenous mixture of the fuel and the oxidizer results in a premixed flame [25].

In premixed combustion, combining of the reactants can be performed by a mixer, a swirler or by diffusion inside a plenum, and the resulting mixture may respect or deviate from stoichiometric proportions. When the mixture is flammable, a deflagration wave propagates through the mixture at a velocity termed the flame speed. If the mixture flows at the same velocity as the flame speed, one can obtain a stationary flame normal to the direction of the flow [26]. A premixture is highly reactive, therefore it is rarely used in practical applications. Instead, a non-flammable partial premixture is often employed [27, 28], where the remainder of the mixing is performed shortly before combustion.

In non-premixed combustion, the diffusion of the gaseous species to the reaction zone is responsible for the mixing, resulting in a diffusion-limited reaction rate [24]. This configuration results in a flame that is stationary (i.e. the flame does not propagate), characterized by stoichiometric proportions of the given fuel-oxidizer pair. To avoid flame quenching or reactant starvation, the reactants must be available at a flow rate equal or slightly larger than the reactant consumption rate [24].

In the following sections, we present the premixed and non-premixed configurations used for the investigation of soot formation, with a special focus on their limitations toward the study of soot morphology.

2.1.2 Premixed flame configurations

2.1.2.1 Bunsen burner

In a premixed Bunsen burner flame, soot formation may be inhibited, as illustrated by the exclusively blue flame in Figure 2.1a, but only for premixtures characterized by a carbon-to-oxygen atom ratio (C/O) much below the theoretical value of 1.0 [29]. To obtain soot, the C/O ratio must be above the threshold value for the fuel considered and hence, lean, stoichiometric and rich premixtures or diffusion flames can be used to generate a soot in this configuration [30, 31], as shown in Figure 2.1b. However, the axisymmetric geometry of the burner is such that the flame location, its structure and the residence time varies as a function of the radial position but also as

a function of the height [32, 33], resulting in a broad range of soot morphologies over relatively small distances [31]. In addition, the interaction between the stream exiting the stack and the quiescent air introduces an additional flow field complexity, leading to coalescent and/or coagulative collisions [34] and ultimately affecting the morphology of the soot.

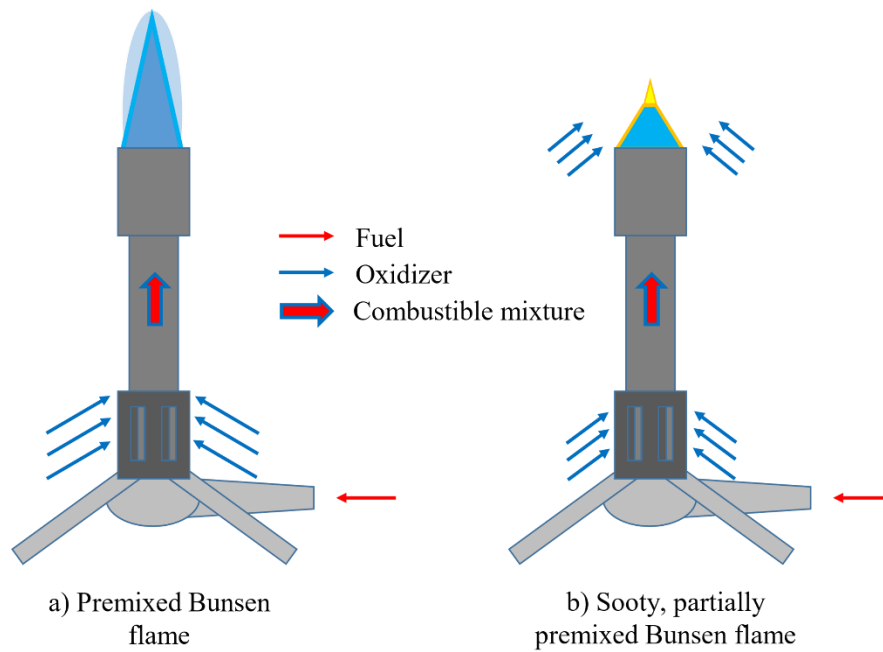


Figure 2.1: a) premixed non-sooty Bunsen burner flame and b) sooty, partially premixed flame

2.1.2.2 McKenna burner

The McKenna burner is another configuration permitting the study of soot in premixed flames [25, 35, 36]. Its advantage over the Bunsen burner is that it produces a flat flame, as shown in Figure 2.2, therefore making it attractive for combustion research because typical parameters of interest such as temperature and flame structure vary only along a single dimension (i.e. parallel to the flow direction) [35]. However, since premixed flames propagate at a constant speed for a given fuel/oxidizer pair and equivalence ratio [26], the resulting soot has a limited residence time in the region characterized by a high temperature and abundant species required for soot growth. As a result, it is much less mature compared to that obtained in diffusion flames [25, 36], such as those

encountered in accidental fires. The particulates contain a considerable amount of volatile material on their surface, strongly correlated with the size of aggregates [36].

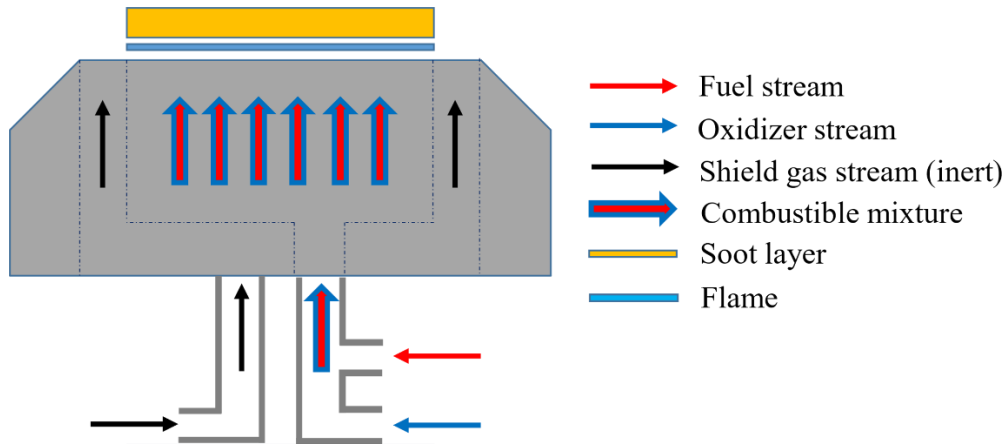


Figure 2.2: Schematic representation of the McKenna burner, the planar flame (blue) and the soot layer (yellow)

From a morphological standpoint, the difference in the maturity of the particles makes the soot from this configuration less relevant compared to that from diffusion flames typically encountered in practical applications. Furthermore, the use of McKenna burners in soot studies recently became a concern due to the observation of a radially non-uniform soot volume fraction profile despite a uniform reactant flow field [35]. This additional complexity, hypothesized to be a result of the material used for the porous plug, hinders the proper understanding of the effect of flame parameters on the observed morphology of soot.

2.1.3 Non-premixed flame configurations

The investigation of the morphology of soot is more adequately performed in a non-premixed flame configuration because it is more relevant to practical applications (gas turbines, diesel engines, etc.), but also because the heat release region is much wider compared to premixed configurations [24], hence allowing for longer soot residence times and a better spatial resolution. The confinement of the flame to a thin sheet and the presence of a fuel-rich and an oxidizer-rich region on either side of the flame make this configuration very attractive for fundamental research

due to the smooth progression of the mixture proportions along the direction of diffusion [24], creating a continuum of thermochemical events. The mixture fraction Z is employed as a universal means of comparing the flame structure across the different non-premixed configurations based on the local degree of mixing [37]. The location of the flame is characterized by the stoichiometric mixture fraction Z_{st} and can vary for the same fuel-oxidizer pair depending on the freestream concentrations of the fuel and oxidizer.

2.1.3.1 Coflow diffusion flame

The construction of a co-flow diffusion burner, shown in Figure 2.3, is similar to the Bunsen burner. It is composed of three concentric tubes; the inner and center tubes transport the fuel and the oxidizer, or vice versa, while a shielding inert gas flows through the outer tube, thereby isolating the flame from the ambient atmosphere.

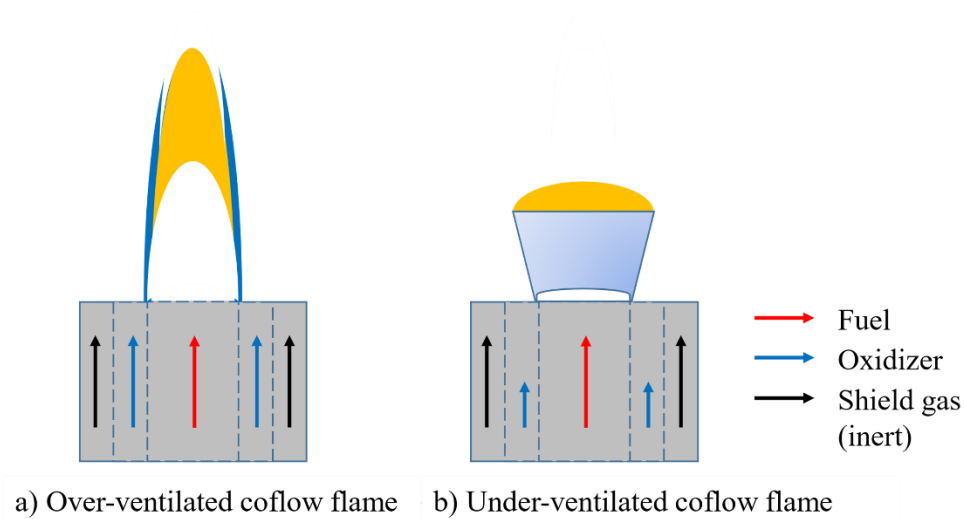


Figure 2.3: Schematic representation of the normal coflow diffusion burner showing a) the over-ventilated and b) the under-ventilated flame geometries. The flames and soot layers are shown in blue and yellow, respectively.

Whether in the over-ventilated (Figure 2.3a) or the under-ventilated case (Figure 2.3b), the flame profile of the non-premixed coflow burner exhibits a complex geometry, which depends on the relative velocities of the reactant flows [37, 38]. At the base, near the burner rim, the mixing of

reactants is enhanced due to the thermal expansion of the gases leaving the flow tubes [14]. Computational fluid dynamics simulations (CFD) [39] have shown that iso-contours of oxygen molar fraction, heat release rate per unit volume and temperature possess a dependence on the axial but also on the radial coordinate. In the over-ventilated scenario, corresponding to an excess of oxidizer relative to the flow rate of fuel and shown in Figure 2.3a, a strong velocity gradient at the interface between the reactant streams can be observed. This region is highly relevant in the study of the lifecycle of soot particles and the complex flow field is not conducive to analysis. The coflow diffusion flame is buoyancy-dominated [14]; therefore, the residence time varies strongly with the axial temperature evolution, except near the burner rim [37]. In addition to a lengthening of the flame [37], an increase in the exit velocity enhances the heat transfer from the burner rim to the reactants, thereby reducing the residence time. Since the presence of soot has a large contribution on the radiative heating of the burner rim [14], the resulting heat transfer loop translates into soot production indirectly affecting residence time, outlining a complex coupling with regards to soot formation.

As such, the soot formation region is characterized by an ensemble of parameters which exhibit a very heterogeneous behaviour depending on the portion considered. To tackle such inhomogeneity, simpler non-premixed configurations are sought, where the flow field in the vicinity of the flame sheet is quasi-one-dimensional. Such configurations will collapse the complexity induced by the flow field into a system described by parameters which exhibit a much smoother variation in space.

2.1.3.2 Counterflow diffusion flame

Counterflow diffusion flames can be obtained using various configurations [24], such as the porous spherical or cylindrical burners, the opposed jets burner, and the one-dimensional chambered flame. The former two, shown in Figure 2.4a and b, are immersed in a slowly flowing oxidizer atmosphere and the flame forms near the forward stagnation plane. Such configurations can also be operated by switching the injected reactant from fuel to oxidizer and by having the ambient reactant as quiescent. Unfortunately, all these variations result in hydrodynamic effects on the flame structure, which also affect soot formation [40]. The latter two configurations, illustrated in

the following subsections, consist of two opposed inlets of reactants, resulting in a flame between them.

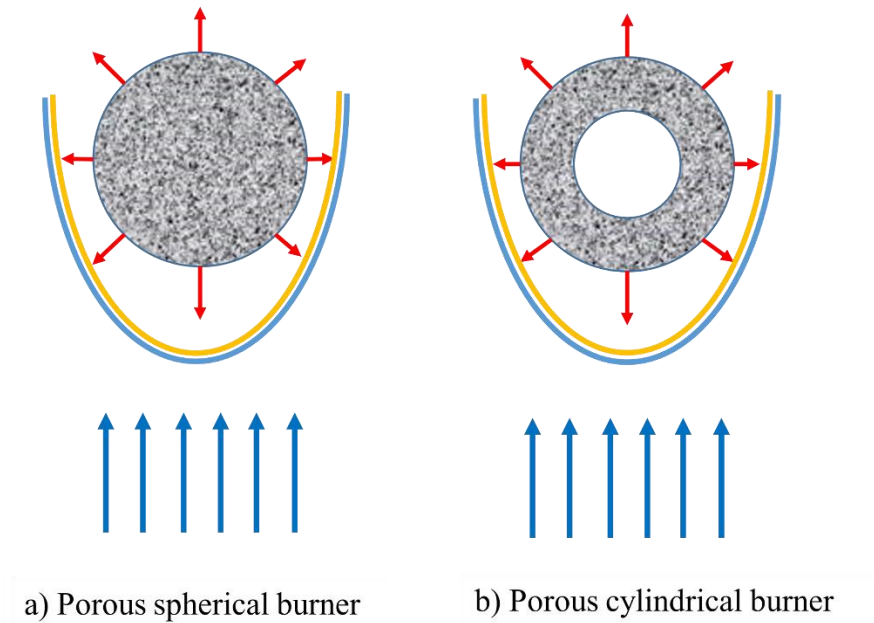


Figure 2.4: Schematic representation of the porous a) spherical and b) cylindrical diffusion burners, qualitatively depicting the resulting flames (blue) and soot layers (yellow)

Counterflow diffusion flames are relevant in the context of the flamelet model, where turbulent flames are discretized into thin reaction sheets that behave as laminar diffusion flames [41]. The designation of *diffusion flame* does not necessarily imply that the transport is purely diffusive [42]. In fact, the first three configurations listed above are characterized by a convective transport component [24], but diffusion is the dominant mixing mechanism given that the flow is laminar.

Opposed jets flame

The opposed jets configuration solves many of the imperfections manifested by its coflow counterpart through the relative simplicity of flow field near the reaction sheet. Since the flame front is planar and stationary within a bulk flow [24], the residence time may be calculated analytically. As its name implies, the opposed jets flame is achieved by opposing two streams of reactants such that they impinge on each other, as shown in Figure 2.5. Each stream is shielded by

a coflowing inert gas, and the velocities of the reactants can be varied, hence changing the spatial velocity gradient of the flow (i.e. the strain rate a) [42, 43] and the residence time. An increase in the strain rate was shown to affect the flame structure, namely by reducing the flame thickness [43]. The flame location can be controlled by diluting/enriching the concentrations of reactants at the boundaries of the system [44], resulting in a flame where the forced convection entrains soot particles either into the oxidizer stream (i.e. soot-formation-oxidation: SFO), or into the fuel stream (i.e. soot-formation: SF) [45], as depicted in Figure 2.5.

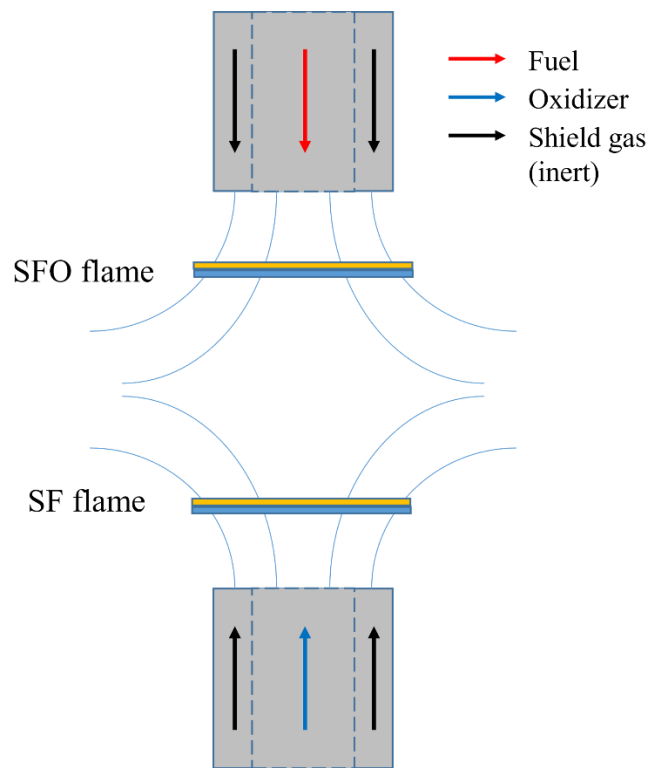


Figure 2.5: Schematic representation of the opposed jets diffusion flame, qualitatively showing the flow field streamlines, the flame and the soot layer in the SFO and SF configurations.

The opposed jet arrangement induces a nonuniform flow field in the reaction sheet of the flame, resulting in flame stretch [46], as highlighted by the diverging streamlines in the figure. As a result, the soot particles follow a complex flow path, which may enhance or inhibit mechanisms of coagulation and/or coalescence, but also chemical mechanisms responsible for soot growth, ultimately affecting the morphology of soot in a significant and hard to predict manner.

One-dimensional laminar diffusion flame

The one-dimensional laminar diffusion flame, shown in Figure 2.6a, was initially introduced as an idealized construct [47], convenient to develop theoretical models but not believed to be experimentally realizable. However, Jacono et al. [48] were able to materialize a proof-of-concept implementation that was later improved and extended by Robert et al. [49], shown in Figure 2.6b.

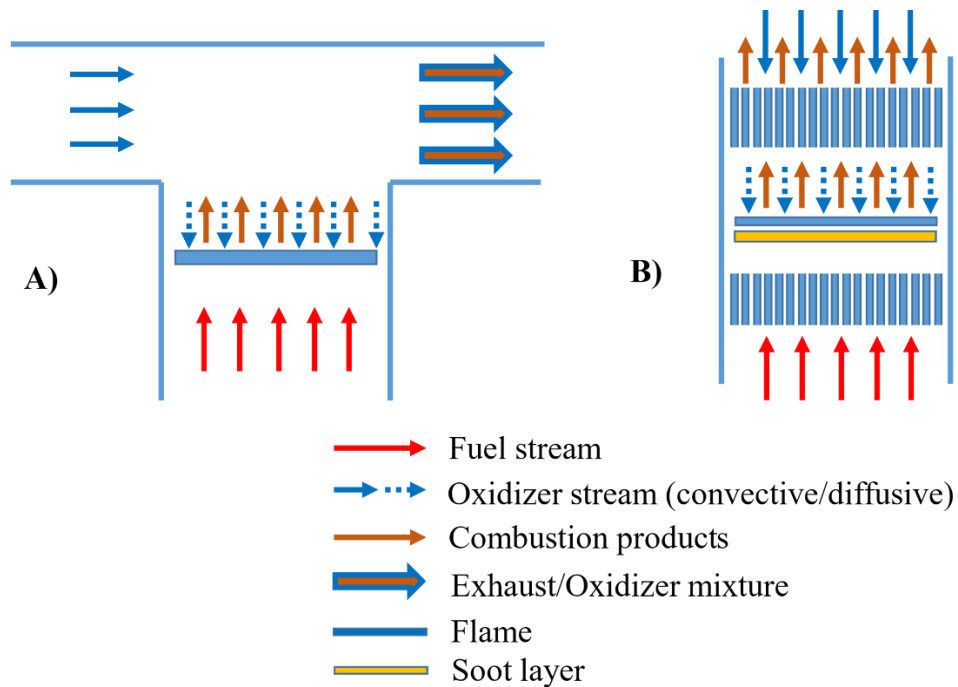


Figure 2.6: Schematic representation of a) the theoretical one-dimensional chambered flame model and b) the one-dimensional unstrained counterflow diffusion flame in a sooting condition

This configuration consists of a chamber of constant cross-sectional area with two opposed inlets, operating at atmospheric pressure. In the experimental implementation, a uniform one-dimensional reactant injection flow field is achieved at the flame with the use of needle arrays as inlets. The fuel is advected to the flame while the oxidizer is injected against the bulk flow, counter-diffusing toward the flame and allowing the exhaust to escape uniformly between the injection needles. The thin layers, herein referred to as ‘injection layers’, immediately downstream of the needle exit planes are characterized by a three-dimensional flow field but only over a distance comparable to

the needle spacing (i.e. 2.5 mm) [50]. The confinement of the flame in a chamber characterized by a one-dimensional bulk flow results in an unstrained planar diffusion flame sheet. It therefore constitutes an interesting configuration for the study of flame structures, but also for soot. Given the thickening of the reaction zone due to the absence of strain [43], thermochemical events can be investigated with a higher spatial resolution compared to the premixed or to the strained counterflow configurations presented earlier. Moreover, the morphology of soot is not affected by a complex flow field in the reaction zone and the flame can be solved analytically to obtain a detailed flame structure, as well as profiles of temperature and axial velocities. From a soot morphology perspective, aggregates formed on the fuel side of this flame are pushed against the bulk flow by thermophoresis (i.e. down the temperature gradient) and can remain trapped in the soot growth region until they grow large enough to be entrained by the aerodynamic drag [51]. This feature results in long residence times, hence a continuum of soot particles with varying and well characterized thermo-chemical histories can be investigated simultaneously.

2.2 Soot emissions sources

Several industries are responsible for soot emissions, namely transport, power generation, waste management but also accidental fires (building, forest and crop fires) [52]. There exist drastic differences between the combustion conditions within each of these categories. Since the formation of soot occurs in fuel-rich regions of a flame, a proper degree of mixing is a critical in the control of particulate emissions [28]. To mitigate local deviations from a desired stoichiometry toward fuel-rich mixtures, turbulent flows are employed to enhance mixing [53]. If combustion is performed at high pressures with inadequate mixing, the problematic fuel-rich regions contain a higher fuel density, hence generating more particulate matter per unit volume [14, 54].

2.2.1 Liquid fuels

In the transport industry, the fuels used in internal combustion engines (ICEs) and gas turbines (GTs) consist mainly of gasoline or diesel and kerosene or natural gas, respectively. Their combustion occurs under at least 8-9 bars of pressure in the case of the former, whereas modern gas turbines such as the General Electric GE9X (i.e. turbofan) may operate at an overall

compression ratio of 60:1. As shown in Figure 2.7a, the injection of gasoline in ICEs is typically performed in the ports of the intake valves (i.e. port injection) [55], while fuel is injected directly into the cylinder for diesel ICEs (i.e. direct injection in Figure 2.7b) [56], ultimately resulting in different means and efficiency of mixing the fuel charge. In gas turbines, there exist various types of fuel injection systems. For instance, pressure-atomizing injectors rely on a high fuel pressure to produce a fine spray, whereas air-blast atomizing injectors operate at lower pressures while exploiting the momentum of primary air to generate and mix the fuel spray [57]. These different types of injection systems encountered in transportation applications are qualitatively shown in Figure 2.7.

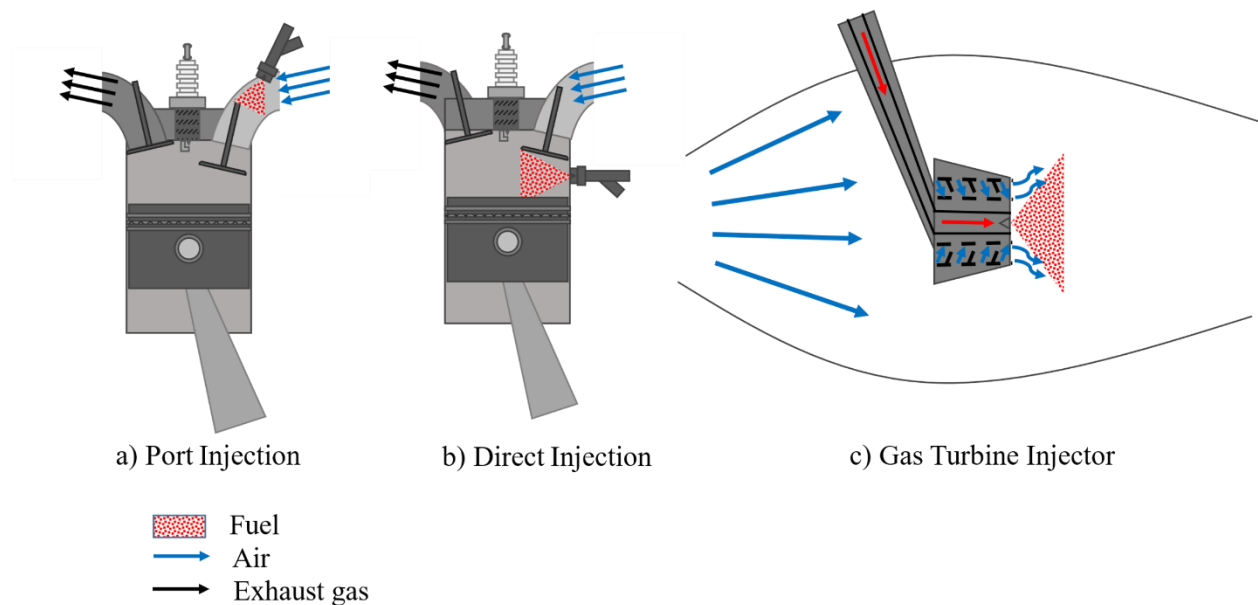


Figure 2.7: Schematic representation of a) ICE port injection, b) ICE direct injection and c) a generic aircraft injector equipped with a swirler

The different fuels [29], injection systems (i.e. means of mixing) [28, 56], and combustion pressures [29, 56] undoubtedly affect the yield and the morphology of soot. In Figure 2.8, a summary of the morphological variability of soot obtained from typical transportation engine types is given in terms of the diameter of primary particles (d_p), the number of primary particles per

aggregate (N_p) and the fractal dimension of aggregates (D_f). Although the fractal dimension is situated in a rather narrow range ($1.75 < D_f < 1.95$), regardless of the engine/fuel type, we may observe that the size of soot clusters and the primary particle diameters are distributed across a large spectrum. By considering various non-premixed configurations, namely two ICEs and a GT, Dastanpour et al. [58] has also shown the existence of a correlation between the size of primary soot particles and the size of the aggregates, whereby larger aggregates were composed of larger primary particles and vice versa. It is important to note that the morphology of soot obtained from practical applications is dependent upon the operating conditions of the given device. In ICEs, the rotational speed of the engine, the type of injection system (direct or port-injection) and the injection timing have all been observed to influence the morphology of soot. In aircraft GTs, the power level is typically the independent variable when studying morphology.

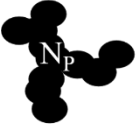
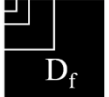
	 Gasoline	 Diesel	 Kerosene	
	20 - 35 nm ^a 8.2 - 43.3 nm ^f 23 - 27 nm ^g	20-30 nm ^b 18-25 nm ^h	3 - 64 nm ^d 12 - 14 nm ^e 0 - 50 nm ⁱ	a – Saffaripour et al., 2015 b – Wagner, 1979 c – Lapuerta et al., 2009 d – Liati et al., 2014 e – Marhabaet al., 2019 f – Uy et al., 2014 g – Bogarra et al., 2017 h – Rohani et al., 2017 i – Liati et al., 2019 j – Saffaripour et al., 2014
	95 – 160 ^g	35 – 90 ^c	1 – 50 ^j	
	< 1.8 ^a	1.75 - 1.95 ^c	1.7 - 1.9 ^e	

Figure 2.8: Summary of the morphological variability of soot obtained from the main engine types used in transportation [59-68], given as the diameter of primary particles (d_p), number of primary particles per aggregate (N_p) and the fractal dimension of aggregates (D_f).

2.2.2 Solid fuels

The soot emitted from solid fuel combustion is morphologically different from that generated in transport applications [69]. Indeed, the combustion of solid fuels involves the pyrolysis of the material [15], thereby emitting gaseous combustible species which are subsequently burned in a diffusion flame.

Coal-fired plants used in the power generation industry burn a mixture of pulverized powdered coal with hot air in an atmospheric pressure environment [54], while municipal waste incinerators operate in a similar fashion, but solid debris are conveyed on a metal grate and burned with two stages of air injection to reduce emissions [70, 71]. In large accidental fires, the initial fuel may be gaseous, liquid, or solid but ultimately, the spread of the fire typically ends up consuming a solid fuel under atmospheric pressure. In such a scenario, natural convection results in a turbulent but poor mixing of the fuel and oxidizer [72], as highlighted by the important radiative heat transfer from the in-flame particulate matter [73]. This flow field enhances the physical mechanisms of coalescence and coagulation [15], that are responsible for the observed morphology. Soot obtained from open flames is also morphologically different depending on the solid fuel under consideration [17]. For instance, during a laboratory-simulated open fire, biomass-derived soot was characterized by primary particle diameters between 28.8 and 32.4 nm and a fractal dimension in the range of 1.65 to 1.71, while its plastic-derived counterpart had a primary particle diameter range spanning from 39.2 to 49.8 nm and a fractal dimension between 1.77 to 1.85. Moreover, soot originating from biomass combustion is noted to contain more oxygenated species [74], whereas that from plastics is typically rich in PAHs [17]. In pulverized coal combustion, soot formed in the boundary layer of the coal particle and the soot yield was noted to have a dependence on the size of the fuel particles [15], suggesting a laminar flame and hence, a poor mixing of the gaseous fuel with the oxidizer. Primary particle diameters ranging from 25 to 60 nm were observed [15], while the fractal dimension of soot from two different types of coal was about 1.75 [75].

These studies highlight the morphological diversity of soot encountered in just a few common scenarios. Nevertheless, they are sufficient to understand that the morphology is sensitive to a large number of parameters. As such, an incremental understanding of the phenomenon, starting from

the morphological quantification of soot in simple experimental flames and progressively adding to their complexity can help elucidate the formation of soot and develop analytical models that give accurate predictions on the quantity and morphology, irrespective of the combustion configuration.

2.3 Morphological characterization of soot

2.3.1 Quantification of the morphology

The morphological characterization of soot aggregates consists in the quantification of the size and spatial arrangement of primary particles within an aggregate [76]. The goal is to capture the way the primary soot particles fill the space and doing so using as few and meaningful parameters as possible. Due to the inherent randomness involved in the aggregation process, the morphological characterization is not an easy task. However, mass fractals have been found to accurately capture the morphology of soot aggregates across a wide spectrum of aggregate sizes and for various fuels [77-79]. The term fractal refers to the repetition of self-similar patterns across different length scales [80, 81]. In the case of soot clusters, the repetitive pattern consists of primary soot particles, coagulating to form a soot agglomerate. The primary particles being spherical, they are readily characterized by their diameter D_p while the aggregate, because of its complex shape, can be characterized by the number of primary particles N_p , the radius of gyration R_g , the maximum length L_{max} , the overlap coefficient C_{ov} , and the fractal dimension D_f [16]. In Figure 2.9a, a few primary particle diameters have been highlighted in a soot micrograph, while the binary mask of the aggregate is shown in b). Image c) illustrates the centroid of the aggregate's binary mask along with its radius of gyration. In Figure 2.9d, the maximum length of the aggregate is shown.

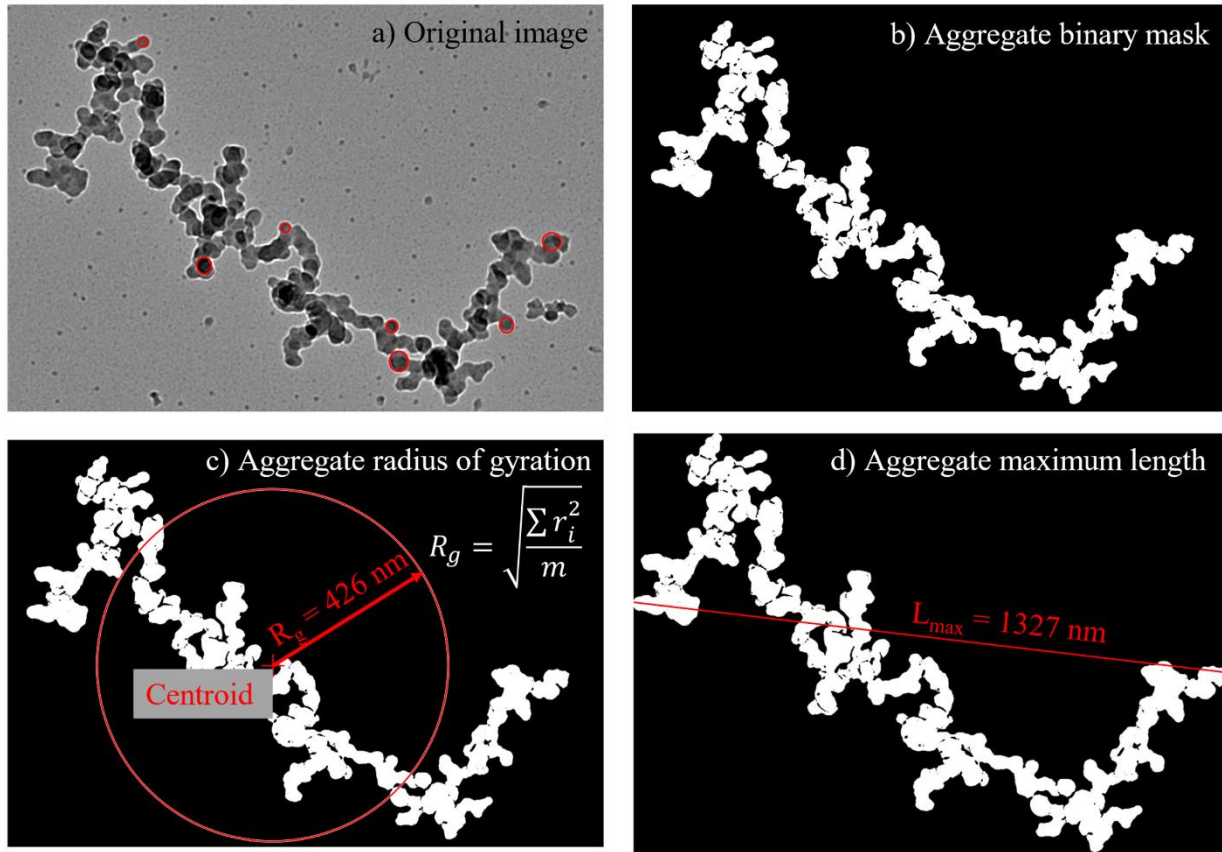


Figure 2.9: Illustration of various morphological parameters of interest, namely a) the primary particle diameters, highlighted in red and b) the binary mask of the aggregate. In c) the centroid of the aggregate's binary mask is shown along with its radius of gyration R_g , while the aggregate's maximum length L_{max} is shown in d).

The following equation shows the relationship between the fractal dimension and the different geometric projection parameters involved, namely the primary particle diameter and the 2d radius of gyration of the aggregate.

$$N_p = k_g (2R_g/D_p)^{D_f}$$

(1)

where k_g is the fractal pre-factor. To determine the fractal dimension D_f and the fractal pre-factor k_g , one must calculate the natural logarithm of N_P and $2R_g/D_P$ for a dataset of soot aggregates, and plot it on a log-log scale, yielding D_f as the slope of the least-squares fit through the data points and $\ln(k_g)$ as the y-intercept. Alternatively, if the fractal dimension is sought for every individual aggregate, the box counting method can be employed, resulting in a distribution of D_f for a dataset of soot aggregates, instead of a single value. Using this method, an image containing an aggregate is divided into a grid and the number of boxes containing at least one aggregate pixel is counted. By progressively refining the grid and repeating this procedure, the fractal dimension is calculated by relating the number of scoring boxes to the side length of the box at every iteration. This technique, however, requires the educated selection of a lower and an upper box size, which affects the obtained value significantly [82]. Using this method, it was possible to observe a negative dependence of the fractal dimension on the size of the aggregates.

The fractal dimension is a geometric property of the aggregates, which is difficult to obtain experimentally by non-intrusive techniques [83]. It provides information on the distribution of the carbon mass of the aggregate in space (i.e. arrangement of the primary particles) and therefore implicitly on the surface area of the aggregate. For example, differential mobility analyzers (DMA) can only measure the equivalent mobility diameter [84] and as a result, the fractal nature of the aggregates is lost, and the surface area is often underestimated.

Since the aggregate size distribution typically lies in the sub-micron domain [85], the most common experimental observation consists of two-dimensional projections of soot from TEM micrographs [86]. It is therefore necessary to relate the observable two-dimensional geometric properties of aggregates with their difficult-to-measure three-dimensional counterparts. This is achieved by numerically simulating 3d aggregates whose geometric characteristics are known from which 2d projections are generated at random orientations and geometric relationships are investigated. The radius of gyration R_g is one of such geometric property and it represents the root mean square distance between any point mass on an object and the center of mass of the object. Koylu et al. [79] simulated soot aggregates composed between $20 < N_P < 1000$ primary particles and have found out that the 3d-to-2d ratio of the radii of gyration is about 1.24 and independent of N_P . Alternatives to the radius of gyration have also been suggested, such as using the maximum

projected length L_{max} or a combination of the geometric mean of the maximum projected length L_{max} and width W , $(L_{max}W)^{1/2}$, resulting in a variation of only 5% in the calculated fractal dimension [87].

We recall that expression (1) requires the number of primary particles per aggregate N_P to be known. In order to obtain N_P , the mean projected area of primary particles A_p and the projected area of the aggregate A_a can be used in the power law relationship (2) below, which found to exhibit a very good agreement for numerical aggregates composed of up to 2500 primary particles [88]:

$$N_P = k_a(A_a/A_p)^{\alpha_a} \quad (2)$$

where k_a is a constant and α_a represents an empirical exponent relating the quantities. The projected area of the aggregate A_a is readily obtained by programmatically counting the number of white pixels in the binary mask of the aggregate, shown in Figure 2.9b. The relationship linking the projected areas of primary particle and aggregates was validated by Samson et al. [89] and Megaridis et al [77] using experimental observations of soot aggregates ($5 < N < 162$) from an acetylene flame. Koylu et al. [79] performed a least-squares fit of these parameters using numerical and experimental aggregates, where both methods have yielded consistent results.

The determination of the mean projected area of a primary particle A_p , however, is the most labor-intensive, tedious, and subjective task when it comes to the morphological characterization of soot aggregates [90]. For this purpose, a large number of primary particles are typically measured manually from electron micrographs, as shown in Figure 2.9a, while expecting a monomer size distribution that is normal or log-normal [86]. Subjectivity may arise from targeting readily distinguishable primary particles in aggregates [91], which are typically located around the aggregate's periphery and may not be representative of all the primary particles composing the given aggregate.

The morphological characterization of soot aggregates would be incomplete without a parameter that captures the level of overlap between primary particles. Overlap arises from partial coalescence and/or soot growth, resulting in a necking effect at the interface between two primary particles [86]. However, as a result of the TEM imaging process, additional overlap is observed in micrographs, which is quantified as follows:

$$C_{ov,proj} = \frac{D_p - D_{ij}}{D_p} \quad (3)$$

where D_p represents the diameter of the reference primary particle while D_{ij} represents the length of the common region between the two overlapping particles along an axis joining their center points. To relate the true overlap, C_{ov} , with the overlap observed in 2d micrographs, $C_{ov,proj}$, Brasil et al. [16] observed 300 numerical couples of primary particles of equal diameter and established the following relationship:

$$C_{ov} = \zeta_1 C_{ov,proj} - \zeta_2 \quad \text{where } \zeta_1 = 1.1 \pm 0.1 \text{ and } \zeta_2 = 0.2 \pm 0.02 \quad (4)$$

An inaccurate estimate of the overlap coefficient can induce important underestimations in the number of primary particles, in the radius of gyration and in the real surface area of the aggregate. However, despite affecting the above-mentioned parameters, the study concludes that the overlap coefficient does not significantly affect the fractal dimension of the aggregates.

2.3.2 Relevance of soot morphology for soot diagnostics

Intrusive flame measurements are often performed in flames, but they should be avoided when possible due to the collateral modifications in temperature, flame structure and soot morphology that they induce locally. For these reasons, non-intrusive alternatives are preferred when available.

For example, a non-intrusive temperature measurement can be performed in sooty flames using the two-color pyrometry method [92]. The temperature of the gas can be coarsely calculated by measuring the glowing intensity (i.e. thermal radiation) of soot particles under the limiting assumption of thermal equilibrium. However, given the fact that particles are cooler than the surrounding gas due to thermal radiation [29], their morphology is necessary to perform a more accurate modeling of the heat transfer [93], thereby yielding a better estimate of the local temperature.

Soot concentration measurements can also be performed using the extinction method by measuring the attenuation (i.e. extinction) of a laser beam passing through a soot-laden atmosphere. An accurate interpretation of the resulting signal necessitates the scattering-to-absorption ratio, which depends on the primary particle diameter and the size of the aggregates [94]. If the particles are spherical, which is seldom the case, the concentration measurement is straightforward [92]. However, when soot aggregates are present and their geometry and hence scattering properties are unknown, the measurement is inaccurate. The optical properties of soot are functions of not only their geometry, but also their maturity [95]. In addition to providing soot concentration measurements, laser-induced incandescence (LII) can be used to determine the mean size of primary particles by modeling the temporal decay of the signal representing the thermal radiation from soot particles following a laser heating event [93]. However, the accuracy of the measurement depends heavily on the precise characterization of the geometrical and optical properties of soot [92, 94-97]. The mean primary particle diameter determined through this method is often biased towards larger particles, which take more time to cool down compared to their smaller counterparts [94].

2.3.3 Relevance of soot morphology for predictive soot models

The morphology of soot is of primordial relevance to models aimed at predicting soot-related quantities. Such models are necessary in the design phase of combustors to ensure that particulate matter yield is within permissible amounts. The absence of predictive soot models can result in a costly iterative process of design, manufacturing and testing until target emission figures are reached [98]. Their development relies on experimental data [99] and various levels of predictive

capability can be encountered. In a review paper by Kennedy [100], the soot prediction models are categorized based on whether they are empirically calibrated, analytical or a combination of both. A striking observation is that, whether these models are empirical or analytical, they do not predict soot morphology. Instead, they typically focus on predictions of precursors, inception particle/aggregate number density and soot loading, expressed as soot volume or soot mass fraction. The morphology of soot particles is nevertheless important because it quantifies the surface area of the particles, which is necessary to predict their growth and oxidation; both mechanisms occurring predominantly at the surface of the spherules [101, 102]. Moreover, the thermal radiation of soot modifies the flame temperature [29] and hence, a coupling exists between soot loading and its morphology and the structure of the flame. Finally, the emission of soot into the environment has far reaching impacts, from adverse health effects on humans to weather pattern modifications, where both phenomena depend on the morphology of the particles. For instance, the presence of soot was noted to be responsible for climate forcing, through modification of the albedo (i.e. reflected proportion of incident light) of soot-contaminated snow and ice [12], effectively contributing to global warming. As such, an accurate prediction of the morphology of soot at the combustion source can help predict the adverse implications resulting from its emission and mitigate these through the implementation of adequate mitigation strategies.

2.3.4 Relevance of soot morphology for soot toxicity studies

The presence of high levels of atmospheric soot has been often linked with increased mortality rates [11]. In under-developed countries where solid fuels including plastic materials are used for cooking and heating purposes, respiratory diseases are more prevalent [103, 104] compared to industrialized countries. The type of cooking fuel used in low- and middle-income countries has been associated with depression [105] as a result of the exposure to the particulate matter formed upon combustion of these fuels [106].

The toxicity of soot stems from the chemical compounds adsorbed onto its surface [21-23, 107]. Indeed, soot can contain a variety of toxic substances such as PAHs and metals [108], depending on the combustible substance and flame conditions from which it originated. The maturity level of the soot particles is also linked with the level of toxicity because young particles (i.e. low flame

residence times) tend to have a much larger amounts of adsorbed substances on their surface [109]. The desorption of these harmful chemical compounds into biological tissues occurs at the interface between the particles and these tissues [23], thus highlighting the importance of the contact area. It has even been shown that the PAHs adsorbed onto soot particles can leech into the water of an aqueous soot solution [110]. It is trivial to understand that the shape, and thus the morphology of the particles govern the contact area following deposition onto a biological tissue. In Figure 2.10, two hypothetical aggregates composed of 7 monomers of equal diameters but with drastically different fractal dimensions are shown in contact with biological tissue (i.e. red line). The chain-like aggregate shown in a) is characterized by a low fractal dimension and has a very large contact area with the biological tissue compared to that shown in b), for which the contact points are limited, thus resulting into a smaller contact area. This considerable difference occurs despite the fact that both aggregates are composed of an equal number of monomers of equal diameters, hence highlighting the importance of soot morphology in the context of assessing its toxicity.

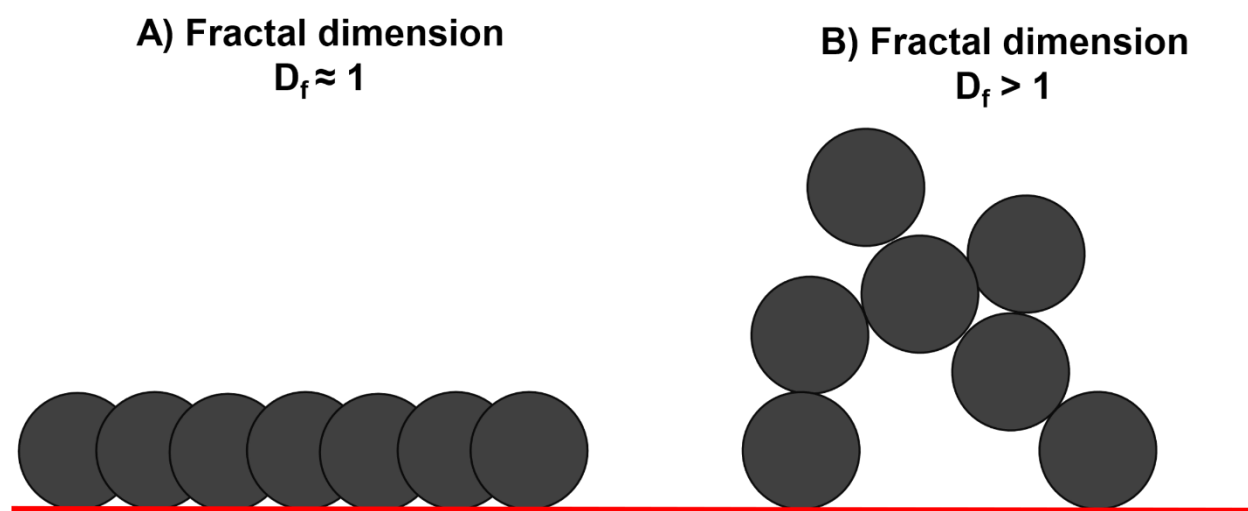


Figure 2.10: Comparative illustration of the contact area between biological tissue (red) and two hypothetical soot particles composed of an equal number of monomers but with drastically different fractal dimensions

2.4 Generic and contextual image processing algorithms

As discussed previously, the morphological quantification of soot involves a manual measurement of primary particles, which can be a tedious, time-consuming, and subjective task. Indeed, a certain level of arbitrariness [111] may arise upon human detection of primary particles in TEM micrographs by focusing primarily on readily distinguishable monomers, which may not be representative of the population of a dataset. To automate this task, researchers have resorted to developing soot monomer detection algorithms that use raw or processed TEM micrographs as input images. These algorithms are often based on existing circle detection algorithms, but they are tailored specifically to the context of soot monomer detection. Some algorithms are dedicated to extracting individual aggregates from TEM micrographs and can therefore be incorporated as aggregate segmentation routines in circle detection algorithms. In the following two sub-sections, generic circle detection algorithms will be discussed followed by the soot monomer detection algorithms derived from them.

2.4.1 Generic circle detection algorithms

Two classes of circle detection algorithms exist, namely pixel-oriented and object-oriented approaches [112]. The former uses the contribution of individual relevant pixels in an image in an attempt to classify a target object, while the latter matches the shape defined by an ensemble of pixels to a target object.

The most common pixel-based circle detection algorithm is the circular Hough transform (CHT) [113]. To detect multiple circles of an equal and known radius R , every edge pixel of the target circles is converted into a circle of radius R in the Hough parameter space. An accumulator array of equal size to the input image counts the number of circle intersections at every point (x,y) in the Hough parameter space, in which the center coordinates of the target circles are given by the coordinates of the maxima. When the radii of the target circles are unknown, the accumulator array becomes three-dimensional. A simple data reduction in the accumulator array was provided by Kimme et al. [114] through the incorporation of the gradient direction at the edge of a target circle (i.e. edge orientation), hence allowing the plotting of an arc in the Hough parameter space instead

of an entire circle. The edge orientation was also employed to achieve a reduction from a three-dimensional to a two-dimensional accumulator array by plotting a ‘spoke’ in the Hough parameter space, hence permitting the detection of circles of various diameters encoded along the length of the spoke [115]. The idea of the spoke was further refined by Atherton and Kerbyson [116] by ‘phase-encoding’ the pixels of the spokes such that for a point to end up in the accumulator array, the pixels of the intersecting spokes must have an equal phase, corresponding to an equal diameter.

The randomized circle detection (RCD) algorithm [117] aimed at reducing the computational complexity of the HT-based algorithms by eliminating the accumulator array altogether. It did this by validating circles sequentially after applying a distance criterion to first determine the likelihood of a circle formed by four randomly selected edge pixels. The selection of true circles, initially tested using a global threshold, was observed to have a selection bias toward large circles. This unwanted behavior was eliminated by imposing a set of threshold values, which depend on size and quality of the circles in the input image. It has been deemed faster for low and moderate noise levels, but when heavy noise is present, a faster performance could be obtained using the HT algorithms [114, 118, 119].

Pan et al. [120] also developed a pixel-based circle detection algorithm. At every iteration, two pixels and their respective edge orientations are used to determine the circle’s center (x_c, y_c, r_c) . A radius-independent probability is calculated for the pixel pair and is associated with the calculated circle parameters (x_c, y_c, r_c) . Finally, all the probability values associated with unique candidate circles (i.e. unique sets of (x_c, y_c, r_c)) are summed up and the maxima of the list of potential candidates are selected as true circles. A comparison with similar circle detection algorithms using natural scene images shows that the accuracy of detection of the circle radius and coordinates is the highest among the tested algorithms. The Euclidean distance mapping [121] method is also a pixel-based method that uses a binary aggregate map as an input, containing an object and a background. The output of the algorithm yields an image of equal dimensions as the input image, in which it assigns to each pixel of the object the Euclidean distance to the nearest background pixel. Using the binary mask of an isolated circle, the EDM algorithm outputs an image where concentric rings of pixels will be assigned values increasingly smaller as they get closer to the

edge of the input circle, while the center pixel is assigned with the value of the radius of the input circle.

With regards to the object-oriented approach, an example is the work of Fisker et al. [122]. The authors used a deformable ellipse characterized by center coordinates, semi-axes lengths and orientation, that is swept around the image of interest, generating a probability based on the difference between the mean intensity of the pixels within the object and that within a band around the object. However, this method requires a priori knowledge of the expected diameter range and the area of the band around the object must be specified depending on the mean distance between the circles in the image. Moreover, a global threshold is necessary to select the final candidates and all the erroneous outcomes are associated with overlapping particles. The use of a shape-matching algorithm typically requires optimized edge detection to segment the characteristic contours of the object [123]. However, unless the input image contrast characteristics are consistent, the edge detection suffers from variability, thus affecting the circle detection performance. To avoid this limitation, it is suggested that the edge orientation of the template object (i.e. circle) should be used instead of the object itself [124]. In addition, the matching criteria of robust object-oriented detection algorithm should be invariant to translation, scaling or even rotation [123].

2.4.2 Soot monomer detection algorithms

Soot monomer detection algorithms are tailored specifically for detecting circular features in micrographs of soot aggregates. For these algorithms to be robust and efficient, a number of pre-processing steps must be performed prior to executing the circle detection routine. In the following subsection, the preliminary image processing steps typically encountered in soot monomer detection algorithms are discussed, followed by the performance and drawbacks of said algorithms.

When a TEM micrograph of soot aggregates is recorded, the level of contrast in the image is a result of the instrument settings and the thickness of the carbon substrate on which the aggregates have been sampled [91, 111, 125]. In addition, the intra-aggregate contrast is a function of the

thickness of the aggregate along the third dimension (i.e. parallel to the electron beam) [126]. Even within a single micrograph, the contrast level at different locations of the viewed area can change due to non-uniformities in the carbon substrate, as shown in Figure 2.11, or due to intrinsic instrument characteristics. As a result, two aggregates from different locations of a micrograph may not be accurately segmented using a global threshold. To tackle such variability, the following image pre-processing steps are typically encountered: 1) individual aggregate extraction from a micrograph, 2) image noise removal, 3) aggregate binary mask calculation, 4) aggregate edge map calculation, and 5) soot monomer detection.

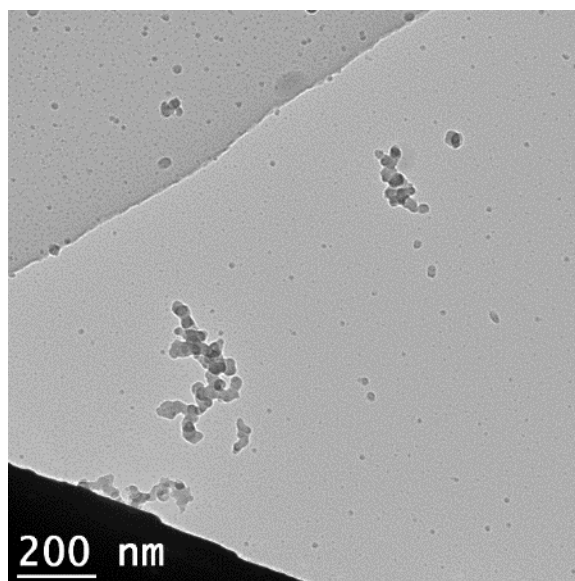


Figure 2.11: TEM micrograph of soot aggregates deposited on a carbon-coated nickel grid, highlighting a contrast variation across the viewing area due to the carbon layer peeling and folding onto itself.

The typical pre-processing steps are briefly covered below to show the different methods employed:

- 1) Individual aggregate extraction from a micrograph

To extract individual and complete aggregates from a micrograph, the manual method consists of cropping the aggregate including a limited portion of its vicinity using an image processing

software. The goal is to obtain an image of the aggregate with a uniform background intensity so that the segmentation step (i.e. step 3) is less prone to yielding artefacts. Another very time-consuming method, which bypasses steps 1, 2, and 3 altogether, consists of manually selecting the pixels around the edge of an aggregate such that the region enclosed within the selected pixels represents only the aggregate [82]. Automated alternatives exist such as the k-means segmentation proposed by Sipkens et al. [125] and the trainable WEKA segmentation (TWS) proposed by Arganda-Carreras et al. [127]. In the former, a TEM micrograph containing soot aggregates is pre-processed into three images, each representing a feature layer, namely the denoised image layer, the texture layer and the adjusted threshold layer. These three layers are then compiled into a 3d array and fed to the *imsegkmeans* Matlab function. Iteratively, individual pixels are first assigned to nearby clusters of pixels (i.e. representing aggregates) by minimizing the Euclidean distance between the given pixels and the centroids of the clusters, followed by the calculation of the new cluster centroids and the repetition of the procedure until convergence (i.e. until clusters remain unchanged). The result of the method is a binary mask where the aggregates are segmented from the background. Compared to a manual segmentation, the k-means typically yields more aggregates due to aggregate splitting/fragmentation, but the area-equivalent diameter is not significantly affected. The TWS algorithm is trained to classify the pixels belonging to the background and the foreground using a representative image in which portions of these two regions are selected and labeled manually by a human operator. Compared to manual contouring, this method slightly underestimates the size of the aggregates, as indicated by their radius of gyration [82]. Aggregate segmentation has also been tested using a convolutional neural network [128], resulting in a more accurate classification of pixels than the k-means and the TWS methods. Although it is overestimating the number of aggregates compared to a manual segmentation, a discrepancy of -14% was observed in the median area-equivalent diameter of aggregates relative to the manual baseline, which can be significantly attenuated by post-processing the segmentation provided by the algorithm. Automated methods may also suffer from the dilation or erosion of the aggregate area, or even fragmentation of a single aggregate into multiple components [82].

2) Noise removal

There exist various sources of noise in electron micrographs ranging from quantum effects to electronic noise picked up by the recording camera (i.e. CCD) [129]. Such noise can hinder the performance of the aggregate segmentation operation but also the performance of circle detection algorithms. For instance, in the former case, when a thresholding operation is performed to obtain the binary mask of an aggregate, the presence of noise may result in the inclusion of additional isolated pixels that are not representative of the aggregate region [111]. In the case of circle detection algorithms, noise can contribute to false positives. The removal of noise is performed by applying spatial-domain filters to the original micrograph such as the median filter [130, 131], the Gaussian low-pass filter [129] and smoothing filters based on morphological operations [91, 125]. Moreover, low-pass and/or high-pass frequency-domain filters can be used through the fast Fourier transform (FFT), depending on the desired outcome [131]. The former smoothens the image signal such that sharp intensity variations in space are minimized, while the latter enhances the regions characterized by sharp signal variations, such as edges. It is important to note that the size of the noise filtering kernels must be tailored to the size of the features to be detected [130].

3) Aggregate binary mask calculation (i.e. segmentation)

A binary mask is typically obtained by applying a threshold to the denoised image of the aggregate. The determination of the threshold value can be performed automatically using the Otsu method [125, 131]. However, this often results into additional aggregates being detected compared to a manual segmentation [125]. Given that a global value for the threshold is not always optimal for all regions of a micrograph [128], it results in the fragmentation of aggregates into multiple components, thereby overestimating their number and underestimating their dimensions. Alternatively, the binary mask can be obtained manually by successively incrementing a threshold value and inspecting the result at every iteration [58, 90]. The goal of the operation is to extract the region representing the aggregate as authentically as possible. This is achieved by maximizing the number of pixels representing the aggregate while minimizing irrelevant artefacts. In addition, it is desired that a single aggregate is represented by a single region of connected pixels in the binary mask, hence avoiding aggregate fragmentation [131]. In the event that there exist unwanted

artefacts in the binary mask of the aggregate, morphological image operations can be performed to eliminate them [91]. A necessary quantity in the morphological operations leading to the calculation of the fractal dimension is the projected area of the aggregate. Once a binary mask is obtained by manual or automatic segmentation, one can estimate this parameter by counting the number of pixels representing an aggregate.

4) Aggregate edge map calculation

The edge map calculation is performed in order to detect the edges of features present in the micrograph. If a gray level image is used as input into an edge detection operation, edges that are internal to the aggregate can also be detected [111, 130], but with more difficulty. Alternatively, the outer edges of the aggregate can be computed using the binary mask of the aggregate as an input image [91]. There exist various edge detection methods but in the context of the image processing of soot aggregates, Canny edge detection [111, 130] and Sobel edge detection [131] are the most common. The desired outcome of the edge detection method is to yield thin edges that are representative of the features of interest, while the pixels associated with edge noise are minimized. The choice of the best edge detection method can depend on the image processing steps performed prior to the operation.

5) Soot monomer detection

Most algorithms aimed at the detection of soot monomers from micrographs are based on the circular Hough transform [91, 111, 130-133]. For instance, Bourrous et al. [132] proposed a CHT-based algorithm that uses the binary mask of the aggregates as input, obtained using a global Otsu threshold, and is capable of determining the median primary particle diameter, the overlap coefficient, and the specific surface area of soot particles. They first analyzed its performance using synthetic images of numerical aggregates with a known particle size distribution, followed by isolated nanoparticles. Finally, a comparison between the manually and automatically measured median diameter for aggregated nanoparticles (i.e. soot) from various sources is made. They have shown that the algorithm is capable of predicting the median diameter and the geometric standard deviation to within 20%, a tolerable discrepancy, shown by the authors to be also expected between

manual measurements performed by two different operators. However, a discrepancy of around 40% was observed for the overlap coefficient between the manual method and the automatic detection. Verma et al. [133] tested a CHT-based primary particle detection algorithm on soot originating from five different types of diesel fuels. While the primary particle diameters were generally overestimated by the algorithm in relation to manual measurements, the trends observed across the different fuels were respected. Moreover, the fractal dimension obtained using the automatically measured primary particles is underestimated when compared to that obtained by manual measurement. It should be noted that for the manual method, the aggregate maximum length was used to calculate the fractal dimension while for the automated method, the aggregate radius of gyration was used.

As mentioned previously, CHT algorithms are sensitive to noise [91, 130, 131, 134], therefore they require clean aggregate edge maps for a satisfactory performance. These algorithms explicitly detect individual soot monomers, but they are sensitive to the lower diameter bound imposed on the algorithm [111, 130, 131, 135]. For instance, using identical images, an increase in the minimum detectable diameter from 4.6 to 8.3 nm shifts the mode of the detected distribution from 11.3 to 17.9 nm. Alternatively, an increase in the maximum detectable diameter from 18.5 to 41.7 nm only shifts the distribution mode toward higher values by 4.6 nm [111]. Moreover, the number of detected particles, especially those closer to the lower diameter bound, increases with detection sensitivity, consisting mainly of false positives. However, the detection sensitivity was noted to have a smaller effect on the resulting particle size distribution compared to the diameter range imposed on the algorithm [130]. A disadvantage of CHT-based algorithms is the need to determine the optimal value of the sensitivity factor for every image. Indeed, a global value for the detection sensitivity may not perform optimally given varying qualities of the soot micrographs [133]. In addition, a negligible effect of the magnification level on the detected particle size distributions was noted [131]. Overall, the size distributions determined by CHT-based algorithms tend to underestimate the mean diameter of soot monomers compared to those obtained by manual measurement [82, 91, 131]. Moreover, the performance of such algorithm was noted to strongly depend on the morphology of the aggregates [82]. That is, aggregates collected from a leaner ethene flame, characterized by a smaller size and a closer packing, resulted in a larger

underestimation in the primary particle size distribution compared to manual measurements. On the contrary, larger aggregates obtained from the richer ethene flame were more accurately characterized by the algorithm in terms of the primary particle diameter.

Although they do not explicitly detect individual soot monomers, alternative algorithms exist that are aimed at determining the mean diameter of soot monomers. One such algorithm is the Euclidean distance mapping surface-based scale (EDM-SBS) [130]. This method can determine the parameters of the soot monomer size distribution, but the type of the distribution must be known *a priori*. It has only been tested using a limited soot dataset from an ethylene diffusion flame and from an aviation engine and, other than the difference in the primary particle diameter between the two sources of soot, the morphology has been determined to be similar for both cases.

The pair correlation method (PCM) is another algorithm capable of determining the mean primary particle diameter from binary images of aggregates [136]. Through manual measurements of the primary particle diameter for a few soot monomers, a critical value P^* of the pair correlation function is found, initially assumed to be only a function of the radius of soot monomers. However, using numerically generated aggregates, the value of P^* was found to also possess a dependence on the overlap coefficient and on the number of primary particles per aggregate, among others. Nevertheless, by determining the P^* value using a few samples of a specific soot dataset, the mean primary particle diameter of the entire dataset can be estimated to within 10%.

2.5 Thermophoretic sampling

Thermophoresis is a physical phenomenon whereby aerosols present in temperature gradient are pushed towards the colder side by the difference in thermal motion of the surrounding gas molecules. This phenomenon is exploited for sampling aerosols present in hot gaseous environments by introducing a cold sampling substrate inside the hot gas [130], in an orientation parallel to that of the flow field [137]. This technique results in a sampling efficiency that is independent of particle sizes under roughly 150 nm [138]. Dobbins and Megaridis [139] estimated the parameters relevant to thermophoretic soot sampling from a coannular ethene diffusion flame. Based on an estimated particle diameter of 12 nm, a soot volume fraction of $1.5 \times 10^{-6} \text{ cm}^3/\text{cm}^3$ and a

gas temperature of 1700 K, the exposure time of a cold substrate in the soot-laden environment must be of about 9 ms to achieve a 10% coverage of the substrate area. A low exposure time is desired to avoid a large particle number density on the sampling substrate and, hence any sampling-induced morphological modifications of the particles. In practice, larger exposure times are employed. For instance, Wang et al. [130] used an exposure time of 100 ms to sample soot aggregates from an ethylene-air diffusion burner; a flame which yields a soot volume fraction considerably larger than a methane diffusion flame [140]. Depending on the type of substrate used, a limitation in the exposure time may be necessary to preserve the structural integrity of the substrate [139]. Impaction sampling may be an alternative to its thermophoretic counterpart, whereby the inertial forces of the particles in a soot-laden flow drives them to strike the sampling substrate that is oriented orthogonal to the flow. However, inertial impaction is size-dependent and is biased towards larger particles compared to thermophoretic sampling [141]. Despite the collision of the soot particles with the sampling substrate, particle fragmentation was not observed [142].

CHAPTER 3 CRITICAL ANALYSIS OF THE LITERATURE AND RESEARCH OBJECTIVES

3.1 Critical Analysis

In the following three sub-sections, the shortcomings identified in the literature with regards to the study of soot morphology are presented. The complexities involved in the typical experimental configurations are first summarized along with the associated limitation of available experimental soot datasets, followed by the improvements required in image processing algorithms aimed at quantifying the morphology of soot. The necessity of incorporating soot from a variety of flames (i.e. for instance, representative of accidental combustion) in the development of robust image processing algorithms is justified. In the last section, the research objectives of this dissertation are stated.

3.1.1 Experimental configurations

The state of the art outlines the current understanding of the soot formation process, as investigated in the different experimental configurations currently available in combustion science. However, these configurations are plagued by the complex fluid dynamics present in the vicinity of the flame, resulting in flow field strain and flame stretch. Undoubtedly, the flow field affects the flame structure as well as the physical mechanisms of coalescence and aggregation of soot particles. Understanding its effects on the already complex pathways of soot formation represents a monumental task. Fundamental studies of soot processes require experimental datasets collected in simple configurations that allow the incremental understanding of the underlying soot formation mechanisms.

In co-flow diffusion flames, a complex hydrodynamic interaction between the reactant streams exists due to the geometry of the configuration. Additionally, most of the studies performed in conventional co-flow diffusion configurations have focused on the formation of soot along the axis of the flame. At this fuel-rich location, soot forms due to fuel pyrolysis and due to the limited abundance of oxidizing species. However, the region in co-flow flames that is relevant for practical

applications is the interface between the reactant streams, which is difficult to isolate and investigate specifically in experiments. In this region the coupling between the flame structure, the strong temperature gradients and the complex flow field affects the particle formation/growth but also the trajectories of these particles, which ultimately contribute to their morphology.

In counter-flow diffusion flames, the impinging reactant jets form a stagnation plane surrounded by a stretched/strained flow field, often propagating beyond the flame sheet. The effects of these important complexities induced by the experimental configurations on the soot formation mechanism are very difficult to quantify and complicate the interpretations of the observations. They affect the flame structure, as well as the mechanisms of coalescence and coagulation of soot particles, which are still poorly understood.

The motivation behind the proposed research project stems from the development of a relatively novel experimental configuration in which the reaction sheet of the flame is situated in a unidimensional unstretched and unstrained flow field. As a result, the soot formation mechanism can be studied without being subjected to complex hydrodynamic effects. In this experimental configuration, it is possible to obtain datasets conducive to study the morphological evolution of soot particles from their inception until close to their oxidation. This investigation should allow the flow-field-independent identification of the domains in the flame structure where inception, surface growth, coagulation and oxidation of soot respectively occur. The observations will be related to the flame structure and temperature, residence time, and any other relevant combustion parameters. Although this configuration has been briefly used to study soot in the past, spatially resolved morphological data required for the development and validation of soot models has not been acquired.

3.1.2 Image analysis of soot morphology

In conjunction with the unique experimental configuration available in our laboratory, our research is further motivated by improvements needed in the image processing algorithms dedicated to the morphological characterization of soot aggregates. Most researchers currently still rely on a manual measurement of primary particles in electron microscope micrographs of soot aggregates

for the morphological characterization. This technique has proven to be reliable but very tedious and time-consuming. Although algorithms aimed at detecting primary soot particles in electron micrographs exist, they are often based on the circular Hough transform and suffer from sensitivity to noise and to the required input parameters, namely the expected diameter range and the detection sensitivity. Alternatives to the circular Hough transform also exist but they require a priori knowledge of the expected size distribution or a calibration using a soot dataset of comparable morphology. While focusing on the detection of particles present around the edge of soot aggregates, these algorithms tend to underestimate the mode of the particle size distribution when compared to a manual measurement. However, a thorough comparison of the aggregate regions exploited by manual measurements and automatic detection algorithms has never been performed and recent publications raised concerns about a potential arbitrariness of manual measurements.

3.1.3 Soot formation and flammability in accidental polymer combustion

Lastly, the toxic nature of combustion-derived particulate matter motivates further research into the particulate effluent generated upon accidental/uncontrolled combustion of polymers. Since the combustion of a solid fuel generates large amounts of flammable gaseous effluent that cannot adequately mix with the oxidizer, a fuel-rich condition is practically always encountered. Moreover, a vast array of gaseous combustible species can be found in such a combustion scenario due to the complex reaction pathways that can occur upon pyrolysis. For example, the growing interest for naturally sourced fiber reinforcements such as cellulose motivates further research on the flammability and particulate matter yield due their relatively lower degradation temperature and inherent oxygen content. For these reasons, the soot collected during the combustion of a solid fuel may be considerably different in morphology compared to that acquired in the 1d burner using methane as a fuel. Currently, morphological information about soot originating from polymer combustion is scarce and often gathered in highly controlled experimental configurations (i.e. process reactors), with the goal of large-scale production of nanoparticles. Morphological data is required from configurations representative of uncontrolled or accidental combustion, such as the Federal Aviation Administration flame spread cabinet [143] or the cone calorimeter [144], for example. In these configurations, a polymer matrix composite is subjected to a pilot flame or a

radiant heat flux, respectively, initiating the thermal decomposition, followed by ignition of the combustible gaseous effluent. The combustion occurs in a buoyancy-dominated flame, thereby resulting in a turbulent flow field which enhances particle collisions. These turbulent flames affect the morphology of the soot aggregates in such a manner that is unexpected to occur in the typical configurations used in fundamental investigations of soot formation. As a result, we propose to develop a soot sampling method in an experimental configuration representative of accidental combustion and incorporate the acquired dataset of soot aggregates into the development of the image processing algorithm to extend its applicability to a broader spectrum of soot morphologies.

3.2 Research objectives

In this section, the objectives of this research project are stated. In addition, their impact on the state of the art in combustion science is assessed.

1. Develop an image processing algorithm capable of analyzing and extracting the morphological parameters of interest from the TEM micrographs of soot from different combustion sources.
2. Perform a spatially resolved morphological mapping of soot aggregates across the thickness and below the luminous soot layer for various flames in the one-dimensional un-stretched/unstrained counter-flow ($\text{CH}_4 + \text{CO}_2 - \text{O}_2 + \text{CO}_2$) diffusion burner.

Sub-objective 1: Develop a soot sample collection method that can be used to collect soot particles from the one-dimensional un-stretched/unstrained counter-flow diffusion flame.

3. Perform a sampling of soot aggregates from the uncontrolled combustion of polymer matrix composites.

Sub-objective 2: Identify a suitable experimental configuration and develop a soot sampling collection method that can be used to collect soot samples from polymer flammability tests.

CHAPTER 4 METHODOLOGY

In this chapter, the experimental methodology implemented to address the objectives stated previously is described. The presentation will be limited to elements of the methodology that could not be included in the research articles of Chapter 5 to Chapter 7. First, the description, construction, and operation of the 1D unstrained diffusion burner is presented. It is followed by the experimental procedure pertaining to gas concentration measurements and to the validation of the one-dimensional assumption of the flow field in the reaction zone. Subsequently, the methodology employed for determining the sooting limits of the burner is presented, followed by the fabrication of a soot sampling substrate holder. Lastly, the selection of a suitable experimental configuration and the procedure for the collection of soot samples from burning polymer matrix composites is presented.

4.1 Description of the 1d burner

Contrary to typical experimental counterflow arrangements, where the exhaust gases flow radially from the stagnation plane, in the experimental burner used in this work the gases flow along the same axis as the injection flow, as qualitatively shown in Figure 4.1. This is achieved by supplying the reactants into a closed combustion chamber through arrays of closely spaced needles, ensuring a uniform injection flow field, while allowing the combustion products to escape between these needles. Such a configuration results in an unstrained one-dimensional flow field in the reaction zone.

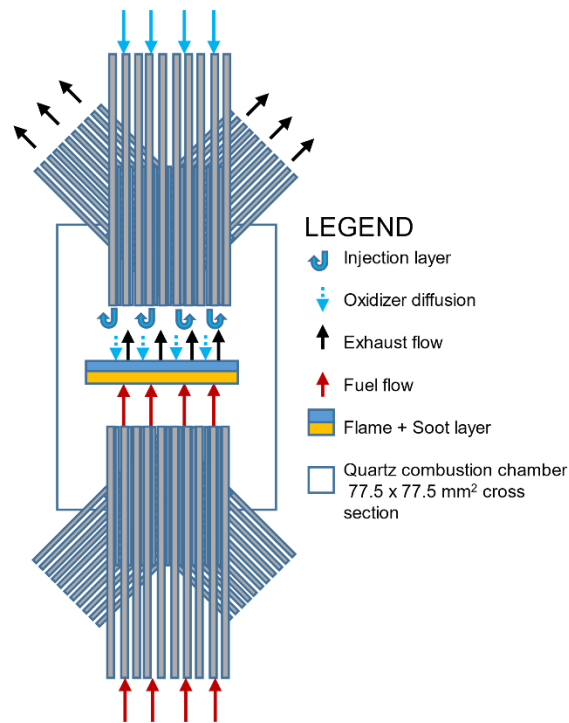


Figure 4.1: Schematic representation of the flow fields in the combustion chamber of the experimental burner, qualitatively showing the flame and the soot layer locations

In this burner, the flow of the counter-diffusing species, most often the oxidizer, is noted to readily reverse in the direction of the bulk flow, but a portion counter-diffuses due to the steep concentration gradient resulting from the flame acting as an oxidizer sink. Consequently, a region characterized by a three-dimensional flow field exists immediately downstream of the oxidizer needles, referred to as the injection layer (Figure 4.1), and it must be far enough from the flame to ensure a one-dimensional flow within the reaction zone. Additionally, the counter-diffusion of the oxidizer towards the flame implies that the effective boundary condition of oxidizer concentration is unknown. However, both the validation of the one-dimensionality of the flow in the reaction zone and the boundary condition can be solved by performing measurements of major species concentrations between the flame and the oxidizer inlet. By first measuring the concentration boundary condition of the oxidizer to perform a numerical simulation of the flame, one can obtain the axial evolution of the major species concentrations. A second concentration measurement,

taken between the boundary condition measurement and the flame, can be used to validate the numerically obtained concentrations. Since the numerical simulation assumes purely diffusive transport of the oxidizer to the reaction zone, the experimental validation of the numerically obtained concentrations implies that the concentration measurement was indeed done outside the injection layer, in a purely diffusive region. The details pertaining to the concentration measurements and to the validation of the one-dimensional assumption are given in sections 4.4 and 4.5, respectively. In the next section, the practical implementation of the burner discussed thus far is presented.

4.2 Construction and operation of the 1d burner

The experimental burner consists of two heated plenums, each featuring an array of injection and exhaust needles. Each injection array consists of $31 \times 31 = 961$ hypodermic needles with an outer diameter of 1.0 mm and a wall thickness of 0.1 mm arranged on a 2.5 mm square grid, fitting within a square cross-section of 77.5 x 77.5 mm. The injection array of the fuel and oxidizer are arranged in a counterflow configuration with an adjustable gap between their exit planes, fixed at 50 mm for the experiments performed herein. Each exhaust array is composed of $32 \times 32 = 1024$ hypodermic needles of 1.2 mm inner diameter, staggered between the injection needles. Only the oxidizer side exhaust is operational during the experiments performed herein. The gap between the inlet planes of the exhaust arrays is 90 mm. The combustion chamber of the burner, shown in Figure 4.2, consists of an 8-mm thick quartz duct with a 77.5 x 77.5 mm inner cross section, equipped with two slits of 26.8 x 3.17 mm. The slits allow for easy access when mounting the soot

sampling device and during operation, they are sealed with machined Macor® plugs, held in place by a spring-loaded rod that applies pressure simultaneously on both plugs.

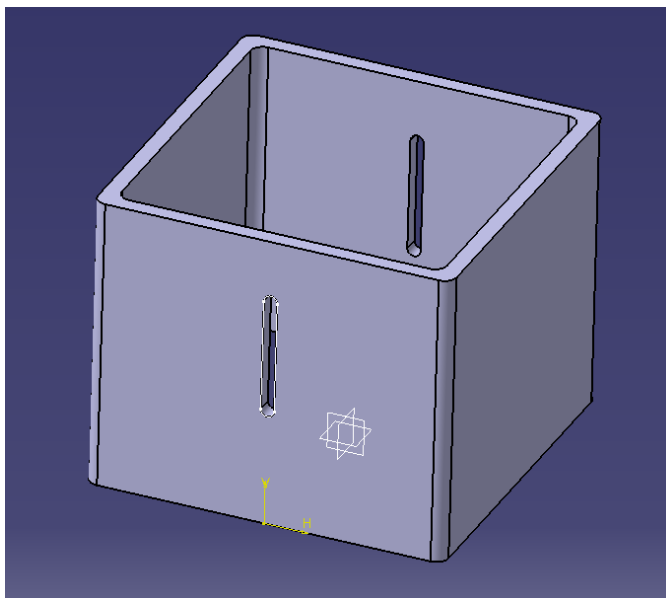


Figure 4.2: Geometry of the quartz combustion chamber

The fuel and oxidizer consist of methane (CH_4 , Praxair 99.0% purity) and oxygen (O_2 , Praxair 99.6% purity), respectively, while the inert dilutant used in both reactant streams consists of carbon dioxide (CO_2 , Praxair 99.9% purity). The burner is always operated with the fuel stream diluted using CO_2 , but the oxidizer stream may be composed of pure O_2 . The purpose of the inert dilutant is to lower the flame temperature and to control the molecular diffusion properties of the mixture to achieve stable flames.

Since the exhaust gas transits through either one of the plenums, they are heated to prevent the condensation of water vapor. For each plenum, the heating system consists of four heater elements electrically insulated in glass tubes. The temperatures of the plenums can be independently controlled with the aid of thermocouples placed at strategic locations inside the shells, namely on the heater elements and on the edge and core of needle array. As such, the temperatures of the injected streams are monitored and can be later used in numerical calculations. The shells that

make up the plenums are insulated with 18-mm-thick flame-retardant silicone foam sheet, which can tolerate temperatures up to 200 °C. The plenum shells have octagonal cross-sections in the horizontal plane and are each equipped with four exhaust tubes allowing the burnt gases to escape into the atmosphere. The exhaust tubes can be closed so that experiments can be performed with the exhaust on the fuel side or on the oxidizer side.

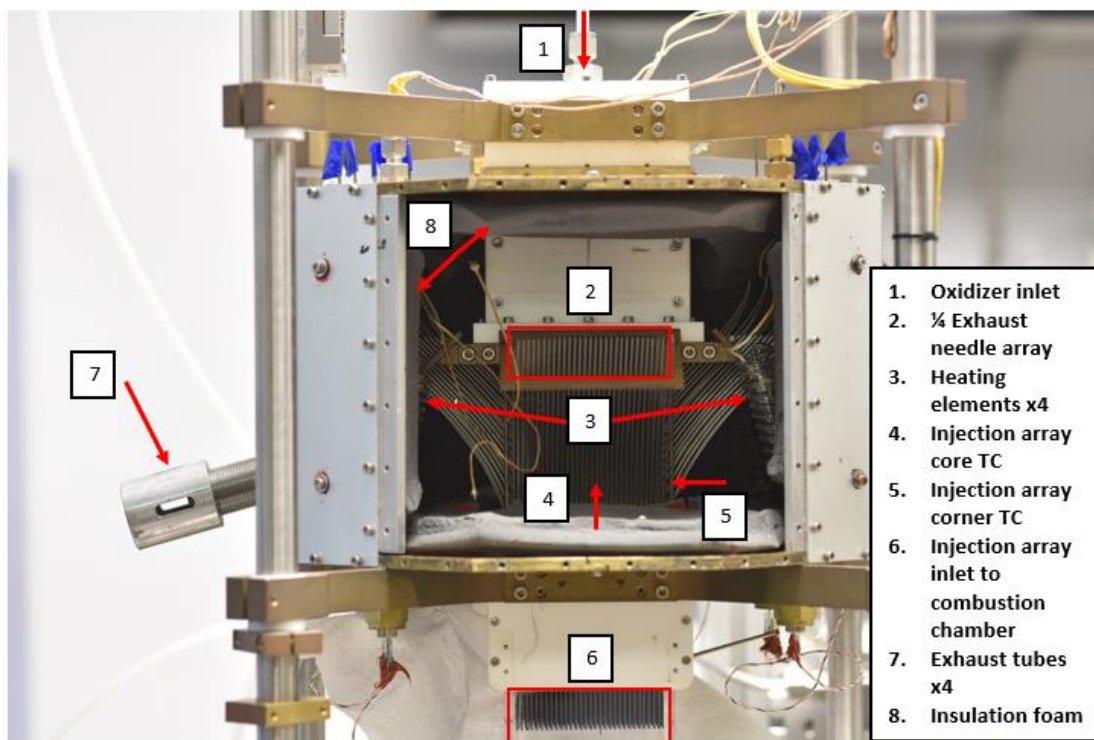


Figure 4.3: Top half of the 1D burner showing the injection and exhaust needle arrays, heating elements, thermocouples (TC)

4.3 Numerical simulations of combustion

A numerical model is built using the Cantera open-source chemical kinetics framework and the GRI-Mech 3.0 detailed kinetic mechanism, designed and optimized to simulate the combustion of natural gas, composed primarily of methane ensuring a reliable modelling of the temperature and

concentration profiles in non sooting flames. The mechanism consists of 53 species and 325 reactions, it provides adiabatic flame temperatures and molar fractions of the chemical species and is capable of predicting the formation of nitrous oxides. However, it is limited to chemical species up to C_2 and does not account for the formation of soot.

The simulation domain implemented to model our burner consists of an axisymmetric and radially infinite flow domain, characterized by a finite length along the flow axis, two inlets and one outlet. The first inlet, namely the fuel inlet, is characterized by a convective flow, whereas the second inlet, namely the oxidizer inlet, is characterized by a diffusive flow. Moreover, the second inlet also acts as a convective outlet to exhaust the combustion products. The governing equations treat the mixture as an ideal gas throughout. The boundary conditions necessary to perform a simulation consist of the reactants' concentrations, volumetric flow rates, inlet temperatures and static pressure. For the fuel, the inlet temperature $T_{f,0}$ is set at 500 K, whereas for the oxidizer, an inlet temperature $T_{O,0}$ of 1250 K is set. The former value has been selected following previous experimental measurements and a sensitivity analysis that revealed a negligible effect on the resulting flame location and temperature. With regards to the latter value, namely 1250 K for $T_{O,0}$, it has been chosen because it is the minimum temperature value resulting in a numerical solution and it also happens to predict quite well the experimental flame location. Unfortunately, experimental temperature measurements have not been performed to validate this temperature assumption at the oxidizer inlet in the present work. However, given the good agreement between the experimental and the numerical flame locations across the investigated flames, it has not been deemed a priority. A schematic representation of the burner's combustion chamber and of the simulation domain is given in Figure 4.4 along with the list of boundary conditions necessary for the simulation.

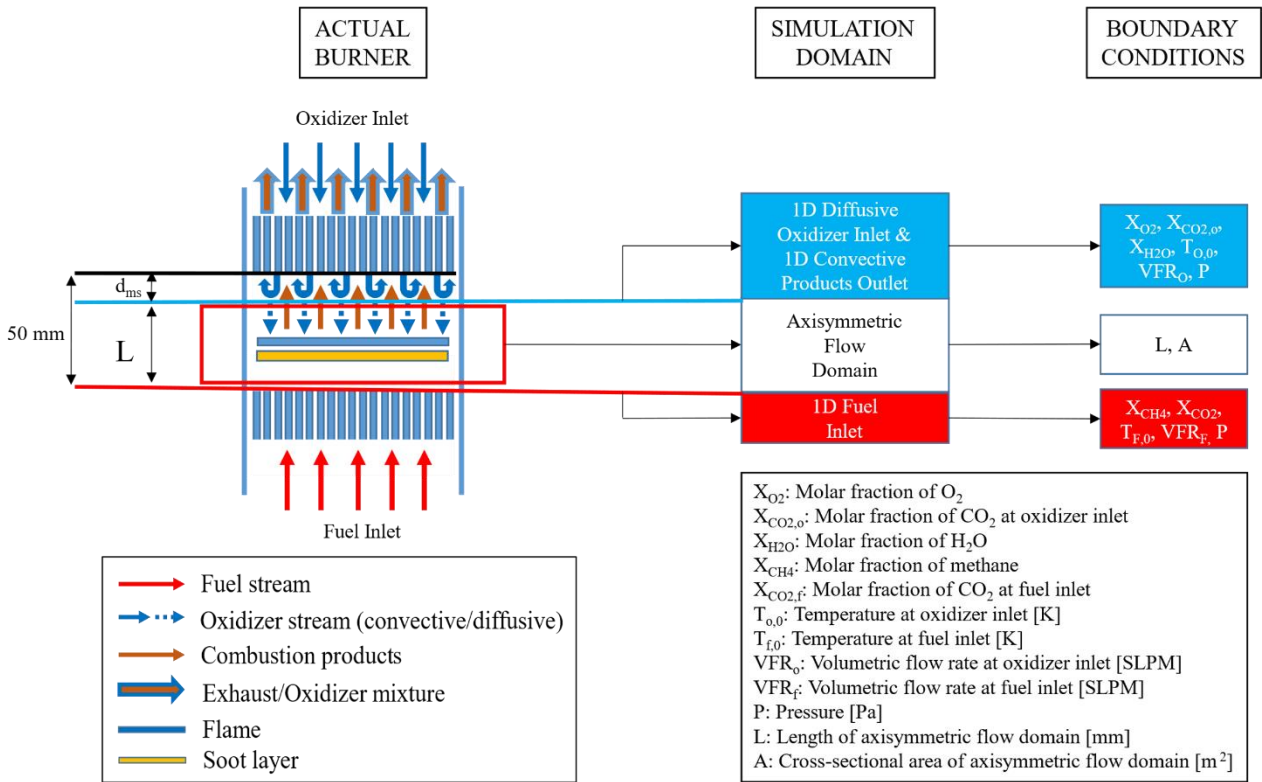


Figure 4.4: Schematic representation of the numerical simulation domain alongside the representation of the experimental burner. The various boundary conditions necessary for the numerical simulation are summarized in the text box.

Given that the numerical model assumes that the transport of species from the oxidizer inlet to the flame occurs by molecular diffusion, the boundary condition of species concentration necessary for this inlet must be measured experimentally in the region downstream of the oxidizer inlet characterized by molecular diffusion. In Figure 4.4, this location is indicated by the solid turquoise line, immediately downstream of the region of three-dimensional flow (i.e. injection layer) represented by the blue curved arrows. The length L of the simulation domain consists of the actual length of the combustion chamber (i.e. 50 mm) minus the thickness d_{ms} of the injection layer. The simulation domain is divided into a grid of 50 equidistant points and is solved without the energy equation, assuming a fixed temperature profile. The steady state absolute and relative error tolerances used are $1.0e-5$ and $1.0e-12$, respectively, while transient state absolute and relative error tolerances are equal to $5.0e-4$ and $1.0e-11$, respectively. Once a preliminary solution is

determined using the fixed temperature profile, the simulation domain is refined with the ratio set to 2, the slope to 200, the curve to 0.05 and the prune to 0.2 and the energy equation is solved.

4.4 Measurement of species' concentration boundary conditions

To obtain species boundary conditions for numerical simulations, we must analyze the composition of the mixture between the counter-diffusing (i.e. oxidizer) inlet and the flame, as mentioned above. In this location, the mixture is composed of the fraction of the oxidizer stream that diffuses towards the reaction zone and the combustion products travelling towards the exhaust. To quantify these species, a mass spectrometer (MKS Spectra Cirrus I) is used. This device is primarily designed for qualitative measurements of individual gases, therefore, to obtain a quantitative measurement for mixtures of gases, the response of the instrument must be mapped using gaseous mixtures of known species and concentrations, representative of the target mixture, as described in [145]. The mapping of its sensitivity to different mixtures composed of oxygen, carbon dioxide and water vapor of varying proportions is performed by preparing such mixtures and recording the raw ionic current generated by each gas. For this purpose, a custom mixture chamber is employed, where steam is generated at a controlled rate and is uniformly mixed with oxygen and carbon dioxide prior to being exhausted through a heated pipe from which the mass spectrometer draws a sample. The mixture chamber is shown in Figure 4.5, labeled as vaporizer/mixer.

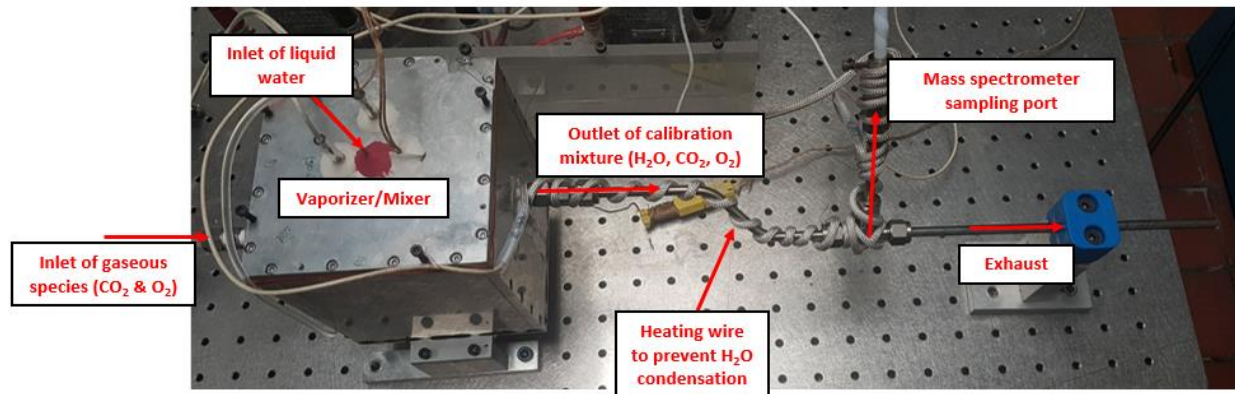


Figure 4.5: Assembly of the equipment employed for preparing mass spectrometer calibration mixtures

The volumetric flow rate of liquid water (H₂O) destined for steam generation is pumped using a diaphragm pump (*SyringePump NE-9000*). The water vapor concentration range of the mixture varies from 0% to 40% v/v using increments of 10% v/v, where the remainder of the mixture consists of carbon dioxide and oxygen. For example, to map the instrument sensitivity at 10% v/v water vapor for the three gases, we define a total volumetric flow rate such that the water vapor generation rate represents 10% v/v of the total. The remainder volumetric flow rate (i.e. 90% v/v) is split among carbon dioxide and oxygen and is swept incrementally from 0% to 100% v/v in carbon dioxide (i.e. increments of 10% v/v), such that the complement always consists of oxygen. As such, a sensitivity map is generated where 5 water vapor points are considered, each with 11 calibration points of various concentrations of carbon dioxide and oxygen. The entire sensitivity map consists of 55 points for which three values are recorded, namely the raw ionic currents of water vapor, carbon dioxide and oxygen. It is then used in experiments to convert the raw ionic currents measured by the instrument into the corresponding volumetric concentrations. Linear interpolations are performed when the measured raw ionic currents do not perfectly match with the points of the calibration map.

4.5 Validation of the 1d assumption at the reaction zone

Experimental major species concentration measurements can be used to numerically validate the assumption that the thickness of the oxidizer injection layer of the burner (i.e. three-dimensional flow field) does not interfere with the flame, hence confirming the one-dimensional nature of the flow field in the reaction zone. An experimental flame characterized by a fuel stream composed of 35% CH₄ / 65% CO₂ and an oxidizer stream composed of 100% O₂ is used for this purpose. Since the numerical simulation domain assumes that the oxidizer diffuses against the bulk flow, a correspondence between the experimental (i.e. blue flame sheet) and numerical flame location is a strong indication that the experimental flame is located outside the injection layer. In Figure 4.6, the correspondence between the experimental and numerical flame location is shown along with the simulated reactants' molar fractions. The dashed green curve represents the molar fraction of oxygen downstream of the counter-diffusing inlet, as measured by the mass spectrometer.

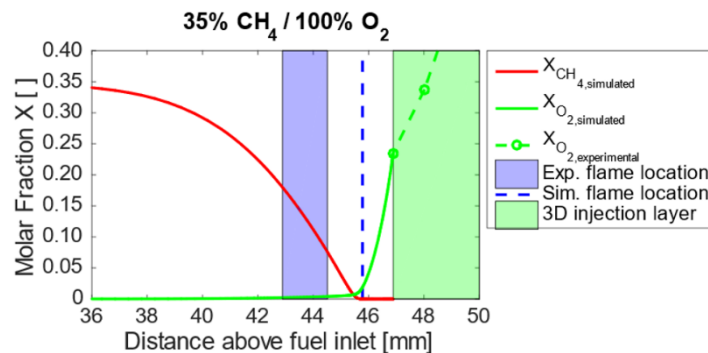


Figure 4.6: Correspondence between experimental and numerical flame locations for a 35% CH₄ / 100% O₂ lightly sooting flame

The agreement between the experimental and the numerical flame location is to within less 1.2 mm, which represents a positional error of 2.5% based on a combustion chamber length of 50 mm. Such error is expected given the various sources of error, namely from the alignment of the photographic equipment used to determine the experimental flame position and the numerical simulation, which does not consider heat radiation from this lightly sooting flame.

4.6 Mapping of the burner's visible sooting limits

An example of the mapping of the sooting limits has been performed at a volumetric flow rate of 7 SLPM in the oxidizer stream as well as 7 SLPM in the fuel stream. To determine the sooting limits, the dilution level of the oxidizer stream is fixed at a desired value. Starting from a fuel stream dilution level where no soot is visible, the fuel concentration in the fuel stream is increased in increments of 1% v/v and left to stabilize for 5 minutes. At the end of the stabilization period, an image is taken at normal exposure and at an over-exposed condition with the laboratory lights turned off. The sooting limit represents the freestream fuel concentration required for the appearance of an orange soot region underneath the blue flame, at the given freestream oxidizer stream concentration. The transition between the non-sooting and the sooting scenarios is shown in Figure 4.7 as a function of the freestream equivalence ratio. In this section exclusively, the freestream fuel equivalence ratio ϕ is calculated based on the concentrations of the fuel and oxidizer streams as measured by the flow controllers, without measuring the effective boundary condition at the counter-diffusing inlet. The idea is to be able to capture the sooting limit with a single parameter and to readily determine the burner settings required to reproduce it from this parameter.

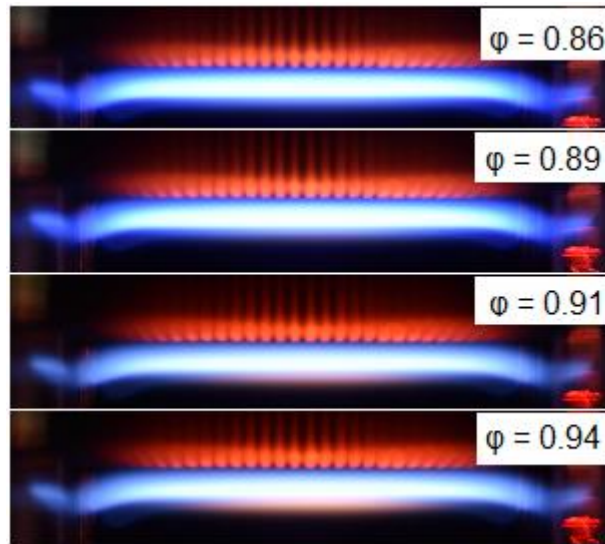


Figure 4.7: Transition between the non-sooting and sooting conditions showing soot appearance (i.e. orange layer below the blue flame front) at a freestream fuel equivalence ratio $\phi=0.91$.

Since the bulk flow velocity affects the soot onset through the residence time, the determined sooting limit is only meaningful if it is accompanied by the volumetric flow rates of the streams and their respective reactants concentrations levels. The sooting limit map has been determined for oxygen concentration levels in the oxidizer stream between 60% v/v and 100% v/v using increments of 10% v/v and is shown in Figure 4.8.

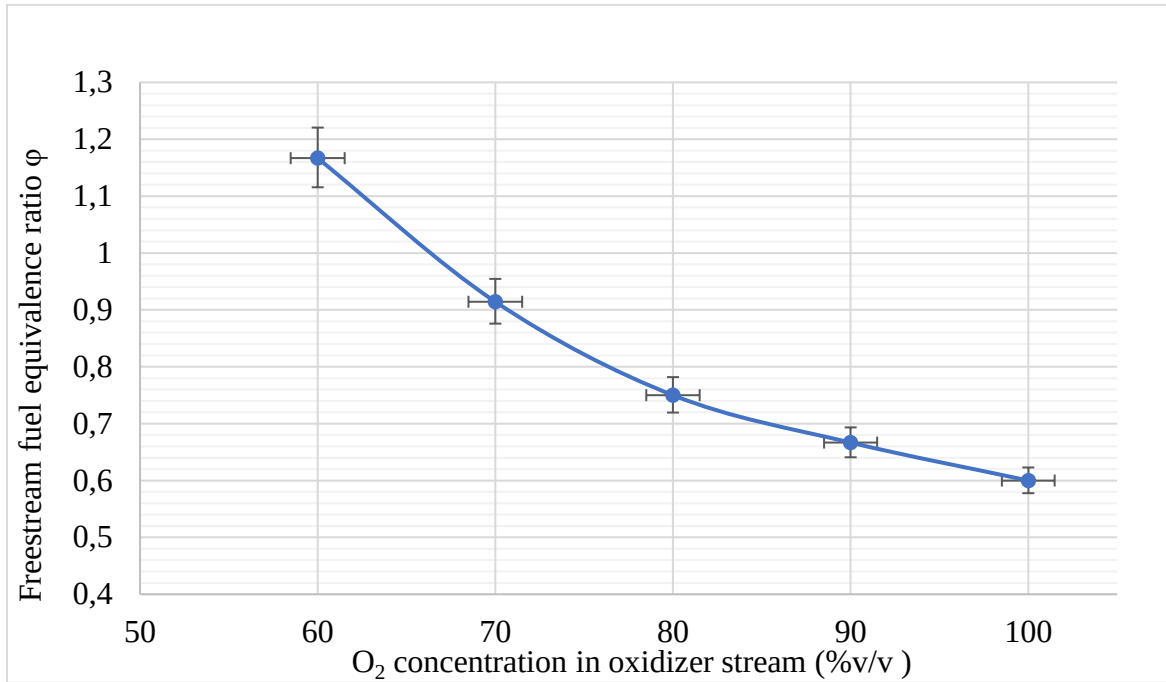


Figure 4.8: Freestream fuel equivalence ratio at the sooting limits of the 1D burner as a function of the freestream oxidizer concentration

4.7 Design of the soot sample substrate holder

The study of soot in the one-dimensional burner requires the acquisition of a spatially resolved dataset of soot aggregates across the thickness of the soot layer. For this purpose, a transmission electron microscope (TEM) sampling substrate holder is necessary.

Several TEM grid holders have been designed and tested throughout the course of this project. The initial criteria of the design was for the sample holder to accommodate up to 4 TEM grids to sample one flame in as few strokes as possible. Moreover, the sample holder should have a low view factor (shape factor) to limit the radiation absorption from the flame prior to insertion in the soot layer. To avoid sampling by impaction, the sample holder should also not exhibit any rocking motion upon reaching the sampling position. As a result, it must be lightweight, and its mass must be concentrated along the axis of the steel wire on which it is supported.

The first iteration, shown in Figure 4.9a, made it difficult to mount the four TEM grids due to the cross shape; the extended manipulation time required resulted in the grids being damaged prior to sampling. In addition, visual inspections of the insertion of this holder into the flame showed an observable decrease in flame and soot layer luminosity. The second iteration, shown in Figure 4.9b, solved the issue pertaining to the mounting of the grids and also incorporated the backing of the grids by a large thermal mass, therefore preserving a temperature gradient for a longer time, yielding a better sampling efficiency. However, this holder exhibited a rocking motion, and its large mass also quenched a considerable portion of the surrounding flame upon insertion. The third unfruitful iteration, shown in Figure 4.9c, conserved the backing of the sampling grids but mounting was again difficult, and the large metal mass proved once again to be intrusive to the flame. Due to the unsatisfactory flame intrusiveness of these holders and the prohibitive costs of TEM analysis, soot samples taken with these versions have not been imaged on the TEM.

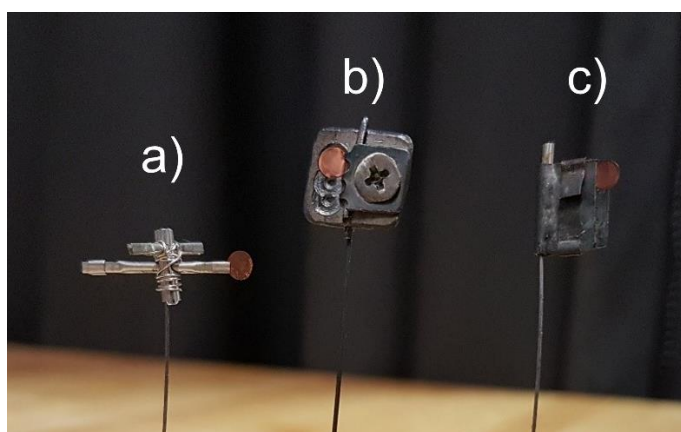


Figure 4.9: Image depicting the early versions of the sampling substrate holders with a TEM grid mounted on each

The design of the holder quickly converged to one accommodating a single TEM grid, axially aligned with the steel wire, shown in Figure 4.10. The previous iterations highlighted the fact that introducing a large mass near the reaction zone was to be avoided, therefore only the sampling substrate shall reach the soot layer. The holder uses two compressible prongs to clamp the grid with minimal contact such that the effective sampling area is maximized. The holder is made of a hypodermic needle of 1.2 mm outer diameter, where one end was ground using a Dremel to form

tweezers, which are compressed by another hypodermic needle of 1.2 mm inner diameter that slides on the holder needle. The final design was very easy to manipulate, and the time required for placing a grid and mounting it in the combustion chamber amounts to less than 5 minutes. In addition, it is very stable upon acceleration/deceleration, it does not observably disturb the flame and its shape results in a low view factor with respect to the heat radiation coming from soot layer, thus maximizing the temperature gradient required for thermophoretic sampling.

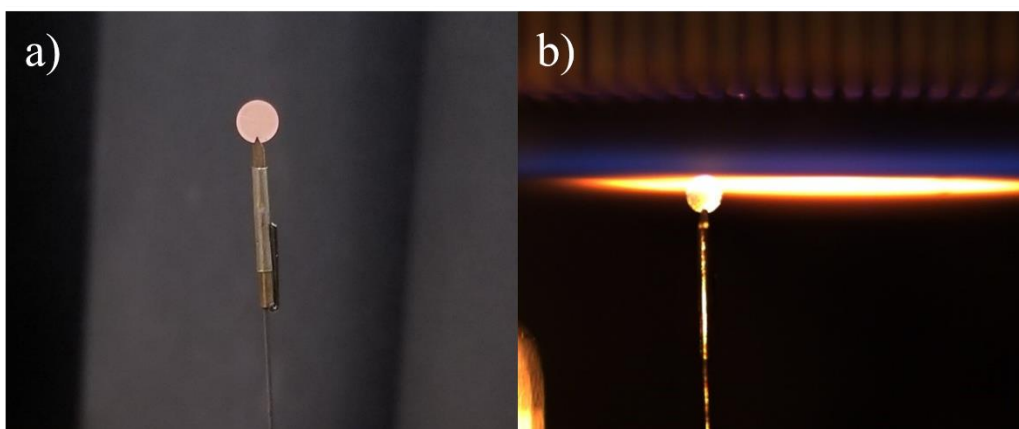


Figure 4.10: Final design of the sample holder with a TEM substrate mounted on it a) outside the flame and b) performing a soot sampling operation in the flame

4.8 Collection of soot samples from the 1d burner

In order to accurately insert the TEM sampling grid in the soot layer, it is primordial to measure the location of the soot layer with respect to a reference point inside the combustion chamber. In fact, the visible soot layer thickness typically ranges between 2-4 mm, while the TEM sampling grids have a diameter of 3 mm. The location of the soot layer is determined by inserting a thin metal probe from the needles of the oxidizer exhaust plenum until it reaches the top edge of the visible soot layer, as shown in Figure 4.11. This metal probe serves as a reference to determine the desired travel of the sampling grid and remains at the reference location until the insertion calibration procedure is complete. Once the location of the top edge of the soot layer has been referenced for a desired flame, the flame is extinguished, and calibration of the soot sampler travel stroke is performed by filming the insertion process using a high-speed camera. Prior to installing

a new TEM grid on the holder, a pinhole is pierced at the edge of the TEM grid and is oriented at 12 o'clock to represent the highest sampling point in soot layer. The pinhole serves as a reference to determine the sampling location from the footage of the high-speed camera, therefore, it should be visible in the video. The TEM grid is then mounted on the sample holder and the holder is placed inside the burner, on the steel wire which serves as a support. The sampling grid is moved to the lowest possible point inside the combustion chamber, where it rests prior to sampling. In the servomotor control code, this position is defined as the “HOME” position or the origin. From the home position, a manual stroke of the motor is performed until the top of the soot sampling grid matches with the metal probe and the stroke distance is recorded from the motor output. It is important to ensure that upon executing the code, the grid indeed travels to the desired position. For this purpose, a few test strokes are performed where, the position and the residence time of the sampling grid inside the soot layer are verified. Once all the sampling parameters are validated, the flame is reignited, and a short waiting period ensues until the top edge of the soot layer matches again with the metal probe. When this condition is fulfilled, the metal probe is removed, and the servomotor code is executed to collect a soot sample. Immediately after the acquisition of the soot sample, the flame is extinguished and both fuel and oxidizer gas lines are purged with carbon dioxide. The purging is performed to avoid any further hydrocarbon cracking and subsequent deposition on the TEM grid, given the high temperature surfaces in the vicinity of the latter. The sample holder is then carefully removed from the combustion chamber and the soot sample is stored in the adequate storage device for subsequent analysis on the TEM.

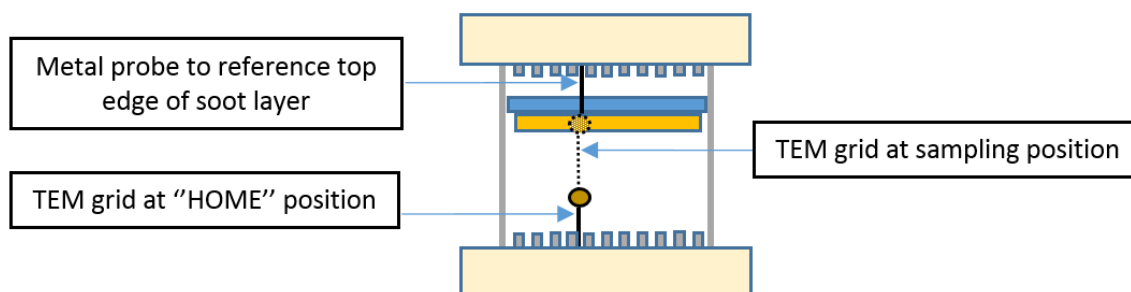


Figure 4.11: Schematic representation of the reference points used upon soot sampling

4.9 Collection of soot samples from burning polymers

To collect soot particles emitted from polymer matrix composites during uncontrolled combustion, suitable experimental configurations were first identified. Two experimental configurations have been considered, namely the Federal Aviation Administration (FAA) flame spread cabinet (Figure 4.12), described in the FAA Aircraft Materials Fire Testing Handbook, and the cone calorimeter presented in the ISO-5660 Part 1 standard.

4.9.1 FAA flame spread method

The FAA flame spread certification test consists of a material with dimension of 75 x 305 mm, oriented vertically or horizontally, subjected to a premixed Bunsen burner flame for 12 or 60 seconds, followed by sustained combustion, if applicable. The test metrics consist of measuring the flame time, the burn length, the rate of flame spread, and the burn time of the dripping material. These are compared to simple pass-fail criteria given in the handbook. This approach suffers from the inability to process materials that drip excessively during combustion. Tests are performed in a 0.15 m³ closed cabinet, where large amounts of particulate matter accumulate throughout the duration of a test. Because the testing method is meant as a procedure for certification purposes rather than as an investigative method, it is practically impossible to install advanced diagnostics equipment inside. Moreover, the collection of soot samples in such a sooty environment would result in a saturation of the sampling substrate, resulting in TEM micrographs of limited value.



Figure 4.12: Federal Aviation Administration (FAA) flame spread test cabinet showing the piloted ignition of a sample material using a Bunsen flame, applied for 12 or 60 seconds in the vertical orientation.

Nevertheless, the FAA test cabinet has been useful in developing a soot sampling methodology for burning polymers using mirror-polished austenitic stainless steel as the sampling substrate. The rationale of sampling on non-magnetic stainless-steel substrates instead of TEM substrates was to be able to record micrographs on the scanning electron microscope, which is much easier to operate than the TEM and can also accommodate multiple samples at the same time. In Figure 4.13a, a burning sample is shown, consisting of cellulose-reinforced (15 wt%) thermoplastic polyurethane, fire-retarded with melamine polyphosphate (5 wt%). The soot sampling substrate is also shown clamped onto an extension of the linear motor. Although it appears in an orientation suggesting inertial impaction sampling, the shaft of the linear motor rotates upon insertion due to the sampling substrate not being clamped along its center of gravity, resulting in a vertically oriented substrate

at the sampling position. Figure 4.13b shows four samples obtained at exposure times of 1) 0.5 s, 2) 3 s, 3) 2 s and 4) 1 s, from left to right, respectively.

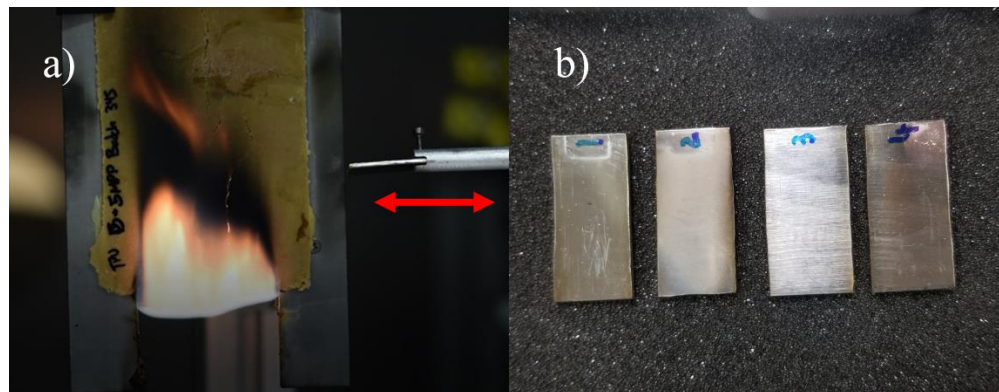


Figure 4.13: a) Thermophoretic soot sampling in the FAA cabinet from a burning sample of cellulose-reinforced (15 wt%) thermoplastic polyurethane, flame-retarded with melamine polyphosphate (5 wt%) and b) mirror-polished austenitic stainless steel sample substrates with flame exposure time of 1) 0.5 s, 2) 3 s, 3) 2 s and 4) 1 s.

In Figure 4.14, scanning electron micrographs of soot taken from sample 4 listed above are shown at various magnification levels. The modest surface density of soot deposited on the substrate at this exposure time does not pose a concern with regards to potential overlapping of aggregates during sampling. In addition, the contrast level is qualitatively comparable to that obtained from TEM images, thus enabling the use of SEM micrographs for morphological quantification using image processing techniques.

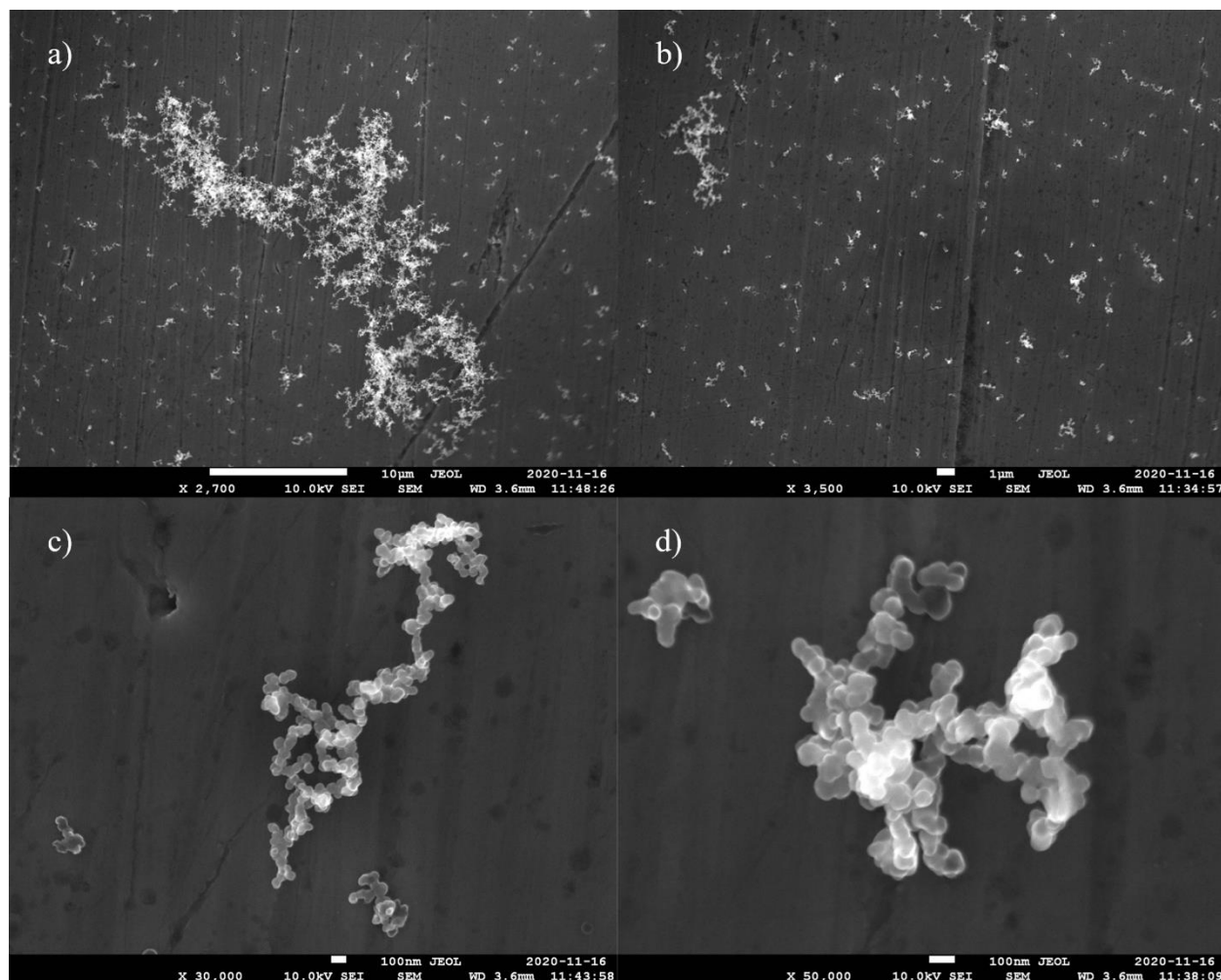


Figure 4.14: Soot micrographs from sample 4 with a flame exposure time of 0.5 s. The scale bar indicates a) 10 μm (2700x), b) 1 μm (3500x), c) 100 nm (30000x) and d) 100 nm (50000x).

In contrast to the micrographs obtained with a flame exposure time of 1 s, Figure 4.15 shows full coverage of the sampling substrate by soot resulting from a flame exposure time of 3 s. In these micrographs, it is possible to distinguish primary particles, but aggregates are overlapping to an extent where their individual nature is lost.

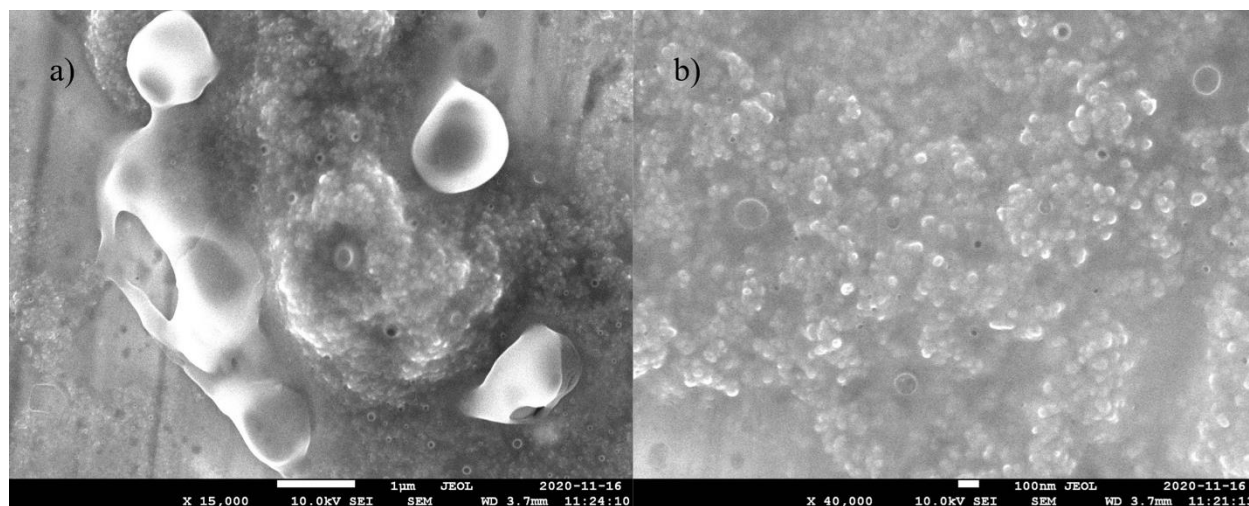


Figure 4.15: Soot micrographs from sample 2 with a flame exposure time of 3 s. The scale bar indicates a) 1 μm (15000x), b) 100 nm (40000x).

4.9.2 Cone calorimeter (ISO-5660)

The cone calorimeter is a device designed to determine the flammability of solid materials by exposing them to a radiant heat element, followed by ignition of the gaseous effluent. A custom-built cone calorimeter was designed and constructed by the author following the ISO-5660-1 (*Reaction-to-fire tests — Heat release, smoke production and mass loss rate Part 1*) standard document [144]. It is composed of a cone heater which irradiates the sample material mounted vertically or horizontally with a heat flux of up to 75 kW/m^2 . As the thermal degradation of the material onsets, a flammable gaseous effluent is emitted and ignited by a piloted spark ignition located 10 mm above the sample. The mass loss of the sample is monitored throughout the duration of the test using a load cell. The products of combustion (i.e. gases and solid particulates) are drawn through an exhaust pipe equipped with a laser obscuration measurement system, which determines the opacity of the combustion products in real time. Moreover, a gaseous sample is drawn continuously from the exhaust pipe, conditioned to remove the humidity and the particulates, and pumped into a paramagnetic O_2 sensor to determine the amount of oxygen consumed by the combustion of the sample material. The heat release rate can be calculated through the oxygen consumption calorimetry method, which, for organic solids and liquids, is

proportional to the amount of oxygen consumed, namely 13100 kJ/kg O_2 with an error of $\pm 5\%$ [146, 147]. The volumetric flow rate in the exhaust is measured by an orifice plate flow meter and it is held constant at a value of 24 L/s throughout the duration of the test. To determine the mass flow rate at various locations of interest inside the exhaust pipe (i.e. laser and orifice plate), thermocouples are used to measure the exhaust gas temperature. The various systems of the cone calorimeter are shown in Figure 4.16.

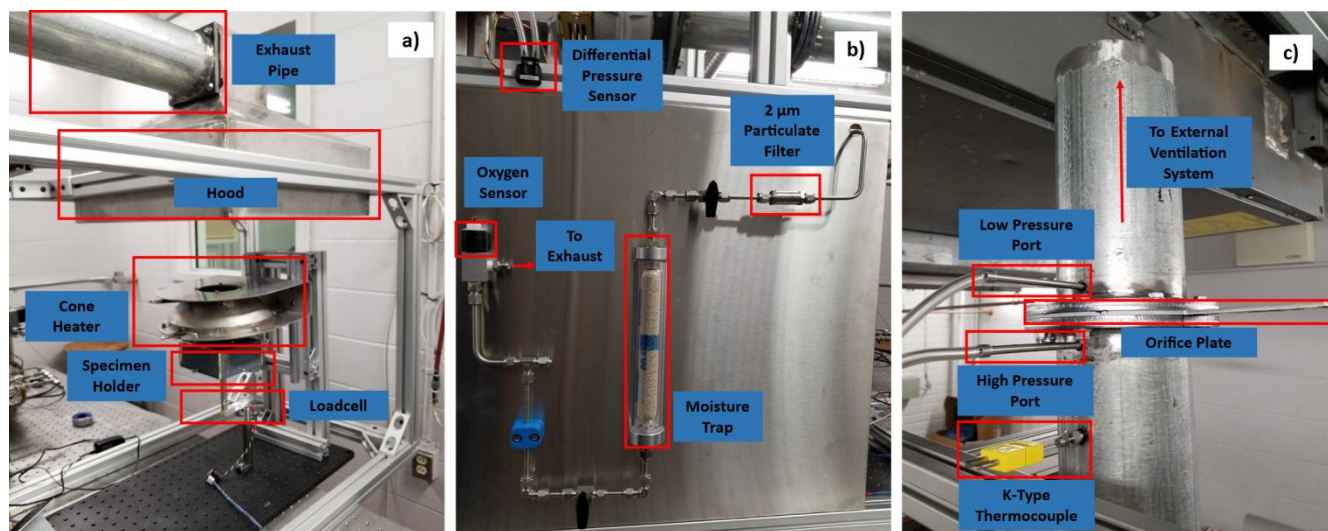


Figure 4.16: Main components of the cone calorimeter arranged in chronological order from the sample burning module to the outlet of the exhaust, namely a) the specimen degradation section and extraction hood, b) the conditioning system of the sampling gas and subsequent O_2 measurement and c) the exhaust flow measurement system.

The most important flammability parameters measurable using a cone calorimeter are the time-resolved heat release rate, the mass loss rate, and the smoke opacity. By integrating the heat release rate signal and by calculating the consumed specimen mass, one can also obtain the mean heat of combustion of the material. The residual specimen mass can also be computed, which can educate on the relative strength of the char formation pathways as a function of the cone heater heat flux, material composition, etc. It is important to note that the behavior of a material in the cone calorimeter cannot be extrapolated to a large-scale fire of the same material. Cone calorimeter tests

are used as a repeatable method to measure and to quantitatively compare the performance of different materials subjected to a radiant heat flux.

The soot sample collection method for these tests is similar to that used in the context of the 1d diffusion flame. A carbon-coated TEM nickel grid is mounted on the sample holder which is inserted in the orange flame of the burning polymer (10 mm above the top face of the sample) with the help of a linear motor, as shown in Figure 4.17. Alternatively, a 4 mm disk, cut from a mirror-polished 0.0254 mm-thick shim stock (18-8 stainless steel) using a punch, can be used as a sampling substrate instead of the TEM grid, for subsequent imaging on the scanning electron microscope.

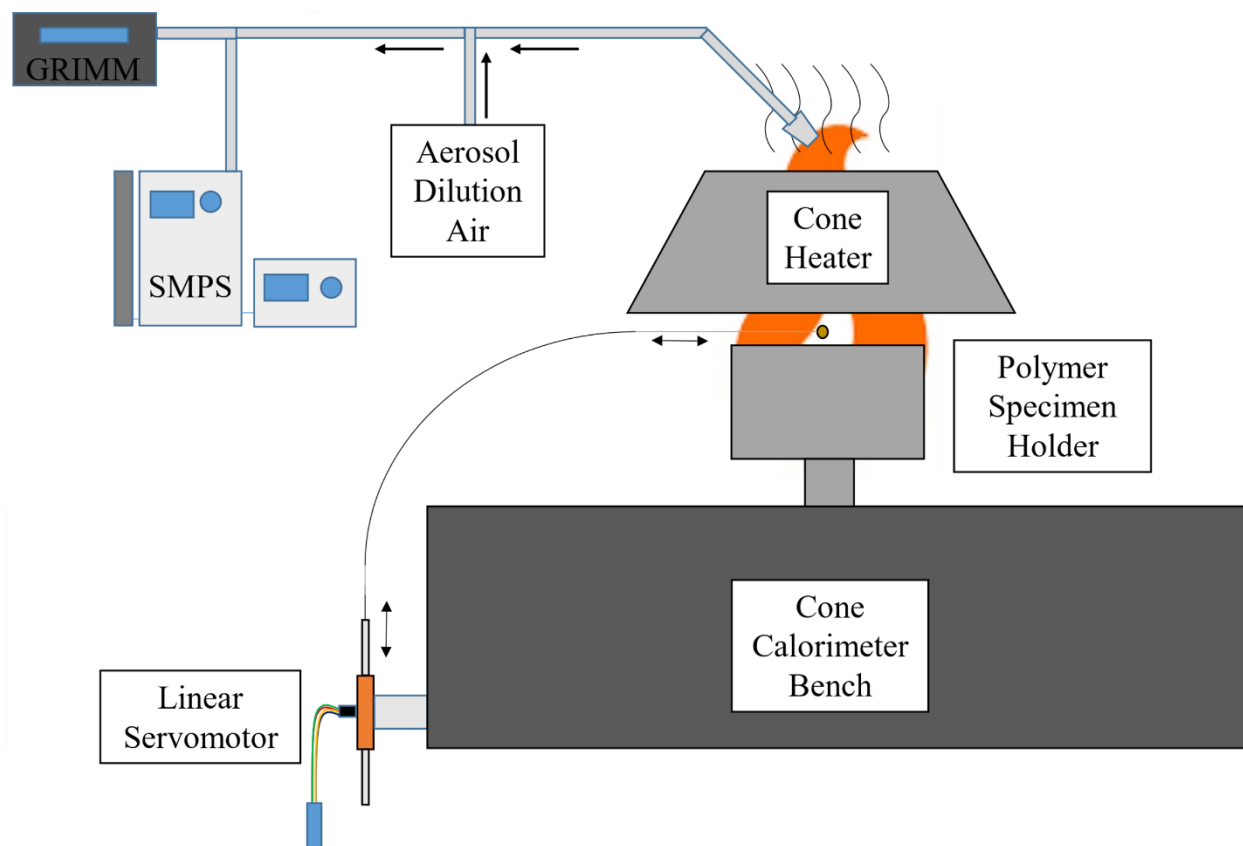


Figure 4.17: Illustration of the burning polymer soot sampling setup mounted on the cone calorimeter

The proposed soot sampling method has been validated in the cone calorimeter using two polymer matrix composite samples, namely an epoxy/carbon-fiber composite and a phenolic/carbon-fiber composite. The material formulation is proprietary, therefore no additional information on the material composition can be disclosed. For the carbon fiber composite, the duration of the sustained combustion in the cone calorimeter was very limited under a radiative heat flux of 35 kW/m^2 , therefore, the sampling was performed in the absence of a flame. In Figure 4.18, four TEM micrographs illustrate the particulate matter deposited on the sampling substrate from the degradation of the epoxy/carbon-fiber composite in the cone calorimeter. We may note the presence of fiber fragments, but no soot aggregates could be observed given the lack of flame upon sampling.

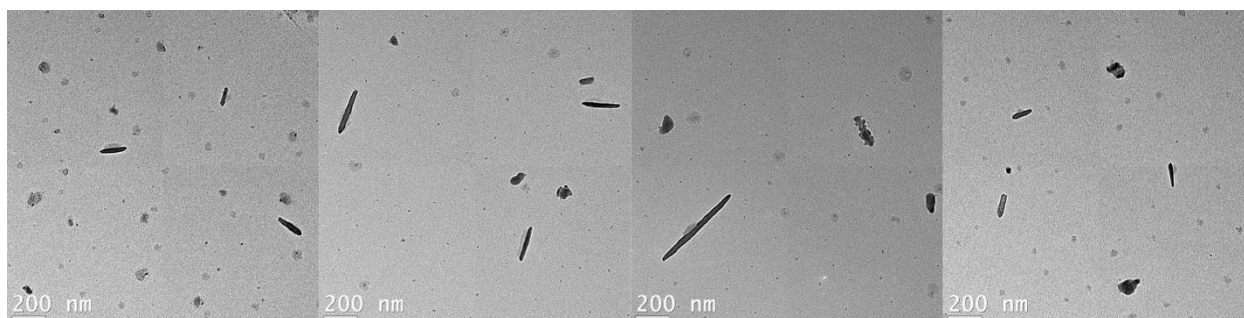


Figure 4.18: TEM micrographs of fiber fragments sampled from an epoxy/carbon-fiber composite material tested in the cone calorimeter under a radiative heat flux of 35 kW/m^2 .

The dimensions of the fiber fragments have been investigated, namely the length and width, using a total of 43 fragment samples. In Figure 4.19, the histograms of the fiber length and fiber width are shown in a) and b), respectively. We may first observe that the sample size is not large enough to reveal a clear distribution type for the fiber length while for the fiber width, the histogram hints at a normal distribution. The bulk of the fiber lengths are between 100 and 200 nm, whereas the mode of the fiber width distribution is located around 40 nm. This is an interesting observation given that the diameter of carbon fibers is typically between 5 and $10 \mu\text{m}$. As such, the fragments observed here may be circumferentially peeling or flaking off the original fiber, but they are definitely not radially-complete segments of the original fiber given their very small width/diameter.

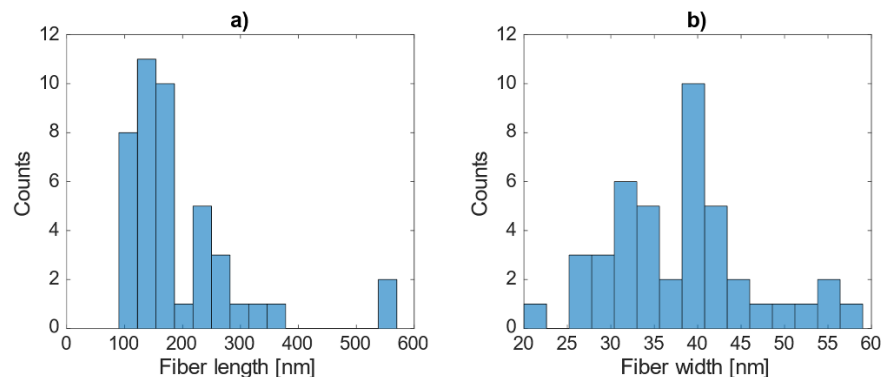


Figure 4.19: Dimensions of the fiber fragments sampled from an epoxy/carbon-fiber composite material tested in the cone calorimeter under a radiative heat flux of 35 kW/m^2 .

In the case of the phenolic/carbon-fiber composite burning in the cone calorimeter, fiber fragments could not be found but soot aggregates were observed, as illustrated in Figure 4.20.

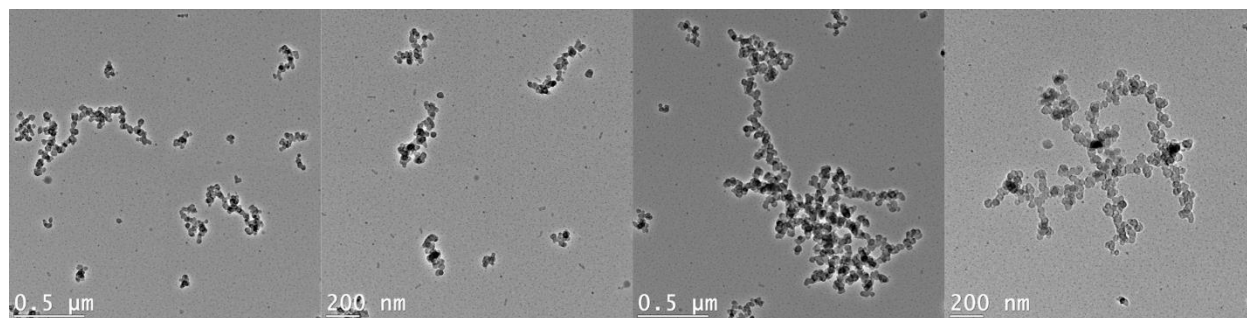


Figure 4.20: TEM micrographs of soot sampled from a phenolic/carbon-fiber composite material tested in the cone calorimeter under a radiative heat flux of 35 kW/m^2 .

By analyzing the morphology of a total of 174 aggregates, histograms of the maximum length and number of primary particles per aggregate have been generated, as shown in Figure 4.21a and b, respectively. The median of the maximum aggregate length is equal to 164 nm while the median of the number of particles per aggregate is of 97 particles and both parameters follow a log-normal distribution. The mean primary particle diameter for these aggregates follow a normal distribution with a 95% confidence interval mean between 32.16 and 33.89 nm and a standard deviation

between 5.99 and 7.21 nm. Using these morphological parameters, the fractal dimension D_{fL} and the fractal pre-factor k_L were estimated at 1.58 and 7.21, respectively.

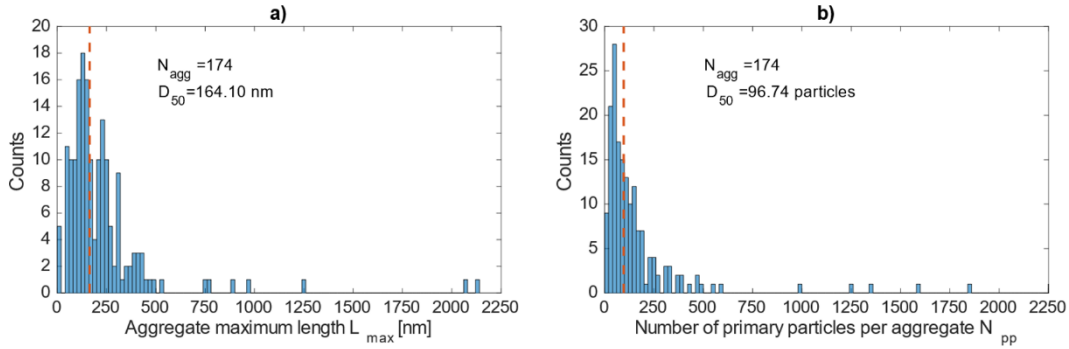


Figure 4.21: Histograms illustrating a) the maximum length and b) the number of primary particles per aggregate sampled from a phenolic/carbon-fiber composite material tested in the cone calorimeter under a radiative heat flux of 35 kW/m².

To complement the soot dataset acquired for electron microscope analysis, aerosol sampling is performed 50 mm above the top hole of the cone heater using two aerosol spectrometers to cover a wider range of particle sizes. The first instrument consists of a scanning mobility particle sizer (SMPS), composed of an electrostatic classifier (TSI Model 3082) and a condensation particle counter (TSI Model 3775), and its particle diameter (d_p) measurement range is $6 < d_p < 240$ nm. The second instrument is a laser aerosol spectrometer (Grimm Mini-LAS 11-R) and its measurement range is $0.25 < d_p < 32$ μ m. To avoid the saturation limits of the instruments, namely 10^7 particles/cm³ and 3×10^6 particles/liter, respectively, dilution of the aerosol is necessary. The dilution setup is shown in **Erreur ! Source du renvoi introuvable.** It consists of a vacuum pump which draws dilution air from a compressed air source whose static pressure can be controlled, along with the aerosol-ridden gas from the combustion source of interest. By increasing the static pressure of the compressed air, the dilution of the aerosol is increased. Tests have been performed to ensure that the dilution of the aerosol does not affect the measured particle size distributions.

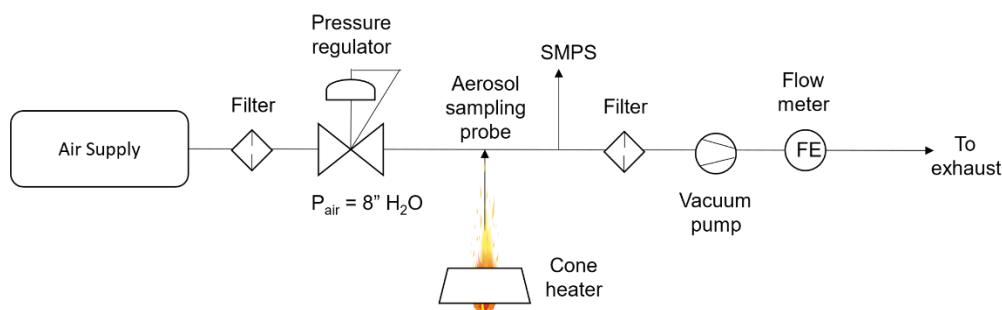


Figure 4.22: Schematic representation of the aerosol sampling system

An aerosol generator (Topas ATM220) provided an aerosol composed of di-ethyl-hexyl-sebacate oil (DEHS) with a controlled particle size distribution between $0 < d_p < 1.0 \mu\text{m}$. In Figure 4.23, the particle size distributions measured at various dilution levels are shown. The legend indicates the static pressure of the compressed air source, in units of inches of water (H_2O). The obtained particle size distributions indicate that besides the magnitude, which is affected by the dilution, the shape of the distribution is preserved. Unfortunately, upon testing the setup in a cone calorimeter flame, the highest achievable dilution ratio was insufficient to avoid saturation of the laser aerosol spectrometer. As a result, the particle size distributions will be limited to those provided by the SMPS.

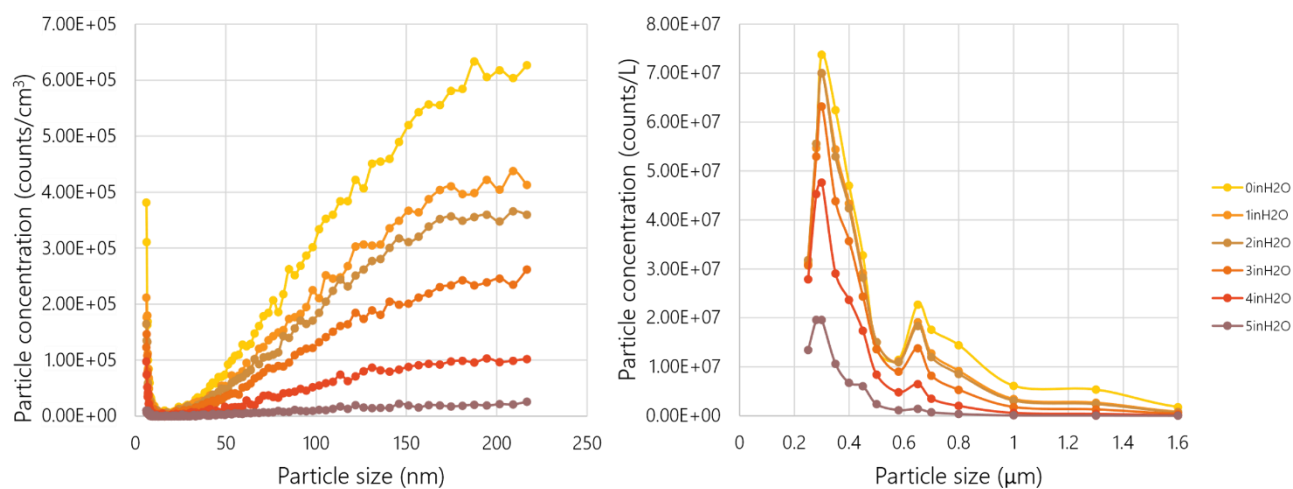


Figure 4.23: Particle size distributions obtained using the SMPS (left) and the LAS (right) at various dilution levels of the aerosol given by the static pressure of the compressed air source in inches of water (in H₂O)

CHAPTER 5 ARTICLE 1: AUTOMATIC DETECTION OF PRIMARY SOOT PARTICLES FROM TRANSMISSION ELECTRON MICROGRAPHS OF SOOT AGGREGATES

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ABSTRACT The morphological characterization of aggregates is an important step in determining the physical and chemical properties of soot, such as cooling rate by radiative heat transfer and surface reactivity. However, the empirical equations currently used for morphological quantification still rely on subjective and tedious manual measurement of soot primary particle diameters. In this work, we propose a soot monomer detection algorithm that uses the binary edge of an aggregate as an input image, generated from TEM/SEM micrographs of soot. Aggregate edge pixels are iteratively paired and using the gradient direction at the edge, the center coordinates and radius of candidate circles are determined. A score capturing the likelihood of candidates representing soot monomers is then attributed to each circle and is used in the final selection. The performance of the proposed algorithm is assessed using soot images from a one-dimensional unstretched CO₂-diluted methane-oxygen diffusion flame along with soot formed during the combustion of polymer matrix composites in a cone calorimeter. The algorithm can effectively capture the shift towards larger primary particles as the fuel concentration is increased but also as the combustion configuration is changed to one resulting in turbulent flame and large soot residence times. A comparison with a manually measured dataset shows that the algorithm slightly underestimates the distribution of the primary particle diameter. To explain this discrepancy, a non-dimensional distance parameter f_{dist} for each circle reveals that the regions where aggregates are preferentially measured manually are different from those considered by automatic detection. The performance of the proposed algorithm is compared with a circular Hough transform algorithm to reveal a more realistic prediction of primary particle diameters.

Keywords – soot, morphology, soot monomer, primary particle, detection, image processing, automated measurement, circle detection, cone calorimetry

5.1.1 Introduction

The morphology of soot is closely related to the structure of the flame in which the aggregates are generated [86, 91, 130, 131]. Non-intrusive laser-based measurements of soot volume fractions require a precise quantification of the morphology [136]. Other aerosol measurement techniques, such as scanning mobility particle sizers provide the electrical mobility diameter [86, 135, 148, 149] but the morphology of the aerosol is overlooked. The accurate characterization of soot morphology from a specific flame requires a large dataset of soot micrographs [111], typically acquired using a transmission (TEM) or scanning electron microscope (SEM). The morphological parameters consist of the mean diameter and mean projected area of soot monomers as well as the number of monomers per aggregate, the maximum aggregate projection length, its two-dimensional radius of gyration and its projected area [16, 79, 86, 130, 150]. Additionally, the fractal dimension, which quantifies the extent to which the two-dimensional projection of the aggregate fills the projection plane, acts as a blueprint of the soot growth mechanism through which the aggregate was formed. Some of these parameters are estimated using empirical equations [16]. Yet, at the core of these empirical equations lies the mean diameter of the soot monomers, which cannot be estimated and must be measured directly from soot micrographs. For a dataset of aggregates acquired in a specific combustion environment, a large number of primary particles must be measured for the resulting distribution to be an accurate representation of the monomer population. Since soot aggregates can be composed of hundreds of monomers and that partial-to-total occlusion can occur due to coalescence but also due to the two-dimensional projection in TEM/SEM imaging, it is a rather complex task to perform this measurement accurately [90]. There is therefore a need for an accurate primary particle detection algorithm using electron microscope micrographs.

A first attempt dedicated to detecting soot monomers using an automated image processing algorithm was done in the last decade by Grishin et al [91], highlighting that this is a rather new endeavor requiring further work. Most automated algorithms for primary soot particle recognition

involve the modified Circular Hough Transform (CHT) algorithm [91, 130, 131, 151]. The main differences between these algorithms lie in the preliminary image processing stages leading to the detection of the outer aggregate edge [91, 111, 130, 131]. As highlighted by the quasi-omnipresent noise removal operations [91, 130, 131, 134], CHT algorithms can be quite sensitive to noise [134]. As such, the edge detection step is crucial to obtaining a satisfactory performance. CHT-based algorithms that consider the internal edges of the aggregate have also been published, such as the work of Kook et al. [111]. The input parameters typically required by the CHT method consist of a sensitivity parameter and an expected diameter range. The former controls the circle detection sensitivity and may vary considerably depending on the complexity of the input edge map [111, 130, 131, 135], while the latter constrains the diameter range for detection. Thus far, in the context of soot monomer detection, CHT-based algorithms tend to underestimate the mean primary particle diameter [91, 131] and are sensitive to the lower bound of the input diameter range [130, 131, 135]. Another image processing algorithm tackling the automated primary particle detection relies on the Euclidean Distance Mapping (EDM) method [86, 90]. This method has the advantage of not requiring an expected diameter range as an input. However, its weakness lies in the requirement for the expected type of the distribution as an input [86, 135]. Contrary to CHT-based algorithms, the mean soot monomer diameter obtained by the EDM-based algorithms is overestimated when compared to manual measurements [135]. The pair correlation method is another type of algorithm used to estimate the diameter of primary particles in soot aggregates [136] but depending on the morphological variability of the aggregates, it must be calibrated against manual measurements.

Unfortunately, the measurement of primary particle diameters has not been yet automated in a satisfactory manner. This can be partially attributed to the imperfect circularity of soot monomers, especially in the case of mature soot, as highlighted in Figure 5.1. A manual measurement of soot monomers is still deemed more reliable than an automated one [135]. The arguments leading to this claim often blame the high sensitivity of the algorithms to the input parameters. More concisely, the discrepancy observed between manual and automatic detection is inherently attributed to the circle detection method itself. At the same time, concerns have been expressed repeatedly regarding arbitrariness in manual measurements [90, 111]. To our best knowledge,

researchers have not yet quantitatively assessed whether this discrepancy arises due to a bias in the region of the aggregate used for measurement between the manual and automatic approaches. Consequently, additional research is needed to determine the source of this discrepancy through a detailed comparison of the results given by the two methods. Moreover, currently published algorithms do not provide an intuitive parameter that captures the quality of the fit between detected circles and input edge map.

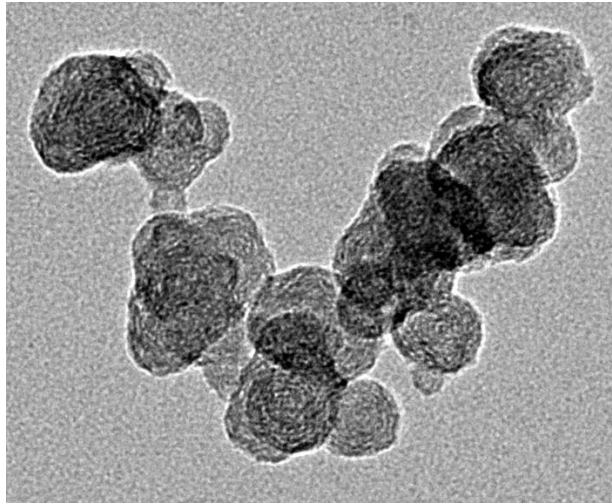


Figure 5.1: Mature soot aggregate adequately illustrating the imperfect circularity of soot monomers

In this work, we propose a new image processing algorithm capable of identifying and measuring the diameter of soot monomers through the detection of the circular arcs composing the outer edge map of the aggregate. We first present the operations required to obtain an edge map that minimizes the computational cost of the circular feature detection algorithm. Following the edge map calculation, edge pixels and their orientations are iteratively paired within a distance representing the maximum expected diameter and are used to simultaneously solve for the center coordinates of the circle and its radius. The resulting candidate circles are compared to the edge map and a score is calculated based on the level of intersection and the number of intersecting fragments. The score is used to perform the final candidate selection by choosing the best candidates in each sub-region of an aggregate. The selected circles are assigned an intuitive quality parameter that indicates the percentage of their circumference intersecting with the edge map. Our

main contribution lies in the definition of the score, which incorporates intuitive factors that are pertinent in quantifying the fit quality between a candidate circle and the edge map. Moreover, the local maximization routine is more transparent compared to other approaches and gives the user more control over the final selection of the candidate circles, by specifying the maximum level of overlap between primary particles, therefore making the algorithm tunable for other types of spherical nanoparticles.

The algorithm is tested on soot aggregate datasets of increasing fuel richness obtained from a highly controlled one-dimensional unstretched carbon-dioxide-(CO₂)-diluted methane-(CH₄)-oxygen-(O₂) diffusion flame along with soot formed during the combustion of polymer matrix composites in a cone calorimeter. The performance of the algorithm is then compared to manual measurements and the observed discrepancy is discussed by defining a non-dimensional distance parameter characterizing the regions of the aggregate exploited by both types of measurement.

5.2 Experimental

5.2.1 Combustion sources for particulate matter

A portion of the soot aggregates used in this work are gathered in a one-dimensional unstrained diffusion burner, developed for the investigation of thermal diffusive instabilities [152] and soot formation [51]. It has been characterized in detail in previous work [49], demonstrating that it indeed allows the experimental realization of the idealized 1D diffusion flame construct. The burner is made of two square arrays of thin stainless-steel needles that are arranged in an opposed jet configuration. The injection arrays are separated by a 50 mm gap and the one-dimensional combustion domain is enclosed in a quartz duct, as shown schematically in Figure 5.2. Each injection array supplies one of the reactants, namely methane or oxygen. For the experiments presented here, the combustion products are forced to exhaust on the oxidizer side, between the injection needles. As a result, the bulk flow in the burner is forced in a single direction, from the fuel inlet (bottom) towards the oxidizer inlet (top), requiring the oxidizer to counter-diffuse to the reaction zone. These physical constraints applied on the flow field result a 1D flow within the reaction zone. The formation of soot occurs upstream of the stoichiometric flame, as indicated in

Figure 5.2, and its thermochemical and morphological evolution depends only on the vertical position. In addition, the thermophoretic force exerted on the particles by the 1D temperature gradient is aligned and opposed to the drag force in the bulk flow, resulting in very long residence times within the soot formation region. Both reactant streams may be diluted with carbon dioxide to control the transport properties of the mixture and reduce the adiabatic flame temperature. The flow rate of the reactants and of the inert dilution gas are controlled using mass flow controllers (Teledyne Hastings HFC-202).

In addition to the 1D diffusion flame, a cone calorimeter built in accordance with the ISO-5660 standard is also used for generating soot in a turbulent flow field that is characterized by high fuel richness and long residence times. The sample materials consist of epoxy/carbon fiber and phenolic/carbon fiber polymer matrix composites subjected to a radiant heat flux of 35 kW/m^2 .

5.2.2 Soot Sampling

The soot sampling apparatus is composed of a linear servomotor (Faulhaber QuickShaft LM1247-100-11) operated by a microcontroller (Faulhaber MCLM-3006-SRS), a carbon-coated nickel TEM grid (Ted Pella #01844N-F) mounted on a tweezer-like holder that sits on a steel wire. The wire is connected to the linear motor, which inserts the grid in the visible soot layer through one of the unused exhaust needles in the bottom array, for a residence time of about 160 ms [130, 153]. The optimal residence time has been determined experimentally to ensure that soot particles have enough time to travel to the grid through thermophoresis while also preserving the structural integrity of the grid. Care has been taken to avoid vibrations in the wire as it reaches the sampling position, to eliminate potential sampling by impaction and the resulting modifications in the morphology of the sampled soot. The insertion of the grid in the flame is recorded by a high-speed camera (Photron Mini AX200) at a sampling rate of 1000 frames per second. Videos of the grid insertion allows the accurate determination of the residence time and sampling location relative to the injection needle arrays and the edges of the visible soot layer. In Figure 5.2 below, the schematic representation of the experimental soot sampling apparatus is shown in the 1D burner. The soot samples from the cone calorimeter are obtained using the same protocol but the high-speed camera is not implemented in this setup.

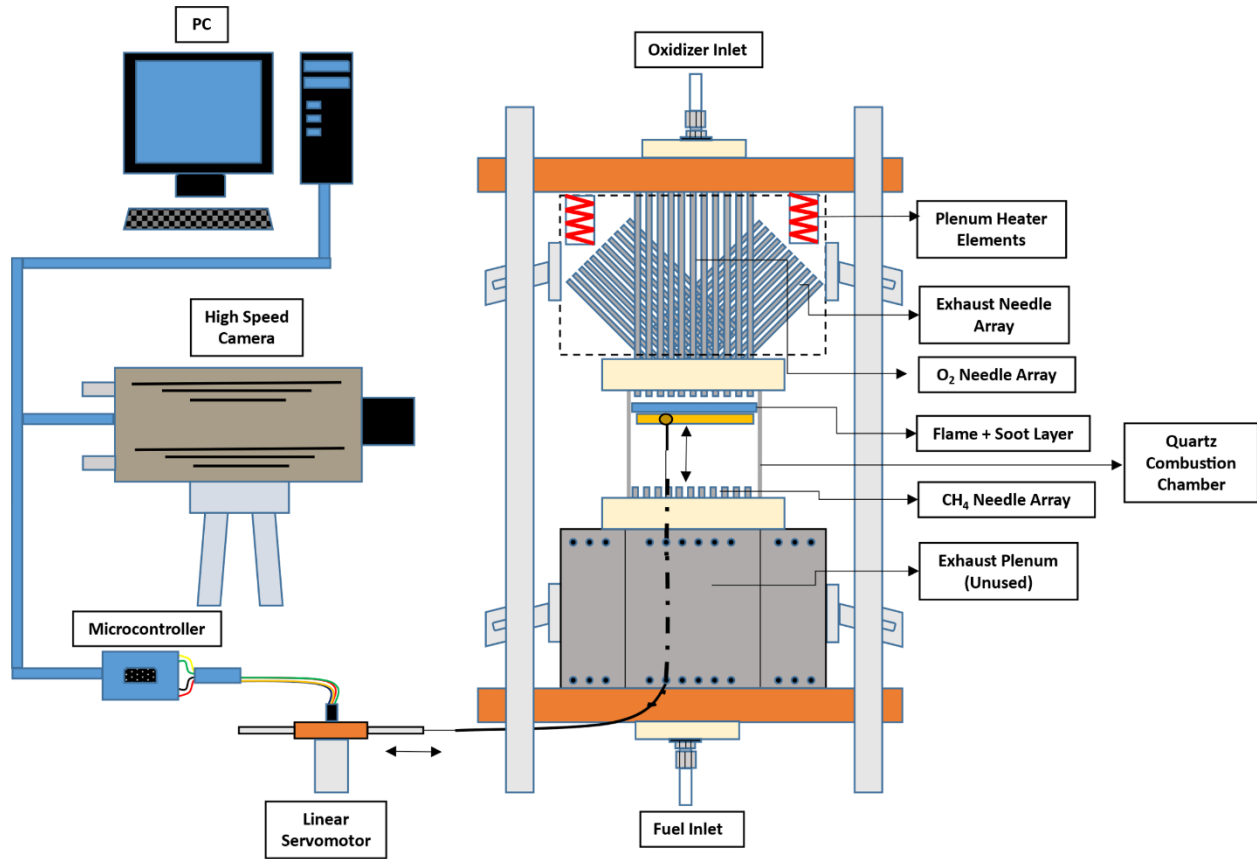


Figure 5.2: Schematic representation of the experimental setup

5.2.3 TEM micrograph acquisition

The sampling disks are imaged on a transmission electron microscope (JEOL JEM-2100F) at an accelerating voltage of 200 KeV. The grayscale micrographs are characterized by a bit depth of 8 and a size of 2048 x 2048 pixels. The resolution range of the acquired micrographs spans between 0.13 and 1.28 nm/px, with the average resolution of the micrographs used in this study is slightly under 1 nm/px.

5.3 Image Processing Algorithm

The main steps composing the soot monomer detection algorithm are detailed in the following sections. We begin by describing the operations leading to a satisfactory edge map of the

aggregate, followed by the calculation of the potential solution circles using pixels pairs and the score associated with each solution point. Redundant solution circles are combined into a single entry while circles that are outside the aggregate area are eliminated from the preliminary list. For each circle, a new score is calculated by incorporating additional factors that are pertinent to quantify the quality of fit between the solution and the aggregate edge map. Ultimately, the final candidate selection routine chooses the highest scoring circle candidates in each region of the aggregate among the cloud of points generated earlier using the edge pixel pairs. The image processing algorithm described here is implemented in the Matlab programming environment and is made available upon request under a creative commons license.

5.3.1 Edge detection

The aggregates are first individually cropped from TEM micrographs. To minimize the computational cost of the circle detection operation, the thinnest possible edge map of the aggregate is desired (i.e. 1-pixel-thick). Because the edge of a feature is a region characterized by a steep intensity gradient, the edge map is best obtained from a binary mask of the aggregate. In this manner, the gradient is maximized only at the interface between the aggregate and the background (i.e. the edge) and assumes a value of zero everywhere else. However, prior to thresholding the cropped aggregate image I , a two-dimensional median filtering is performed to remove noise. The size of the filtering kernel is 4x4 pixels and is independent of the magnification level of the input image. The segmentation of the aggregate from the background is performed manually. To achieve this, the median-filtered image I_{median} is subjected to a thresholding operation starting from an initial threshold value of 0.6. The value is manually incremented in steps of 0.01 until a qualitatively satisfactory outcome is achieved. Our criteria of a good threshold value are to simultaneously maximize the number of aggregate pixels while accurately segmenting it from the background.

In Figure 5.3, images b), c) and d) depict the outcome of the thresholding operation for an underestimated, overestimated, and optimal threshold value t , respectively. As indicated by the green arrows, the aggregate is fragmented for suboptimal values of t and becomes filled as the threshold value is increased. If t is overestimated, the pixels representing the background merge

with the pixels representing the aggregate (Figure 5.3c, red arrow) and the segmentation of the aggregate becomes impossible. The thresholding operation results in a binary mask $I_{binary,1}$ that serves as input to the *bwconncomp* Matlab function to isolate the aggregate from the background. The output of this function lists the various connected regions in the input image; only the region representing the aggregate is conserved as it represents the binary mask of the aggregate, I_{binary} . The binary mask is used to generate an edge map I_{edge} of the aggregate using the *edge* function with the ‘*Roberts*’ method. This method has been chosen following a qualitative comparison with the *Sobel*, *Canny*, *Prewitt* and *Laplacian of Gaussian* edge detection methods. The edge map I_{edge} is then used as an input into the *imgradient* function using the *Prewitt* method to calculate the direction of maximum gradient for each pixel (i.e. the angle normal to the edge), resulting in image $I_{edge, normal}$. Using the image with the optimal threshold value t (Figure 5.3d), one can readily isolate the aggregate from the background (Figure 5.3e) and generate the edge map of the aggregate (Figure 5.3f) using the operations described above.

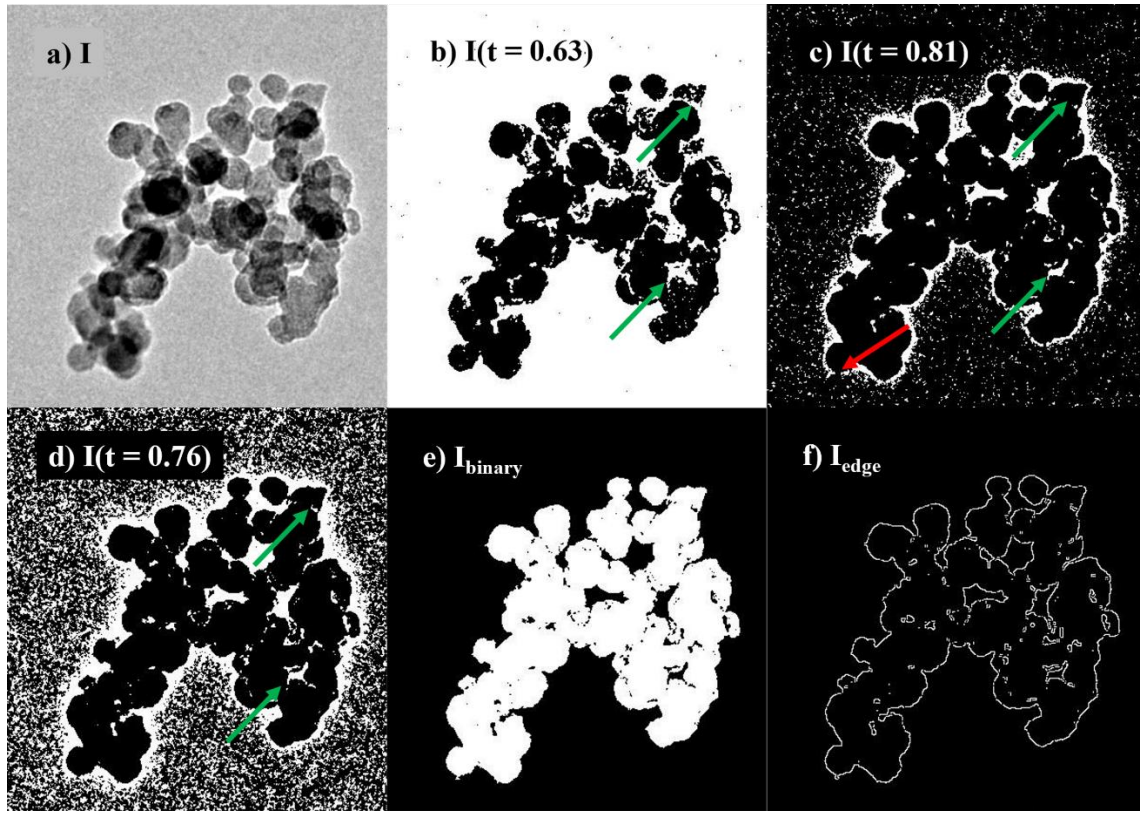


Figure 5.3: Manual thresholding of the aggregate shown in a) with a b) underestimated threshold value where the evolution of the aggregate fragmentation is indicated by green arrows, c) overestimated threshold value where background merges with aggregate, indicated by a red arrow and d) optimal threshold value. Image e) shows the binary mask of the aggregate using the optimal threshold t and image f) shows the aggregate edge map

5.3.2 Circular feature detection

The circular feature detection algorithm is based on the work of Pan et al. [120] and uses both I_{edge} and $I_{edge, normal}$ as input images. The circle is parametrized in a three-dimensional space of (x, y, r) and detection relies on the fact that a line coincidental to the normal of a circle's edge ideally passes through the center of the circle. By parametrizing the circle using two edge points, p_1 and p_2 , and their respective normal vectors $\vec{n}_1$ and $\vec{n}_2$, one can solve for the intersection of the projection lines l_1 and l_2 , yielding the center coordinates of the circle as well as its radius, represented by (x_c, y_c, r_c) . The list of edge pixel pairs V_{pairs} is then computed by calculating all the

unique edge pixel combinations while imposing a distance constraint $D_{\max} = 60$ nm, representing the maximum expected primary particle diameter [29], converted to pixels using the resolution of the image.

Due to the discrete nature of pixels, a seemingly perfect circle from a digital image invariably deviates from the ideal case represented in continuous space. As a result, the projection lines $\vec{l}_{1,i}$ and $\vec{l}_{2,i}$ will often be skew in the three-dimensional parameter space (x, y, r) characterizing the circle. Consequently, the solution $(x_c, y_c, r_c)_i$ to element i of V_{pairs} is determined by calculating the center point of the shortest line segment $\vec{l}_{3,i}$ that joins both skew lines $\vec{l}_{1,i}$ and $\vec{l}_{2,i}$, through points $(x_{c1}, y_{c1}, r_{c1})_i$ and $(x_{c2}, y_{c2}, r_{c2})_i$, respectively. By definition, $\vec{l}_{3,i}$ is perpendicular to both $\vec{l}_{1,i}$ and $\vec{l}_{2,i}$.

In Figure 5.4, a schematic representation is shown for the non-ideal case of a discretized circle resulting in skew projection lines. It illustrates the parametrization of the circle using two edge points and their normals, and the solution (x_c, y_c, r_c) in (x, y, r) space to one iteration of the algorithm for an image containing a single circle.

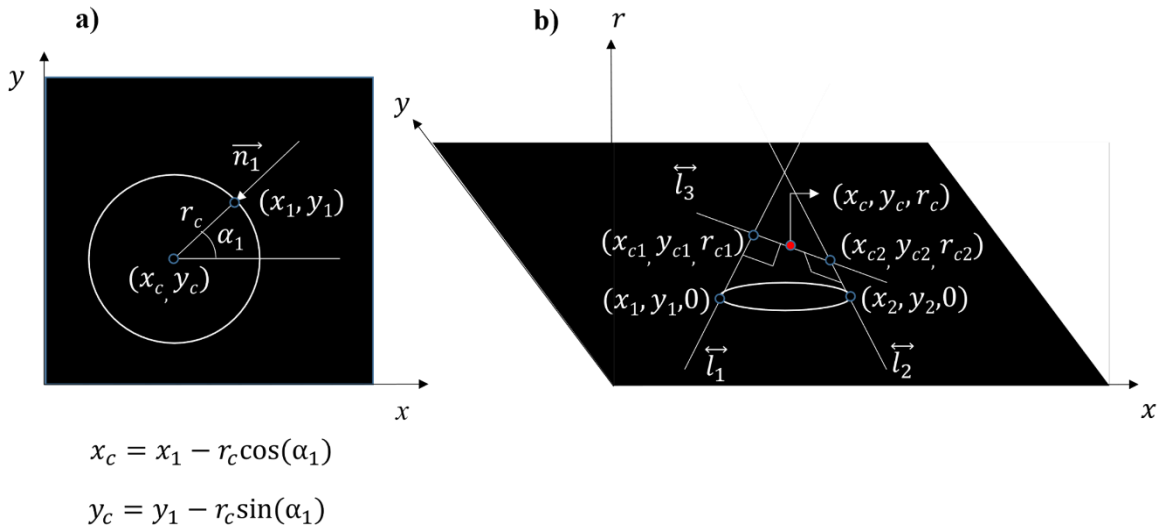


Figure 5.4: Schematic representation of a) the parametrization of the circle, b) the solution to one iteration of the circle detection algorithm for a single circle. The loop index i has been omitted to simplify the labels.

The characteristic parameters of the candidate circle are given by:

$$(x_c, y_c, r_c)_i = \frac{(x_{c1}, y_{c1}, r_{c1})_i + (x_{c2}, y_{c2}, r_{c2})_i}{2}.$$

In addition, the minimum distance $d_{min,i}$ between skew lines $\vec{l}_{1,i}$ and $\vec{l}_{2,i}$ is given by:

$$d_{min,i} = \|(x_{c1}, y_{c1}, r_{c1})_i - (x_{c2}, y_{c2}, r_{c2})_i\|.$$

Subsequently, a score $S_{1,i}$ capturing the likelihood that a pair of edge points is part of a circle is calculated as follows:

$$S_{1,i} = \begin{cases} \exp\left(-\frac{d_{min,i}}{r_{c,i}}\right) & \text{if } \frac{d_{min,i}}{r_{c,i}} < 1.0 \\ 0, & \text{otherwise} \end{cases}$$

After processing all the elements of V_{pairs} , the algorithm outputs a list A of entries representing potential solutions (i.e. circles) for the input image I , each characterized by center coordinates, a radius and a score, namely (x_c, y_c, r_c, S_1) . Since pixel coordinates may only take integer values, (x_c, y_c, r_c) are each converted to the nearest integer. This operation often leads to duplicate entries of (x_c, y_c, r_c) in list A . To eliminate these duplicates, list A is ordered in ascending order of x_c and for all equal values of x_c , the resulting sub-list is ordered in ascending order of y_c . Subsequently, the algorithm combines the duplicated circle entries of list A into one, where S_1 is the sum of the individual S_1 's of the duplicates. The resulting list is labeled A_I .

5.3.3 Elimination of the out-of-bounds candidates

The following data reduction operation performed on A_I eliminates the entries that have center coordinates (x_c, y_c) outside of the region representing the soot aggregate. To achieve this, a gray-level image I_{S1} of the same size as I is generated and the pixels (x, y) corresponding to (x_c, y_c) are set to their respective score S_1 , the rest to 0.

$$I_{S1}(x, y) = \begin{cases} S_1 & | (x_c = x, y_c = y) \quad \forall (x_c, y_c) \in A_1 \\ 0, & otherwise \end{cases}$$

I_{S1} is then multiplied elementwise (i.e. Hadamard-Schur product $\circ$) with the binary mask of the aggregate, I_{binary} .

$$I_{S1'} = I_{binary} \circ I_{S1}$$

The resulting image $I_{S1'}$ conserves only those entries of A_1 that are located within the aggregate; the new list is referred to as A_2 .

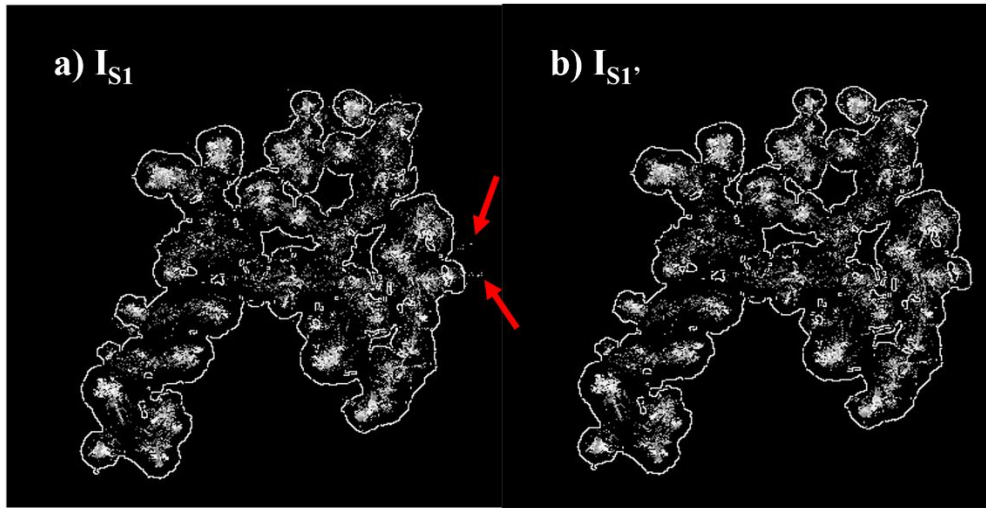


Figure 5.5: Gray-level images illustrating the score $S_1(x, y)$ using a) the raw solution points containing aggregate outliers (red arrows) and b) the solution points after elimination of aggregate outliers. For visual purposes, the score value is normalized to 255 (8-bit) and the aggregate edge map is added for context.

5.3.4 Refinement of the definition of the score

To improve the accuracy of the score S_1 at measuring the likelihood that a candidate circle is valid, a combined score S_C is calculated. This new score S_C is a product of the initial score S_1 and two additional sub-unitary coefficients f_c and f_{frag} . The former is a ratio between the number of pixels of the edge map coinciding with the edge pixels of a solution circle (i.e. $I_{edge} \cap I_{circle}$) and the number of edge pixels of the solution circle. The latter, f_{frag} , decreases exponentially with the number of fragments of the edge map that coincide with the edge pixels of the solution circle. When combined into S_C , the coefficients f_c and f_{frag} respectively ensure that 1) the number of aggregate edge pixels confirming a given solution circle is maximized while 2) the number of separate fragments that these pixels form is minimized.

For each entry of A_2 , a binary image I_{circle} is generated which contains a candidate circle with center coordinates (x_c, y_c) . The radial span of the circle is given by:

$$r_c - 1 < r < r_c + 1.$$

I_{circle} is a mask used to extract the pixels of I_{edge} that coincide with the solution through an elementwise multiplication, as previously. In Figure 5.6, the extraction of the number of edge points that coincide with a solution circle, n_{common} , is illustrated for a synthetic test aggregate.

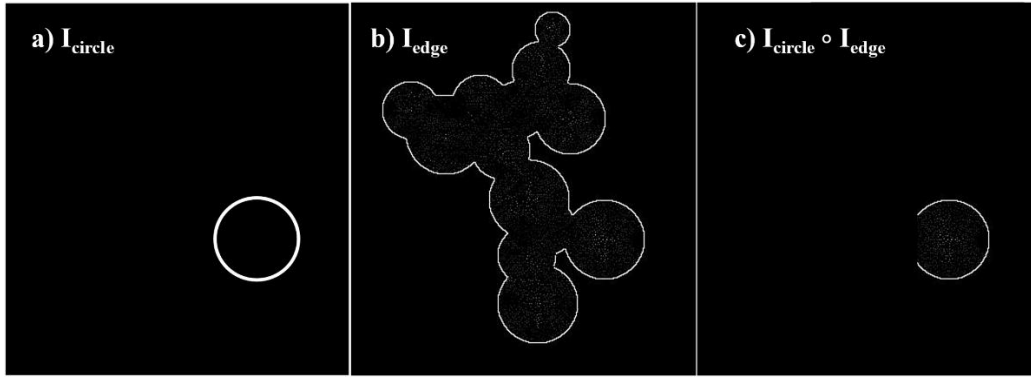


Figure 5.6: Representation of the image operations leading to the extraction of the edge points that coincide with a solution circle for the edge map of a synthetic aggregate

However, the determination of a reliable value for n_{common} requires an additional condition, illustrated in Figure 5.7. The blue contours represent a hypothetical edge map composed of 3 circles, namely A, B and C. The red contour represents a suboptimal solution to circle C. Circles A and B are located close enough to C to falsely increase the value of n_{common} , potentially resulting in the red circle being chosen as the most probable solution to circle C. To avoid counting the pixels of circles A and B into the value of n_{common} for the solution to circle C, the orientation of the normal edge vector (shown by white arrows) must result in an angle comparable with the normal edge vector of the solution circle (shown by red arrows). With this additional condition, n_{common} is limited to the pixels of region 1, where the common pixels must also share a common edge orientation. Region 2 shows the pixels that are rejected from n_{common} because the edge orientations do not match, despite the edge pixels coinciding with the solution circle.

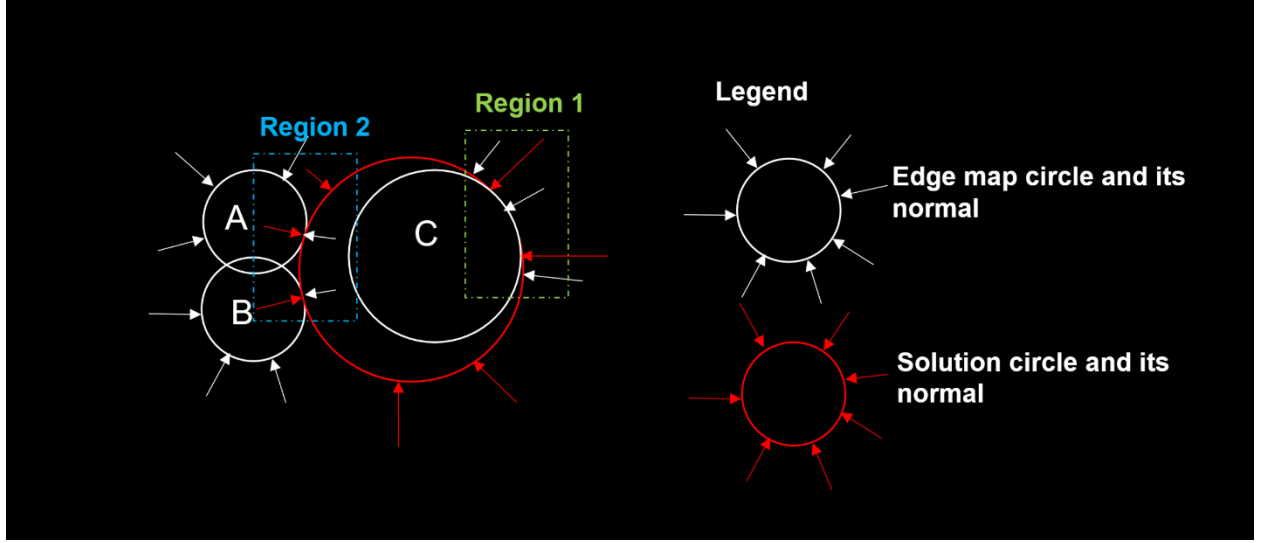


Figure 5.7: Illustration of a scenario where edge points of adjacent circles falsely increase the value of n_{common} .

This operation is performed elementwise by taking the ratio of the normal vector α_{circle} of image I_{circle} , with the normal vector α_{edge} of image I_{edge} for every pixel location that is common to both I_{edge} and I_{circle} (i.e. $I_{edge} \cap I_{circle}$). Although theoretically we should only conserve the pixels for which the ratio $\alpha_{circle}/\alpha_{edge} = 1.0$, we conserve all those that are in the range $0 < \alpha_{circle}/\alpha_{edge} < 2.0$.

Now that a reliable value for n_{common} is obtained, we may calculate the quality parameter f_c as follows:

$$f_c = \frac{n_{common}}{2\pi r_c}.$$

This quality metric quantifies the fraction of a solution circle's edge pixels that coincide with the pixels of the edge map of the input image. If the value of f_c is low for a candidate circle, the confidence that its diameter was accurately measured is also low.

The second factor used to calculate the combined score S_C captures the level of fragmentation f_{frag} of the portion of the edge map that coincides with the solution circle (i.e. $I_{edge} \cap I_{circle}$). For this purpose, the intersection of the edge map with the solution circle, $I_{edge,sol}$, is calculated through:

$$I_{edge,sol} = I_{circle} \circ I_{edge}$$

The operation is illustrated in Figure 5.8 for an intersection constituted of one (images a, b, c) and two (images d, e, f) components.



Figure 5.8: Illustration of the operations leading to the quantification of the edge fragmentation matching with a solution point for an edge with low fragmentation (images a, b, c) and high (images d, e, f) fragmentation

Using $I_{edge,sol}$ as an input, the number of connected components, $n_{conncomp}$ are returned by the $bwconncomp$ function using an 8-pixel connectivity. The factor f_{frag} is calculated as follows:

$$f_{frag} = \exp(-\varepsilon * (n_{conncomp} - 1))$$

Due to the higher level of fragmentation, the solution circle in the Figure 5.8d case yields a lower f_{frag} value, thus lowering the overall score S_C . The combined score S_C is then given by:

$$S_C = S_1 * f_c * f_{frag}$$

The factor ϵ controls the rate of decay of the exponential function responsible for generating the sub-unitary coefficient f_{frag} that multiplies the overall score. As such, the combined score S_C is a product of different pertinent factors that measure the likelihood that a solution point represents a soot monomer, and it can take values between 0 and 1.0.

5.3.5 Local maximization routine

Thus far, we have assumed that the circle detection algorithm yields the optimal r_c value for the solution point (x_c, y_c, r_c, S_1) . To ensure that an optimal value of r for a given solution point (x_c, y_c, r_c, S_1) is obtained, we perform the operations outlined in this section iteratively while varying the value of r in a radius range characterized by r_{tol} as follows:

$$r_c - r_{\text{tol}} < r < r_c + r_{\text{tol}}$$

At the end of the iterative process on r for a single solution element (x_c, y_c, r_c, S_1) , we select the value r_c' which results in the highest score S_C and accumulate the solution point (x_c, y_c, r_c', S_C) into a new list, namely A_3 . The process is repeated for all the elements of A_2 . Prior to running the final candidate selection routine, also referred to as local maximization, list A_3 is ordered in increasing order of r and for each unique value of r , the sub-list is ordered in decreasing order of score S_C . The ordered instance of list A_3 is referred to as A_4 . The elements of list A_4 that have a low likelihood of representing a circular feature in the input image may be eliminated by the application of a threshold $S_{C,th}$ on the value of S_C . This operation is written as:

$$A_5 = \{A_4 \mid S_C > S_{C,th}\}$$

The local maximization is performed over the aggregate region of the input image by looping through list A_5 . Using each solution candidate (x_c, y_c, r_c', S_C) , we extract all the solution points located within the region characterized by $f_{\text{ov}} * r_c'$ around (x_c, y_c) and from these points, we select the circle with the largest S_C value. Prior to executing the next loop, list A_5 is updated to exclude all the points that have been considered in the current loop. The final solution points are accumulated into A_F , which represents the final list of solution elements to input image I .

The overlap factor f_{ov} controls the extent of the region $f_{ov} * r_c'$ around (x_c, y_c) . For example, setting f_{ov} to 1.0 forces the final candidate selection routine to consider only the solution points contained within a distance r_c' around point (x_c, y_c) . If a high degree of overlap exists between the circles of the input image, the value of f_{ov} should be far below 1.0. For example, if the value of f_{ov} is large and a high level of primary particle overlap exists, the solutions to primary particles that are adjacent to the one currently considered may be eliminated. As such, the value of f_{ov} can provide an additional level of control over the solution points that are selected by the algorithm depending on the level of overlap that is expected from the soot aggregates. Moreover, this additional level of control enables the use of this algorithm for other types of particles that may exhibit high levels of overlap.

The ordering of the solution from list A_3 to list A_4 discussed above ensures that the local maximization begins in increasing order of primary particle radius r_c' and decreasing order of score S_c . It is justified by the fact that upon final selection of a solution point, all other solution points contained within the circle given by the selected solution point are eliminated. As such, if the list was ordered in decreasing order of r_c' , the likelihood of eliminating valid solution points is larger because it has a dependence on r_c' .

5.4 Results

The performance of the algorithm is tested using soot aggregates originating from different flames, summarized in Table 5.1. Three flames (i.e. 1, 2 and 3) from the 1D unstretched diffusion burner were sampled, representing progressively richer flames and thus visibly more abundant soot. The freestream fuel equivalence ratio ϕ_∞ and the volumetric flow rates (VFR) in the burner are given therein. The various tunable parameters of the algorithm are also given in the table for each dataset. The values chosen for these parameters have been determined by visually validating the algorithm's performance using a few aggregates. Additionally, the flames of epoxy/carbon fiber and phenolic/carbon fiber composite samples burning in the cone calorimeter were also sampled (i.e. flame 4). The soot from burning composites will be discussed as one dataset, irrespective of the matrix type. The performance of the proposed algorithm is assessed using an additional dataset

of soot aggregates acquired in flame 2 for which a manual measurement was performed. This dataset does not appear in Table 5.1.

Table 5.1: Summary of the soot aggregate datasets used for testing the performance of the algorithm

Flame ID	ϕ_∞	VFR _F / VFR _O (SLPM)	N _{aggregates}	D _{p,min} / D _{p,max} (nm)	ϵ	r _{tol} (pix)	S _{C,th}	f _{ov}
1	3.389	7/7	92	0/60 and 10/60	1/10	10	0	1.0
2	3.733	7/7	1556	0/60 and 10/60	1/10	10	0	1.0
3	4.320	7/7	818	0/60 and 10/60	1/10	10	0	1.0
4	N/A	N/A	596	0/60, 10/30, 10/40, 10/50	1/10	10	0	1.0

5.4.1 Performance of the local maximization routine

Figure 5.9 illustrates the characteristics of the solution dataset before and after local maximization for flame 1. The plots in column a) show the raw distributions of the detected circles' diameters, the initial score S_I and the quality parameter f_c , respectively, as given by the circle detection algorithm for a diameter range corresponding to $0 < D_p < 60$ nm. The last frame in a) shows the mean S_I and mean f_c for each diameter bin. Column b) consists of the same plots as in a) but after a local maximization with a diameter range of $0 < D_p < 60$ nm and with a redefinition of the score to S_C . Since smaller circles tend to yield higher scores due to fewer pixels composing them compared to larger ones and because mature soot monomers are typically larger than 10 nm, in column c), the results are reproduced for a diameter range of $10 < D_p < 60$ nm.

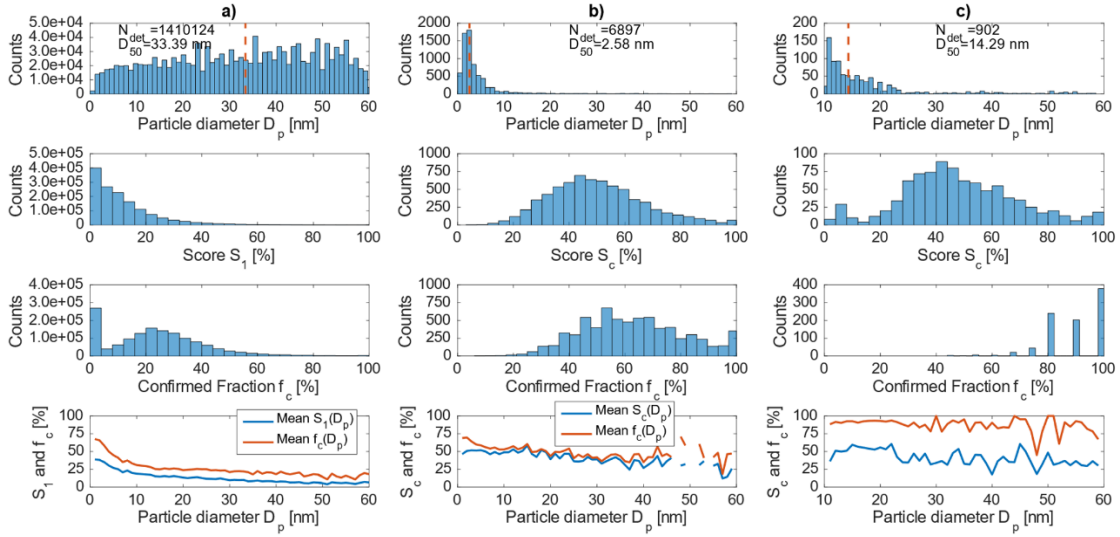


Figure 5.9: Evolution of the distributions of the solution circles' diameters D_P , scores S_1 and S_c , along with the quality parameter f_c , a) prior to local maximization ($0 < D_P < 60$ nm) and post local maximization for particle diameter ranges of b) $0 < D_P < 60$ nm and c) $10 < D_P < 60$ nm for flame 1 ($\phi_\infty = 3.389$)

Prior to local maximization, the distribution of the detected circles' diameters D_P is uniform across the entire diameter range, but the total number of detected circles is unrealistically large ($N_{\text{det}} = 1.4 \times 10^6$), averaging 1.5×10^4 circles per image. In fact, the aggregates from this flame contain on average less than 30 primary particles. The median of the diameter distribution (i.e. D_{50} value) is located at 33.39 nm, which represents a reasonable size for soot. However, the mean values of S_1 and f_c as a function of D_P show a bias for circle diameters under 10 nm, which must be corrected.

Upon redefining the score and applying the local maximization routine for the original diameter range (i.e. 0 to 60 nm - Figure 5.9b), we observe that most of the selected circles have a diameter under 10 nm, with a distribution median located at 2.58 nm. The outcome is illustrated in Figure 5.10 for three aggregates and outlines the preferential selection of very small circles, along with very large ones to fill in the unsolved regions of the aggregate. This performance highlights the necessity of *a priori* knowledge on the expected diameter range, but also the importance of avoiding the resolution limit of discretized (i.e. digital) circles. Nevertheless, the performance of

the local maximization is evident given the rightward shift in the modes of S_c and f_c , compared to the former case.

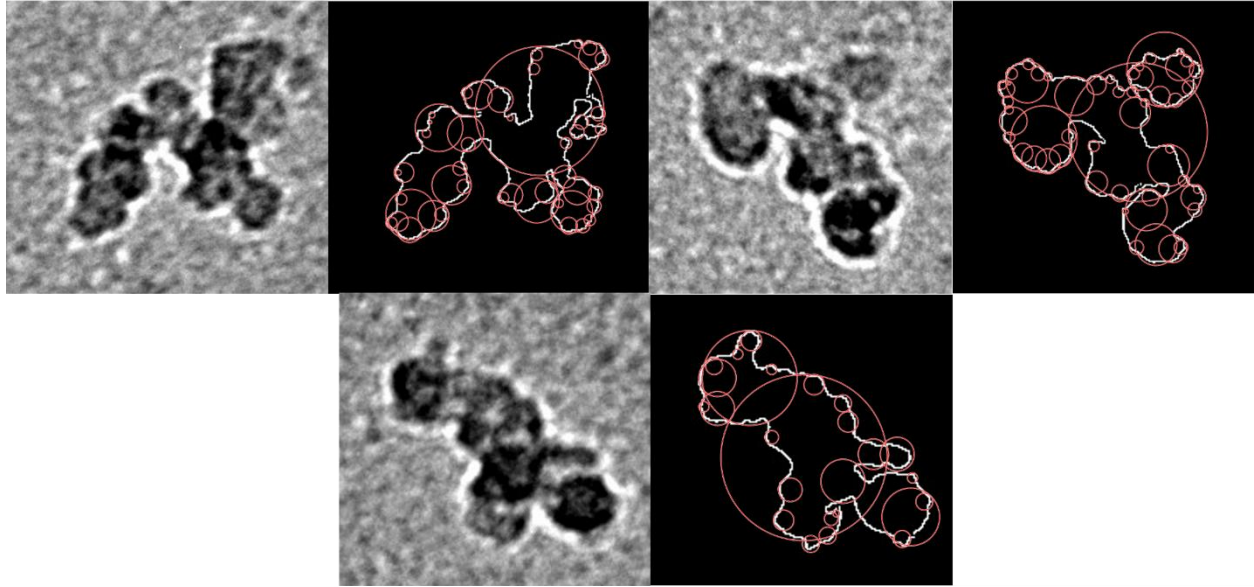


Figure 5.10: Visual output of the algorithm for a diameter range of $0 < D_p < 60$ nm, showing the input aggregate edge map (i.e. white pixels) and the detected circles overlaid in red for three aggregates originating from flame 1 ($\phi_\infty = 3.389$)

Particles under 10 nm are unlikely to represent the bulk of the distribution of mature soot monomers [29, 91, 130] as these may burn out due to their small size prior to aggregation [154]. Consequently, we may confidently constrain the diameter range to $10 < D_p < 60$ nm, as shown in Figure 5.9c, thereby also avoiding the resolution limit of discretized circles. In doing so, we obtain a monomer diameter distribution concentrated between 10 and 25 nm with median at 14.29 nm; a value which is within the expected range for mature soot monomers. The strong increase in the quality parameter f_c ($> 50\%$) for the entire diameter spectrum after restriction the diameter range suggests a better fit between the detected monomers and the edge map than previously. In Figure 5.11, the output of the algorithm is illustrated for the same three aggregates after local maximization with a diameter range of 10-60 nm.

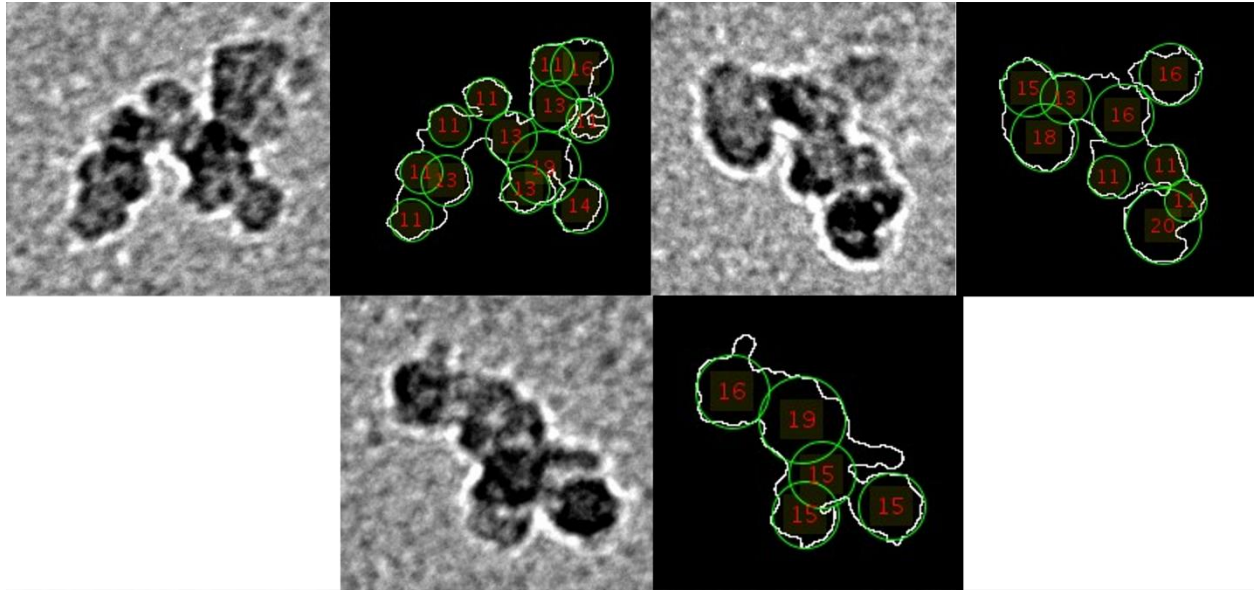


Figure 5.11: Visual output of the algorithm for the range $10 < D_p < 60$ nm showing the TEM micrograph of the soot aggregates and the input aggregate edge map with the detected circles in green (diameters shown in [nm]) for three aggregates representative of the soot dataset acquired in flame 1 ($\phi_\infty = 3.389$)

5.4.2 Sensitivity analysis on the upper limit of the D_p range

To assess the effect of changing the higher limit of the D_p range, we resort to a soot dataset obtained from burning polymers (i.e. flame 4) because compared to gaseous fuel flames, these aggregates consist of larger primary particles, subjected to longer residence times, and an enhanced sooting tendency due to a higher polycyclic aromatic hydrocarbon (PAH) yield [155].

The soot was sampled in the cone calorimeter, 20 mm above the top face of the burning sample specimens while these were subjected to an external radiative heat flux of 35 kW/m^2 . Three polymers/composites have been considered, namely neat thermoplastic polyurethane (i.e. TPU), a composite TPU reinforced with 15 wt% cellulose nanofibers (i.e. TPU/CNF) and a composite phenolic reinforced with carbon fiber (i.e. Phenolic/CF). The TPU/CNF was sampled twice, namely 30 and 100 seconds after ignition. In Table 5.2, the number of aggregates (i.e. $N_{\text{aggregates}}$) and the number of primary particles measured manually (i.e. $N_{p,\text{meas}}$) are shown for each material.

The manual measurements resulted in normal distributions for each material, and their respective fit parameters (i.e. mean μ_{DP} and standard deviation σ_{DP}) are calculated considering a 95% confidence interval. Moreover, the smallest and largest particles measured in each dataset are also given, namely $D_{P,min}$ and $D_{P,max}$. As highlighted by the mean primary particle diameter, located in the 30 nm range, this dataset is well suited to investigate whether the algorithm can detect a shift towards larger primary particles in relation to soot produced by a gaseous fuel diffusion flame.

Table 5.2: Range, mean and standard deviation of the primary particle diameter D_P obtained by manual measurement for the polymer soot dataset.

Soot dataset			Primary particle diameter D_P [nm]					
Material	$N_{aggregates}$	$N_{p,meas}$	$D_{P,min}$	$D_{P,max}$	μ_{DP} (95% CI)		σ_{DP} (95% CI)	
TPU	26	257	11.13	54.94	32.02	34.06	7.65	9.10
TPU/CNF _{30sec}	20	272	18.38	58.94	37.94	39.86	7.40	8.76
TPU/CNF _{100sec}	21	243	14.22	57.75	33.31	35.32	7.29	8.72
Phenolic/CF _{30sec}	21	223	17.33	60.15	32.16	33.89	5.99	7.21

In Figure 5.12, the first column of plots shows the distribution of D_P prior to local maximization. The remainder of the columns represent the solution dataset post local maximization with a D_P range of b) 10-30 nm, c) 10-40 nm and d) 10-50 nm, respectively. The raw dataset has a particle diameter median value located at 10.86 nm. By restricting the range of the particle diameter to $10 < D_P < 30$ nm, it shifts to a value of 16.29 nm, which is mainly associated with the elimination of the solution candidates that are inferior to 10 nm and do not correspond to real monomers in the

aggregate, as shown previously for flame 1. Increasing the upper limit of the D_p range to 40 nm results in a median of 18.10 nm, which remains constant even after a further increase by 10 nm to 50 nm. Given that more than 95% of the manually measured primary particle diameters are below 40 nm and that imposing an upper bound of 50 nm does not affect the distribution significantly, we may conclude that the sensitivity of the algorithm to the upper bound is low. Nevertheless, the median value of 18.10 nm determined by the algorithm is low compared to the manually measured mean primary particle diameter of approximately 35 nm. However, relative to flame 1, the algorithm could detect the expected increase in the median diameter for polymer soot. For the test cases considered, the quality parameter f_c as a function of D_p oscillates between approximately 40% and 60%, which indicates a reliable match between the edge map and the selected circles. We may also observe that the extension of the D_p range from 30 nm to 40 and to 50 nm does not significantly affect the magnitude of the distribution in the 10-30 nm range.

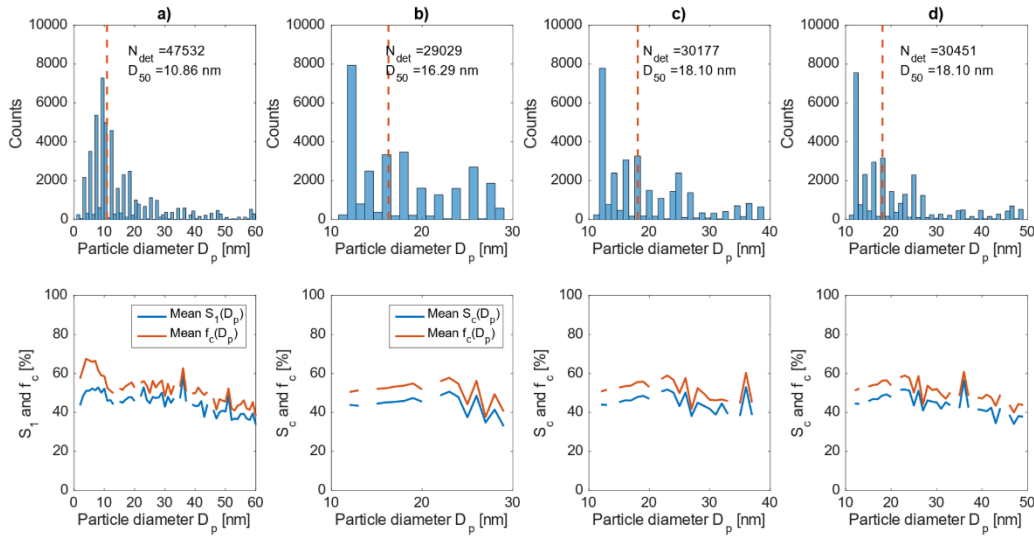


Figure 5.12: Evolution of the distributions of the solution circles' diameters D_p and scores $S_1(D_p)$ and $S_c(D_p)$, as well as the quality parameter $f_c(D_p)$, a) prior to local maximization ($0 < D_p < 60$ nm) and post local maximization for particle diameter ranges of b) $10 < D_p < 30$ nm, c) $10 < D_p < 40$ nm and d) $10 < D_p < 50$ nm for burning composite soot (i.e. flame 4)

5.4.3 1D burner soot characterization

To assess the relative performance of the circle detection algorithm, soot obtained from the 1D diffusion burner is used, in which the freestream fuel concentration, and hence the freestream equivalence ratio, is progressively increased, namely flames 1, 2 and 3. In these datasets, the primary particle diameter is expected to increase progressively with the fuel concentration, which controls the abundance of the chemical species driving inception and monomer growth through surface adsorption. In Figure 5.13, the distributions of the primary particle diameter are shown for these flames along with the median particle diameter. As the freestream fuel concentration is increased, we note a shift the median from 14.29 nm to 16.29 nm and ultimately to 17.95 nm, highlighting the sensitivity of the algorithm at detecting subtle changes in the particle diameter as a result of increasing the equivalence ratio.

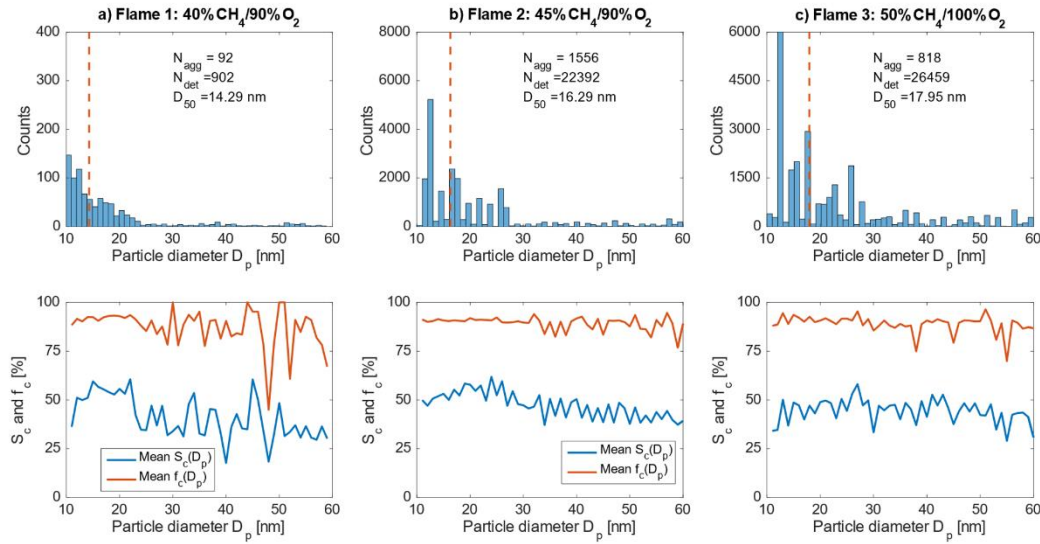


Figure 5.13: Distributions of the solution circles' diameters D_p , combined score $S_c(D_p)$ and quality parameter $f_c(D_p)$ post local maximization for a particle diameter range of $10 < D_p < 60$ nm for a) flame 1 ($\phi_\infty = 3.389$), b) flame 2 ($\phi_\infty = 3.733$) and c) flame 3 ($\phi_\infty = 4.320$)

5.4.4 Comparison with manual measurements

In Figure 5.14a, we compare the particle diameter distributions resulting from manual measurement and automatic detection. For this purpose, a dataset of soot aggregates corresponding to the conditions of flame 2 is used. Two conditions are imposed to match a manually measured monomer with its automatically detected counterpart: 1) the distance between the respective centers must be less than 10 nm and 2) the automatic-to-manually-measured diameter ratio must be within $\pm 15\%$. For most candidates detected by both methods, the difference in the location of the center is less than 4 nm while the diameter ratio is within $\pm 10\%$. Figure 5.14b depicts the manually measured particle size distribution and that of circles common to both methods (i.e. $\text{Manual} \cap \text{Algorithm}$). To quantify the location of a monomer within the aggregate, a non-dimensional distance parameter f_{dist} is calculated through division of the distance d_{cc} from the centroid of the aggregate's binary mask to a given monomer center by the distance d_{ce} from the centroid to the edge, along the line defined by d_{cc} . The distribution of f_{dist} is given in the bottom frame of Figure 5.14b for both measurement methods.

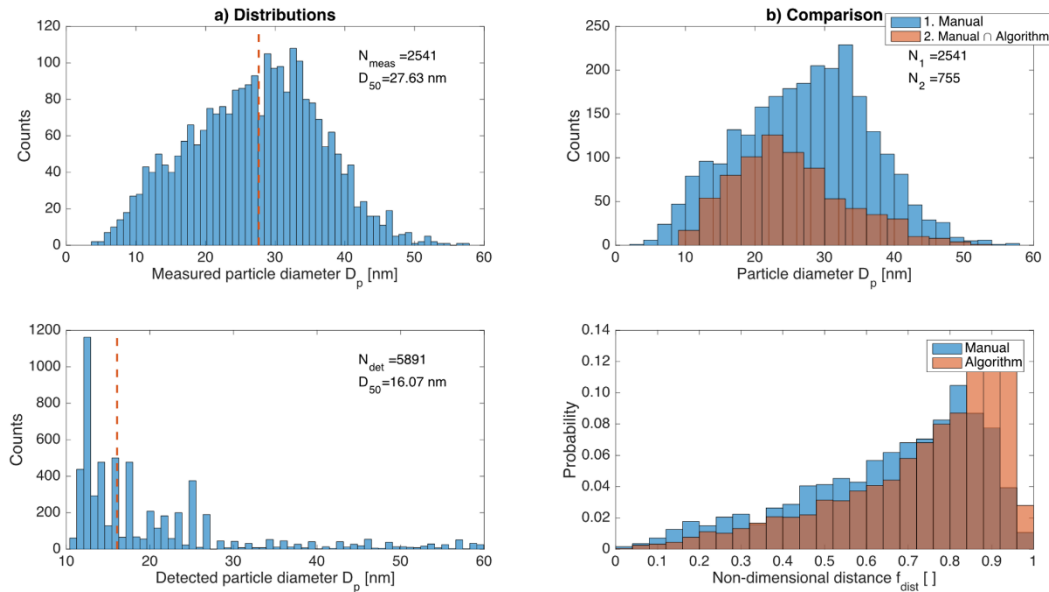


Figure 5.14: Primary particle size distributions for flame 2 obtained by a) manual measurement and the proposed algorithm, with a $10 < D_p < 60 \text{ nm}$, b) comparison of primary particle size distributions for

manual measurement and algorithm detection and probability histogram of f_{dist} for both measurement methods.

Figure 5.14a shows that manual measurement yields an approximately normal distribution with a mode around 30 nm, whereas automatic detection results in a roughly log-normal distribution with a mode located at 13 nm, outlining an underestimation of the mean particle diameter by the algorithm. Moreover, the mode of the common distribution (i.e. $\text{Manual} \cap \text{Algorithm}$ in Figure 5.14b) is much closer to that from manual measurement but it is still underestimated. This is suspected to be a consequence of the manual measurement, which is not limited to primary particles present around the periphery of the aggregate. To confirm this hypothesis, we refer to the histogram showing the probability of obtaining a given f_{dist} value according to the two types of measurements (Figure 5.14b). We note that manual measurements yield a higher probability of detecting particles up to an f_{dist} value of 0.85 but the algorithm is more likely to detect particles with high f_{dist} values (> 0.85), given its focus on the edge of aggregates. Consequently, the underestimation given by the algorithm is at least partly attributed to a higher likelihood of finding small particles around the periphery of the aggregate. If the manual measurement is assumed to be unbiased with respect to the primary particle diameter, it follows that the automatic detection algorithm must consider monomers that are closer to the centroid of the aggregate's 2D projection to yield the true distribution. The obtained mean value of f_{dist} between 0.6 and 0.7 suggests that manual measurements are characterized by a preferred region in f_{dist} -space. However, this region may also depend on the morphology of the aggregates and therefore on the combustion source generating the particulate matter. In Figure 5.15, the primary particles detected by the algorithm by manual measurement are shown. We note that the algorithm detected many of the particles that have been identified through a manual measurement. However, a few additional small particles are detected, especially in the case of the aggregate shown in Figure 5.15a. This behavior can be mitigated either by increasing the lower bound or by applying a threshold on the score prior to the local maximization routine, especially for the smaller particles. In this way, the smaller particles must achieve a stricter fit with the edge map in order to qualify as final candidates. Large circles that do not represent soot monomers have also been detected in aggregates of Figure 5.15a and b. The selection of such unlikely candidates can also be mitigated by applying a threshold on the score, as evoked above.

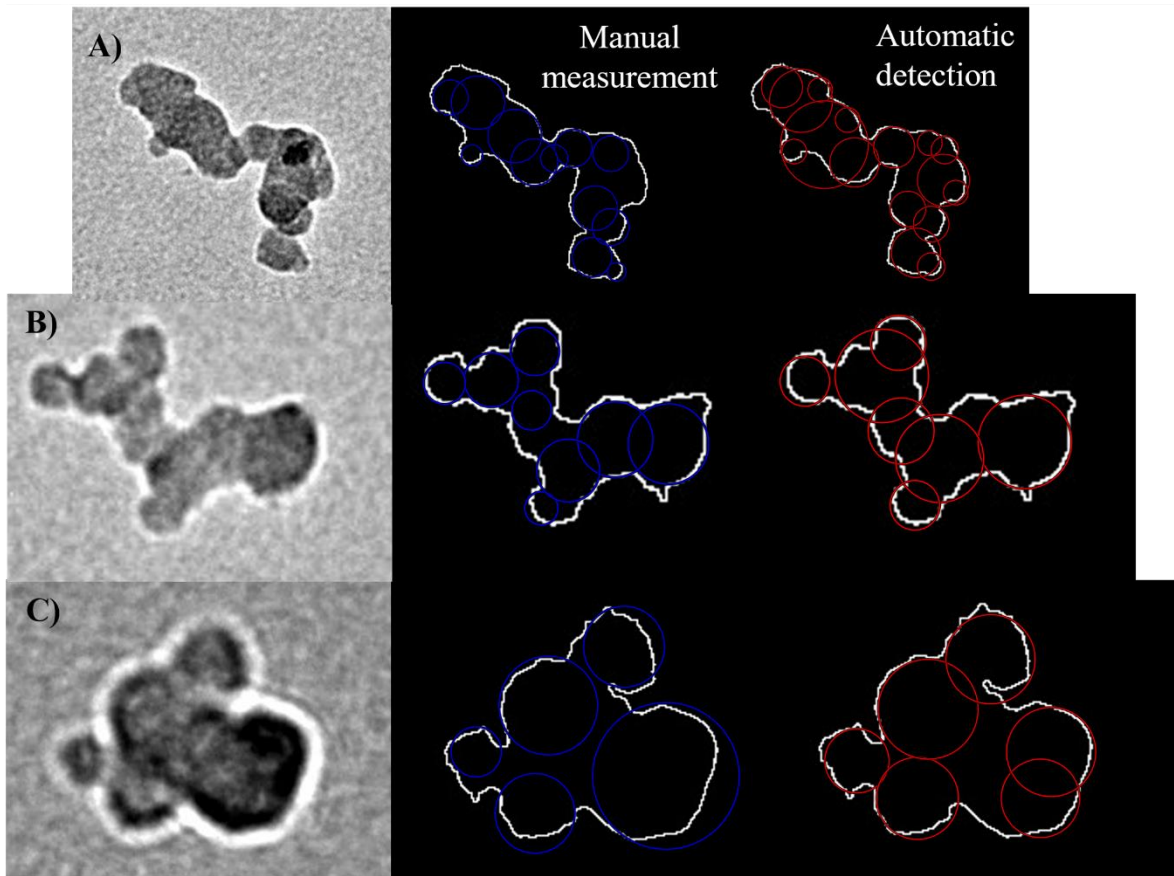


Figure 5.15: Original TEM micrographs of aggregates and visual comparison of the primary particle measurement by the manual method (i.e. blue circles) and automatic detection using the proposed algorithm with a diameter range of $10 < D_p < 60$ nm (i.e. red circles)

To complement f_{dist} , we have also defined the fraction of the area processed f_{agg} (Figure 5.16) as the ratio between the area of measured/detected circles and the area of the aggregate but the pixels that are common to two partially overlapping monomers are only counted once. We observe that a manual measurement typically covers a larger percentage of the aggregate's area, despite a larger number of monomers detected by the algorithm ($N_{\text{det}} = 5891$ vs. $N_{\text{meas}} = 2541$), indicating that larger primary particles are preferentially found closer to the aggregate's centroid. This constitutes an additional argument that justifies the need for the automatic detection algorithm to measure particles that are not limited to the edge of the aggregates.

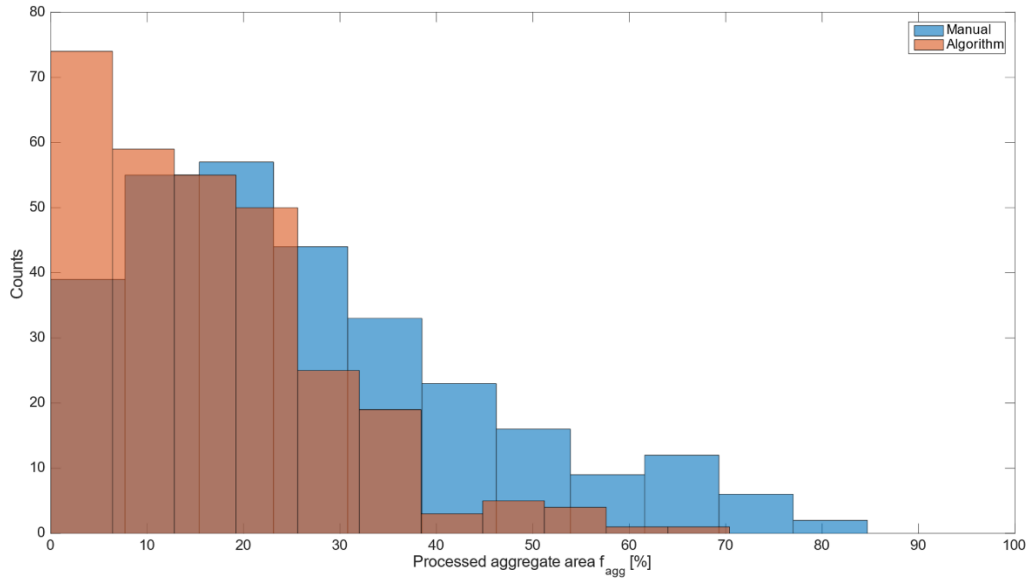


Figure 5.16: Distributions of the processed aggregate area f_{agg} for manual measurement and algorithm detection

5.4.5 Comparison with a circular Hough Transform algorithm

Given the popularity of circular Hough transform algorithm for the detection of soot monomers, but also its sensitivity to the lower diameter bound and the underestimation of the particle size distribution, we deemed it important to put into perspective the performance of the proposed algorithm with that of a CHT-based algorithm for soot. For this purpose, the algorithm proposed by Kook et al. [111] has been used on the soot dataset obtained from flame 1. Three values have been considered for the sensitivity of the algorithm, namely 0.85, 0.90 and 0.95, while the remainder of the parameters were set according to the values suggested by the authors in Table 6 of their manuscript. The primary particle diameter range for the algorithm was set to $8 < D_p < 60$ nm; a range comparable to that tested for our algorithm. The particle size distributions given by the algorithm are shown in Figure 5.17 in order of increasing CHT sensitivity value. We note a median value evolving from 10.71 nm to 10.00 nm as the sensitivity value is increased, outlining the preferential selection of small candidates circles as a result of this increase. Irrespective of the

tested sensitivity value, a median primary particle diameter between 10 and 11 nm is very low, unlikely to represent the bulk of primary particles composing the aggregates of flame 1.

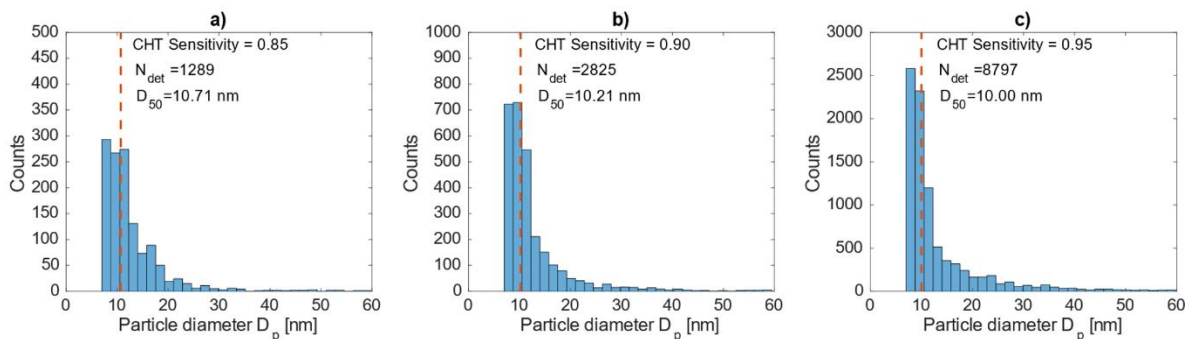


Figure 5.17: Primary particle size distributions obtained for flame 1 using Kook et al. [111] algorithm with a CHT sensitivity value of a) 0.85, b) 0.90 and c) 0.95 and a diameter range of $8 < D_p < 60$ nm.

In Figure 5.18, the preferential selection of smaller candidate circles is clear upon increasing the CHT sensitivity value. Moreover, the algorithm fails to constrain the selection of candidates to the region represented by the soot aggregate, resulting in final candidates detected in regions of image background. Nevertheless, if we focus on the performance of the algorithm solely within the region represented by the aggregate, we can note that the larger the sensitivity, the more soot monomers are detected. However, with a CHT sensitivity of 0.95, many false positives seem to be detected even if we only consider the aggregate region.

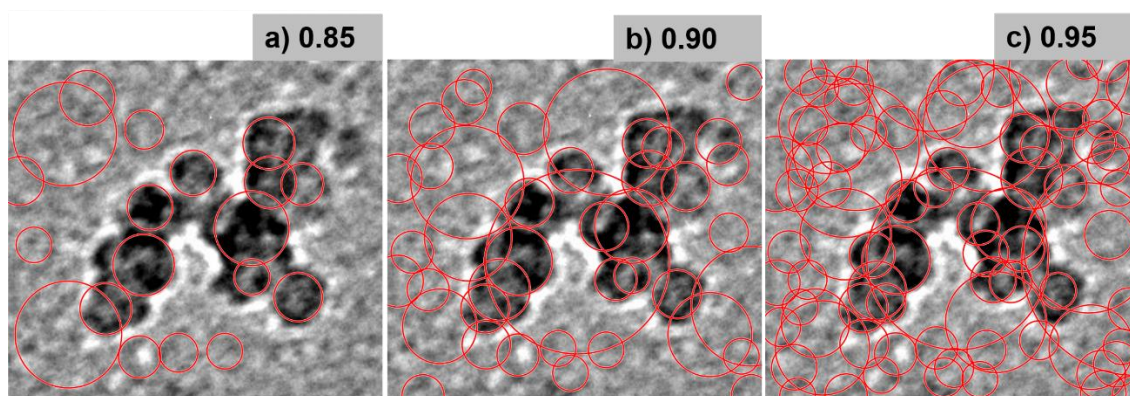


Figure 5.18: Visual output of the algorithm proposed by Kook et al. [111] with a CHT sensitivity value of a) 0.85, b) 0.90 and c) 0.95 and an input diameter range of $8 < D_p < 60$ nm. The detected circles are shown in red, overlaid on the original TEM micrograph.

5.5 General discussion

The automatic detection of soot monomers using the edge map of the aggregate has been shown to be especially sensitive to the lower bound of the diameter range imposed on the algorithm, thus requiring *a priori* knowledge of the expected lower particle diameter. The sensitivity analysis performed on the upper bound of the diameter range indicates that even if this is overestimated, the distribution is not significantly affected. Moreover, given soot datasets from three diffusion flames of increasing equivalence ratio, we were able to observe that the algorithm can detect the expected shift toward larger particle sizes, using the same input diameter range of $10 < D_p < 60$ nm. Unfortunately, the algorithm cannot predict the particle size distribution in a way comparable to a manual measurement, while focusing exclusively on detecting the soot monomers present around the edge of the aggregate. This observation applies for the soot obtained in the diffusion burner as well as that obtained from polymers. Nevertheless, some bias is expected from manual measurements [111], which may translate into the operator focussing towards larger and thus, readily distinguishable particles. However, assuming that the manual measurement is unbiased, the mode of the distribution given by the algorithm is largely underestimated and f_{dist} suggests that manually measured monomers are generally closer to the centroid of the aggregate compared to the automatic monomer detection. Consequently, the algorithm must focus on a region of interest

of the aggregate to yield a comparable distribution. For this purpose, edges that are internal to the aggregate must be detected, potentially through an iterative method that is limited to the pixels representing the aggregate, combining multi-level thresholding followed by edge detection. Internal edges have been previously considered in the context of CHT algorithms, but the proposed procedures resulted in noisy edge maps characterized by missing edges [111, 130]. The comparison of our algorithm with a CHT-based algorithm for primary particle detection has shown that a more realistic median primary particle size can be obtained by the former, an observation most probably associated with a lower sensitivity to the lower diameter bound. In addition, our algorithm constrains the selection of final candidate circles to the region represented by the aggregate.

5.6 Conclusion

In this work, we have proposed an automatic soot primary particle detection and measurement algorithm. It uses the binary edge map of a soot aggregate as an input, which is generated from the binary mask of an aggregate's TEM micrograph following a manual thresholding operation. The score S_c is used to select the best candidate circles from the preliminary list while the quality parameter f_c provides an intuitive metric to quantify the fit between the detected circle and the edge map. The performance of the algorithm was assessed using three soot aggregate datasets acquired in a 1D unstrained diffusion flame, where the median of the detected monomer diameter distribution was observed to increase in tandem with the freestream equivalence ratio. Soot obtained from polymer matrix composites burning in a cone calorimeter revealed a larger median diameter compared to the diffusion flame, highlighting the performance of the algorithm at detecting subtle differences in particle sizes across two drastically different sources of combustion particulates. Compared to a manual measurement, the algorithm underestimates the mode of the particle size distribution because it focuses exclusively on the monomers present around the edge of the aggregate, as demonstrated through the definition of a non-dimensional distance parameter f_{dist} , which captures the location of the measured/detected soot monomer in relation to the centroid and the edge of the aggregate. The definition of f_{dist} is a first attempt at understanding whether soot monomers are preferentially found at specific distances between the centroid and the edge of the

aggregate depending on their size. It enabled us to determine that for a specific flame, regions of the aggregate exploited by manual and automatic detection are distinct. The proposed algorithm was also shown to perform better than a CHT-based algorithm designed for the automated detection of primary particles, namely by yielding a more realistic median primary particle diameter and by constraining the detection to the regions of the image representing soot aggregates.

CHAPTER 6 ARTICLE 2: SPATIALLY RESOLVED MORPHOLOGY OF SOOT AGGREGATES IN A ONE-DIMENSIONAL UNSTRAINED METHANE/OXYGEN DIFFUSION FLAME

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ABSTRACT Using an experimental configuration characterized by a one-dimensional reaction zone, the formation of soot is decoupled from complex fluid mechanics and long soot residence times can be obtained. We characterize the morphology of soot aggregates as a function of position within the unstrained soot layer. Four flames of increasing freestream equivalence ratio are considered. Numerical simulations are performed to obtain the flame temperatures, chemical structure and particle residence times. In three flames, the collected soot samples reveal the ubiquitous coexistence of isolated primary particles and soot aggregates throughout the entire thickness of the soot layer. The size of isolated primary particles follow a log-normal distribution and are considerably smaller than the primary particles included in aggregates, whose size is normally distributed. The morphological parameters such as the primary particle diameter, the number of particles per aggregate, the maximum aggregate length, the overlap coefficient, and the fractal dimension are strongly and positively correlated with the freestream fuel concentration. The aggregates from the high equivalence ratio flame begin with a high fractal dimension which decreases when approaching the flame sheet, whereas those from the low equivalence ratio flame initially have a low fractal dimension that increases progressively. The simulated flame structure reveals that soot is accompanied by important levels of acetylene but scarce levels of atomic hydrogen. Soot has been collected at locations characterized by an adiabatic temperature below the critical soot inception temperature of 1250K, with the upstream edge of the visible soot layer (fuel-rich edge) typically characterized by temperatures between 750K and 1100K for the flames considered herein.

Keywords – soot, morphology, soot monomer, primary particle, image processing, fractal dimension, flame structure, size distribution.

6.1 Introduction

The current energy demands are fulfilled in majority by fossil fuel combustion [156, 157] for electricity generation [158, 159], transportation [160, 161], and industrial sectors [162]. In addition, from an economic perspective, the use of fossil fuels as an energy source is still more advantageous compared to available low-carbon energy sources [156, 157, 163]. Most combustion processes as currently implemented, from internal combustion engines to thermal power plants, result in the emission of solid particulates which are detrimental to health [23, 164, 165] and the environment [165, 166]. The ubiquitous presence and important magnitude of combustion processes surrounding us is cause for concern and justifies the implementation of stringent emissions limits and the deployment of a sustained research effort to minimize emissions.

Soot is an air pollutant common to all sectors heavily reliant on hydrocarbon combustion [167]. It is an aggregate of carbon particles resulting from incomplete combustion and is characterized by the crowding of quasi-spherical primary particles into clusters. This particulate effluent presents adverse effects on the efficiency and structural integrity of mechanical components [29] involved in combustion devices, such as internal combustion engines [168] and gas turbines [169]. The complexity inherent to the soot formation mechanisms makes the task of numerically predicting soot-related quantities very difficult [100]. Indeed, the accurate prediction of the soot yield in experimental and practical combustion applications is often confined in a narrow range of the combustion parameter space. The accuracy of soot prediction models in terms of soot yield is often limited to a specific fuel-oxidizer pair, in a narrow range of equivalence ratios, where they have been calibrated against experimental data [100]. Moreover, these models often cannot give information on the morphology of soot [170], which is of primordial importance for the estimation of the radiation heat transfer [171] and thus, for the measurement of soot volume fraction using laser diagnostics [172]. Indeed, the transfer of heat depends on the radiation emitting boundaries of the soot particles. The limited knowledge of soot morphology also affects the prediction of the

soot growth and oxidation rates [100] and toxicity [173], which are functions of the surface area of soot exposed to growth/oxidizing chemical species and adsorbing media, respectively.

We present an experimental investigation focused on the detailed characterization of the morphology of soot particles acquired in a highly controlled, simple, and readily modelled combustion environment; a 1D unstrained diffusion flame. The morphology of soot particles is mapped as a function of position in the burner throughout their evolution from inception until burnout within the combustion domain. Such a simple combustion environment is conducive to investigate the combustion parameters at play in the soot formation/destruction mechanism, and their effect on the size of primary particles and aggregates, as well as on the fractal dimension of the latter. In the literature, the experimental configurations typically used for this purpose, such as co-flow and counter-flow diffusion flames, make it more difficult to link a specific soot particle to the precise conditions it was exposed to since its inception. Consequently, the relative importance of the physical and chemical phenomena involved is challenging to assess due to their strong coupling with the flow field. The experimental configuration used in this work is characterized by a strictly unidimensional flow field throughout the reaction zone. As a result, fluid mechanics effects are limited to changes in the residence time of the reactants and of the soot particles formed in the reaction zone. In addition, the absence of flame stretch and strain ensures that coalescence and coagulation are only minimally affected by physical mechanisms pertaining to the non-uniformity of the flow field. The resulting diffusion flame allows the observation of the thermochemical evolution of soot particles from the onset of the luminous soot region until the high-temperature oxidation region, thus permitting the study of the complete high temperature history of soot.

6.2 Experimental Methods

6.2.1 Burner

The burner used here, presented in detail in previous work [49], is characterized by two square arrays of needles spaced 2.5 mm apart and arranged in an opposed jet configuration. The burner was developed to study thermal diffusive instabilities [152] and to validate models for the stability

of unstretched flames [174]. Needles carrying the exhaust gases are staggered between the reactant injection needles. Each injection array supplies one of the reactants, namely methane or oxygen. In the experiments presented here, the combustion products are forced to exhaust on the oxidizer side, as indicated by the black arrows in Figure 6.1. As a result, the bulk flow in the burner is forced in a single direction, from the fuel inlet (bottom) towards the oxidizer inlet (top), requiring the oxidizer to counter-diffuse to the reaction zone. Both reactant streams may be diluted with carbon dioxide to control the transport properties of the mixture and reduce the adiabatic flame temperature. The flow rate of the reactants and the inert dilution gas are set using mass flow controllers (Teledyne Hastings HFC-202).

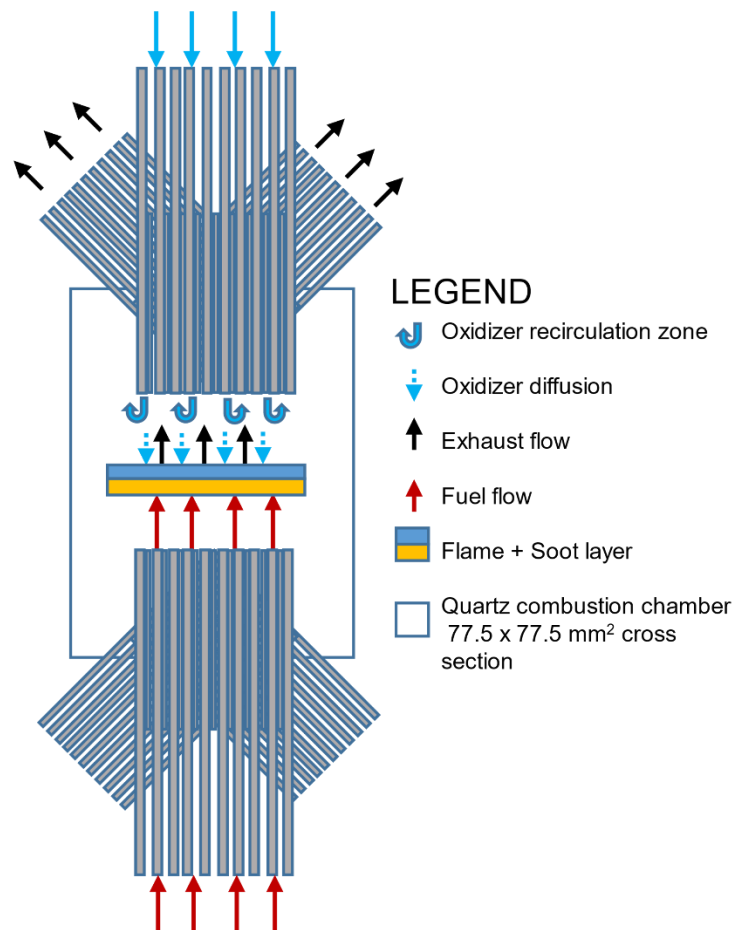


Figure 6.1: Qualitative representation of the flow field in the combustion chamber

6.2.2 Soot Sampling

The soot sampling apparatus consists of a microcontroller-operated linear servomotor (Faulhaber MCLM-3006-SRS and Faulhaber QuickShaft LM1247-100-11), a TEM nickel grid (Ted Pella #01844N-F) coated with a layer of carbon on both faces and a TEM grid holder mounted on a steel wire. The wire is connected to the linear motor which inserts the grid in the visible soot layer through one of the unused exhaust needles in the bottom array, for a residence time between 100 and 200 ms [130, 153]. This range for the optimal residence time has been determined experimentally to ensure that soot particles have enough time to travel to the grid through thermophoresis while also ensuring that the structural integrity of the grid is preserved. Moreover, irrespective of the flame sampled, the concentration of particles on the grid should not be large enough to suggest aggregation on the sampling substrate. Care has been taken to avoid vibrations in the wire as it reaches the sampling position, to eliminate potential sampling by impaction and the resulting modifications in the morphology of the sampled soot. The insertion of the grid in the flame is recorded by a high-speed camera (Photron Mini AX200) at a sampling rate of 1000 frames per second. The illumination necessary for the high acquisition frequency of the camera is supplied by a fiber optic lamp (ThorLabs OSL2 Fiber Illuminator). The video of the grid insertion allows the accurate determination of the residence time and the sampling location relative to the injection needle arrays and the edges of the visible soot layer. In Figure 5.2 below, a schematic representation of the experimental soot sampling apparatus is shown.

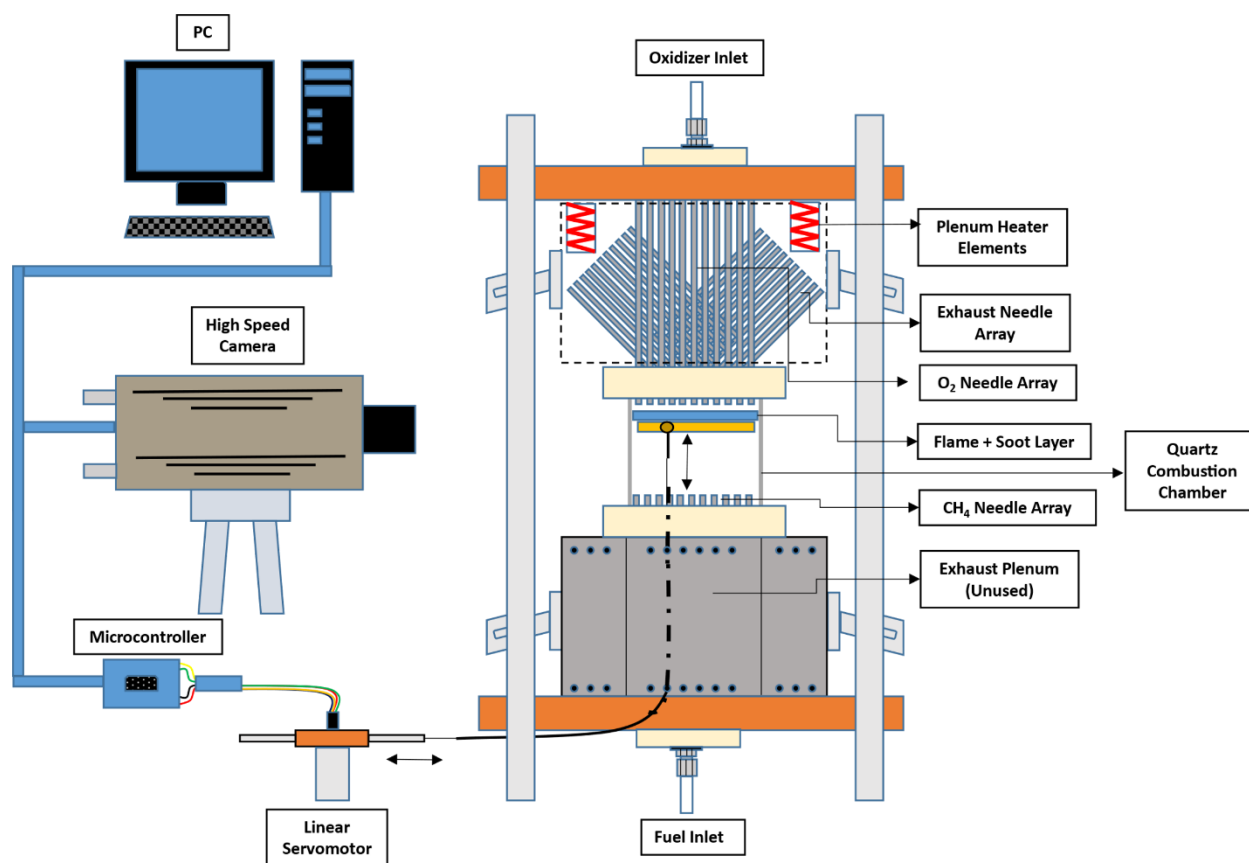


Figure 6.2: Schematic representation of the experimental setup

6.2.3 Transmission Electron Microscope Imaging

The sampling disks are imaged on a transmission electron microscope (JEOL JEM-2100F) at an accelerating voltage of 200 KeV. The 8-bit grayscale micrographs are 2048 x 2048 pixels. The Cartesian coordinate system used to navigate on the TEM grid exploits the number of holes on the grid, namely 32 holes along its 3 mm diameter. The origin is located at the center of the grid; the x and y coordinates span from $-16 < x, y < 16$ and since the centerline of the grid does not contain holes, the origin is taken at location (1, 1). For example, a soot aggregate recorded at the position (1, 16) on grid is located at the topmost point on the grid, immediately to the right of the centerline. All soot aggregates imaged within the same grid hole are assigned with the same location label,

therefore the relative position within a hole is not measured. Since we are interested in the morphological evolution of the soot aggregates along the vertical axis of the burner, the region viewed on the TEM is limited to the vertical array of holes adjacent to this axis of the TEM grid. For each sampling substrate, a total five equidistant locations are analyzed. The list of holes imaged typically consists of coordinates (1, 16), (1, 8), (1, 1), (1, -8), (1, -16) or any adjacent holes around those listed if the former are damaged. Figure 6.3 below depicts the coordinate system and the typical grid positions investigated in this morphological soot study.

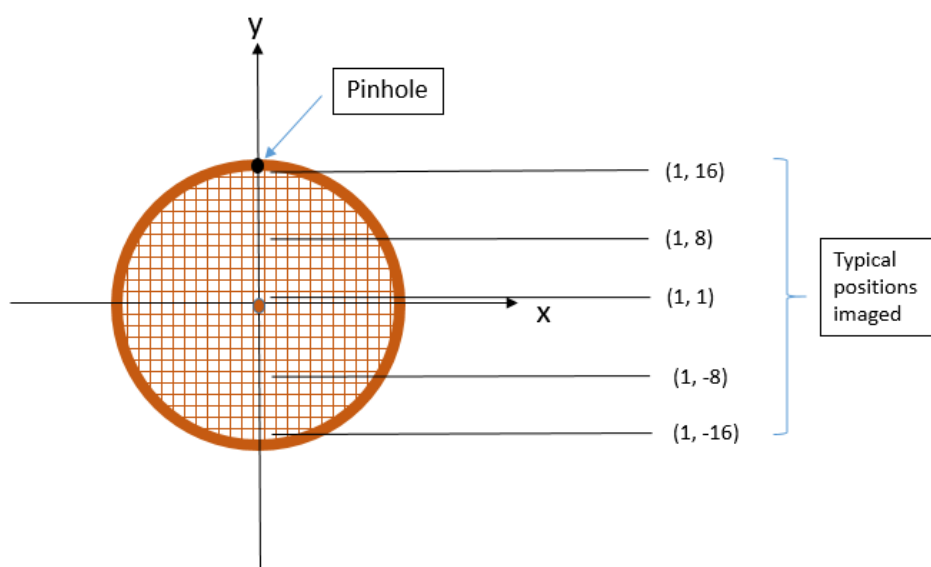


Figure 6.3: Representation of a TEM grid, showing the coordinate system and typical locations imaged

6.2.4 Numerical simulations of combustion

To obtain the temperature and concentration profiles through the combustion chamber, a numerical model is built using the Cantera open-source chemical kinetics framework and the GRI-Mech 3.0 chemical mechanism. GRI-Mech 3.0 is designed and optimized for the simulation of the combustion of natural gas and methane, ensuring a reliable modelling of the temperature and concentration profiles in non sooting flames [51]. However, it does not include heavy hydrocarbon condensation and particulate formation mechanisms that would be needed to account for effects

due to the presence of soot. The results from this model are therefore carefully interpreted when experimental observations reveal the presence of soot.

The numerical simulations rely on boundary conditions measured experimentally for the inlet fuel temperature and reactive species/products at both ends of the burner. A major challenge with the burner geometry used here is that the boundary condition at the counter-diffusing inlet (i.e. oxidizer stream - top side) cannot be known only from the properties of the gas stream supplied to the reaction chamber. Due to the mixing of combustion products with the incoming oxidizer stream shown in Figure 6.1, the effective boundary condition deviates from the freestream oxidizer concentration. As such, the molar fractions of oxygen (X_{O_2}), carbon dioxide (X_{CO_2}) and water (X_{H_2O}) must be measured at the counter-diffusing inlet. This is done here using a quadrupole mass spectrometer (MKS Cirrus), to identify the extent of the one-dimensional diffusion region between the reaction zone and the needle array of the counter-diffusing inlet. The calibration of the mass spectrometer has been carried out by generating 55 mixtures of the three gases in the concentration ranges of interest for the application, following the procedure described by Robert [145]. The inlet fuel temperature is measured at the center of the exit plane of the fuel injection array by a K-type thermocouple. The sensitivity of the numerical simulations to the inlet fuel temperature $T_{f,0}$ was verified as negligible and therefore, a value of 500K was used for all flames while a value of 1250K is used at the opposite end of the combustion chamber, namely $T_{o,0}$. In Table 6.1, the values for the boundary conditions used in the numerical simulations are listed. For each flame, the distance d_{ms} below the oxidizer inlet plane is given for the sampling point of the mass spectrometer. The simulated length of the combustion chamber spans from the fuel inlet until the sampling point of the mass spectrometer, namely $(50 - d_{ms})$ mm. The remainder of the combustion chamber length, immediately downstream of the oxidizer inlet is characterized by 3d flow and is referred to as the injection layer. Figure 6.4 shows images of the combustion chamber with the investigated flames, where the mass spectrometer sampling location is indicated by a pale red dot above the flames.

Table 6.1: Boundary conditions for temperature, molar fractions of the major combustion species used in numerical simulations

Flame ID	$T_{f,0}$ (K)	$T_{o,0}$ (K)	X_{O_2}	X_{CO_2}	X_{H_2O}	d_{ms} (mm)
f_1	500	1250	0.2168	0.6539	0.1293	3.1
f_2	500	1250	0.2301	0.6433	0.1266	2.1
f_3	500	1250	0.2455	0.6315	0.1230	1.8
f_4	500	1250	0.2467	0.6032	0.1501	1.6

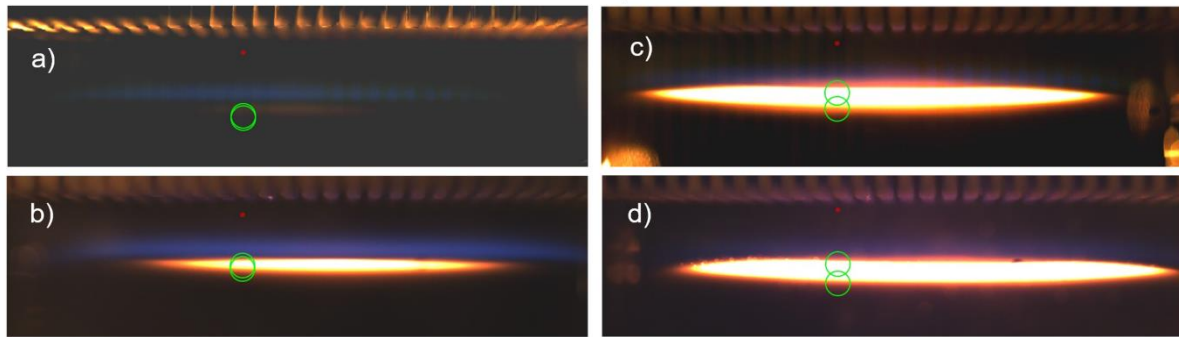


Figure 6.4: Soot and mass spectrometer sampling locations for flames a) f_1 , b) f_2 , c) f_3 and d) f_4 .

The green circles represent the sampling location of the TEM substrates, and the red dots represent the tip of the capillary inlet of the mass spectrometer

The simulation domain consists of an axisymmetric flow with two opposed inlets, where one inlet can also act as an outlet. The cross-sectional area of the inlets as well as that of the outlet are set to the physical values of the burner. The axisymmetric flow domain ensures that the flow moves in a unidimensional fashion and the inlet and exhaust flow rates are set to those used in the

experiments. Since the physical combustion domain contains a region characterized by three-dimensional flow immediately downstream of the counter-diffusing inlet, the geometry of the simulation domain is set to only contain the unidimensional flow portion of the burner.

6.3 Image processing methodology

The morphological characterization of soot consists of measuring the mean primary particle diameter D_p , the mean overlap coefficient C_{ov} , the aggregate projected area A_a and the aggregate maximum length L_{max} from TEM micrographs of soot. By using these parameters into established correlations [16], it is possible to obtain the remaining morphological parameters, namely the number of primary particles per aggregate N_p , the fractal dimension D_{fL} and the fractal pre-factor k_L . Upon inspecting the acquired soot micrographs, we have observed that alongside the soot aggregates, many isolated soot monomers are also present on the sampling grids. As such, we will investigate the morphological evolution of soot aggregates but also the size evolution of the isolated primary particles as a function of the flame parameters and of the location within the burner.

6.3.1 Isolated primary particles

The locations of the isolated soot monomers are detected by manually applying a global threshold on a TEM micrograph until all the features of interest appear on the resulting binary mask. Unwanted features (i.e. smaller or larger than the target features) are eliminated from the binary mask by applying two manual constraints using an image processing program developed in-house using Matlab; one for the minimum and one for the maximum number of pixels composing the target features. The resulting binary image contains all the isolated primary particles, but not at their true size due to the global threshold applied previously. Indeed, background intensity variation within the micrograph area and non-uniformity in the thickness of the carbon film makes the accurate segmentation of features practically impossible using a single threshold value. In Figure 6.5, a TEM micrograph depicting a large number of isolated primary particles is shown, which also contains three large soot aggregates that are eliminated from this initial analysis. With the locations of the isolated primary particles determined by the operations above, a region of

interest encompassing each feature and its immediate surrounding is taken and an automatic Otsu threshold is applied to this region. This operation determines the optimal threshold value based on the local contrast and ensures that the true size of features is retained in the binarized version of the micrograph. Since the isolated primary particles are exclusively quasi-spherical, their size is then determined programmatically using the *regionprops* function, from which the primary particle aspect ratio can also be deduced. The large number of isolated primary particles present on micrographs justifies the calculation of the surface density of soot monomers on the sampling substrate. This parameter can serve as a proxy for the in-flame number concentration and help interpret the morphological evolution of aggregates. For a micrograph, the surface density is calculated by dividing the number of isolated primary particles by the total area over which these particles are spread. For a flame, the average surface density at each location in the burner is calculated by summing the surface density of all micrographs from a given location and dividing it by the total number of micrographs taken at that location.

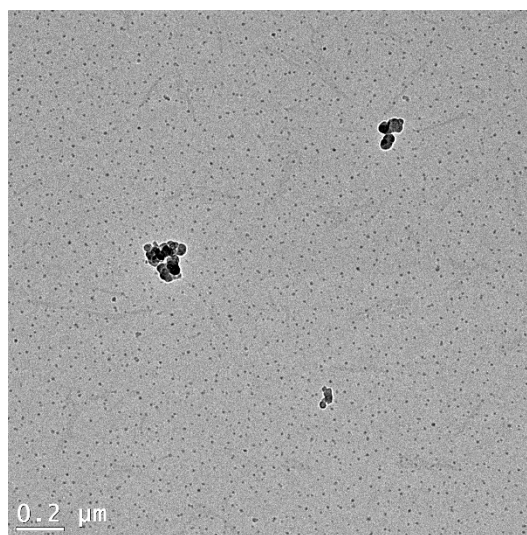


Figure 6.5: TEM micrograph of soot from flame f_4 clearly depicting the large number of isolated primary particles.

6.3.2 Soot aggregates

The segmentation of soot aggregates from TEM micrographs begins with the cropping of each individual aggregate and the application of a 4x4 median filter for noise removal; the kernel size is independent of the micrograph's magnification level. A manual threshold is applied to the median-filtered micrograph starting at a value of 0.6 using increments of 0.01, followed by visual inspection of the outcome. Our criteria of a good threshold value are to 1) simultaneously maximize the number of aggregate pixels while 2) isolating the aggregate from the background. Once an acceptable threshold value is determined, a binary mask is generated by conserving only the region characterizing the aggregate and eliminating any irrelevant artifacts. From the binary mask of the aggregate, the projected area of the aggregate a_a is obtained by counting the number of pixels composing the aggregate. For each flame, the mean primary particle diameter, D_p , is determined by manually measuring 50 primary particles from the micrographs at every location and calculating the mean value. The results presented here are therefore manually measured with the primary particle diameters and the center coordinates of the respective monomers used to estimate the mean overlap coefficient C_{ov} for all the overlapping pairs of measured soot monomers. Since the values of k_a and α_a required for estimating the number of primary particles per aggregate N_p depend on the value of C_{ov} , the data points given by Brasil et al. [16] are fitted to obtain the relationship between C_{ov} and k_a and α_a . With this relationship, one can estimate k_a and α_a using the mean value of C_{ov} obtained previously for a given flame and location prior to calculating N_p using the following relationship:

$$N_p = k_a \left(\frac{A_a}{A_p} \right)^{\alpha_a}$$

In addition to the above-mentioned parameters, the aggregate maximum length L_{max} is also measured, ultimately leading to the determination of the fractal dimension D_{fL} and the fractal pre-factor k_L for each location of each flame through the following equation:

$$N_p = k_L \left(\frac{L_{max}}{D_p} \right)^{D_{fL}}$$

The parameters enumerated above are assigned to the flame and to the location within the burner from which they originate, hence allowing to track the morphological evolution of the soot aggregates within a flame with respect to location within the burner.

6.4 Results and discussion

In this section, we present the morphological results obtained for the four flames labeled as f_1 , f_2 , f_3 and f_4 . In *Table 6.2*, the operating parameters of the burner are given, namely the freestream molar fractions of fuel and oxidizer (X_{CH_4} , X_{O_2}) along with fuel and oxidizer stream flow rates (VFR_F , VFR_O). The numerical non-dimensional flame locations (Z_f), flame temperatures (T_{flame}), freestream fuel equivalence ratio (ϕ_∞), the experimental visible soot layer thickness (t_{soot}) and the number of aggregates (N_{agg}) analyzed for each flame are also included therein. The non-dimensional flame location Z_f is calculated as the ratio of the distance from the fuel inlet to the flame location and the length of the combustion domain, namely $(50 - d_{ms})$ mm. The sampling substrate residence times (τ_{samp}) are given for each of the two substrates used to sample each flame.

Table 6.2: Summary of the burner operating conditions and the resulting flame soot related parameters

Flame ID	X_{CH_4}/X_{O_2}	VFR_F/VFR_O (SLPM)	Z_f	T_{flame} ($^{\circ}K$)	ϕ_∞	t_{soot} (mm)	τ_{samp} (ms)	N_{agg}
f_1	35/100	7/7	0.976	1946	3.019	1.68	146/121	N/A
f_2	40/90	7/7	0.977	2008	3.389	2.64	163/169	93
f_3	45/90	7/7	0.978	2069	3.733	3.57	147/173	1557
f_4	50/100	7/7	0.979	2075	4.320	3.64	150/191	816

We first analyze the size distributions of the isolated primary particles and the primary particles composing aggregates irrespective of the sampling location, followed by the numerical results of the pertinent soot formation/oxidation species, the temperature evolution in the combustion domain and the simulated residence time of particles depending on their size. Subsequently, we investigate the evolution of the morphology of soot as a function of the non-dimensional location within the combustion domain. More specifically, for aggregates, the diameter and number of primary particles per aggregate, the aggregate maximum length, the overlap coefficient, the fractal dimension, and fractal pre-factor are presented. As specified in Table 6.2, for flame f_1 , no aggregates have been observed on the sampling substrates, as this flame is close to the visible soot onset. On the contrary, in flame f_4 , soot aggregates were very large, and some could be seen glowing with the naked eye, as shown in Figure 6.6 below.

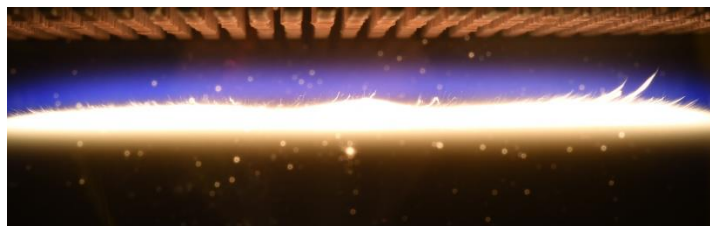


Figure 6.6: Macroscopic soot appearing as streaks at the interface between the soot layer and the blue flame. The white dots of various sizes are dust particles on the quartz combustion chamber reflecting light and should be disregarded.

6.4.1 Size distributions of isolated and aggregate primary particles

In Figure 6.7, the size distribution of the isolated primary particles is shown for each flame, irrespective of the location in the soot layer where they have been sampled. The upper bounds of the size distributions have been truncated at 50 nm. Each histogram is composed of two datasets, namely the major and the minor axis length, divided into 51 bins. For both datasets, a lognormal fit has been performed with a 95% confidence interval; the intervals for the mean and the standard deviation are given Table 6.3 in units of nm for the major axis dataset only. The mean aspect ratio of the particles is determined using the center of the mean interval of the major and minor axes.

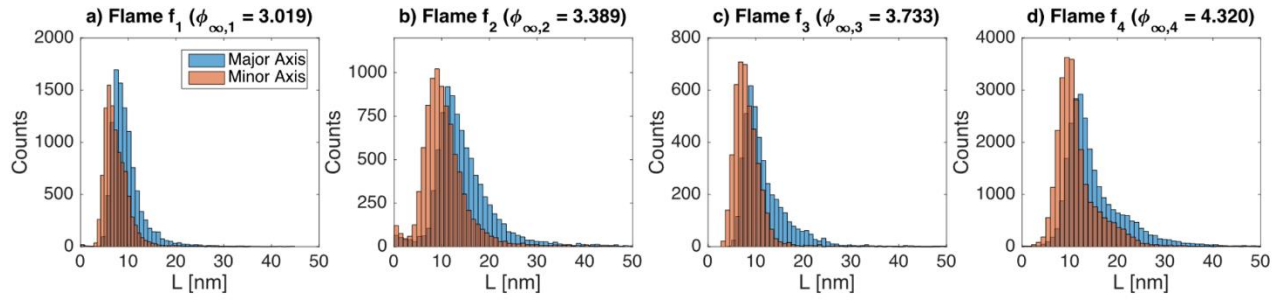


Figure 6.7: Size distributions of the isolated primary particles for flames f_1 , f_2 , f_3 and f_4

Table 6.3: Lognormal distribution fit parameters for the major axis length and mean aspect ratio for flames f_1 , f_2 , f_3 and f_4

Flame ID	Major axis length				Aspect ratio
	μ [nm] (95% CI)		σ [nm] (95% CI)		
f_1	9.0755	9.1921	1.3847	1.3973	1.2917
f_2	13.1277	13.4118	1.6574	1.6827	1.4067
f_3	10.9590	11.1851	1.4017	1.4221	1.4139
f_4	14.1124	14.2411	1.4468	1.4561	1.3162

Isolated primary particles sampled from these flames are characterized by a mean size ranging from 9 to 14.25 nm, indicating that they are at the inception stage of their lifecycle. As expected from the monotonically increasing freestream fuel equivalence ratio ϕ_∞ and the rising flame temperatures, the mean primary particle size also increases monotonically, except for flame f_3 . The aspect ratio of these particles indicates that they are not perfectly spherical. It is uncertain whether

the aspect ratio is a result of uneven growth from the one-dimensional species and temperature gradient evolution or whether it is due to the particles still being in a liquid state and deforming upon landing on the sampling grid.

With regards to the size of primary particles found in aggregates, shown in Figure 6.8, we note that they are much larger than the isolated ones and their size is also positively linked with the freestream fuel equivalence ratio ϕ_{∞} . The size distribution also becomes wider with increasing equivalence ratio, as outlined by the standard deviation given in Table 6.4.

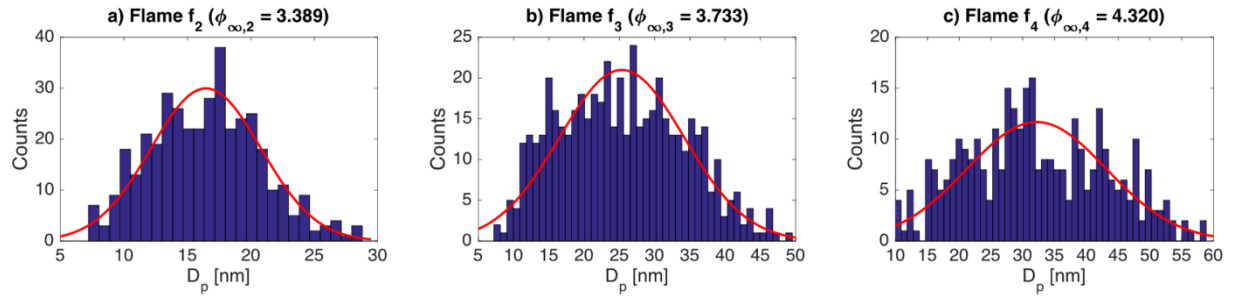


Figure 6.8: Size distributions for the primary particles composing the aggregates for the flames where aggregates were observed, namely flames f_2 , f_3 and f_4

Table 6.4: Normal distribution fit parameters for the primary particle diameter composing aggregates for flames f_2 , f_3 and f_4

Flame ID	Primary particle diameter D_p			
	μ [nm] (95% CI)		σ [nm] (95% CI)	
f_2	16.031	16.8910	4.0508	4.6612
f_3	24.5800	26.1250	8.3222	9.4170
f_4	31.0096	33.3676	10.1813	11.8541

The primary particles found in aggregates for flame f_4 have a mean diameter of about 32.2 nm while the isolated primary particles from the same flame exhibit a mean major axis length of approximately 14.25 nm. This size difference can be explained by an increased propensity for surface growth species to condense on a large aggregate compared to a small isolated primary particle. Indeed, outside the coalescence regime where soot has solidified through dehydrogenation, a large aggregate irradiates a considerable amount of heat and as a result becomes colder than the surrounding gas. This cold region, shown in Figure 6.9 as a dark halo surrounding large soot particles, may be ideal for condensation of growth species but can also act as a sink for small liquid-like inception particles that are drawn towards the colder aggregate by thermophoresis, given the strong temperature gradient.

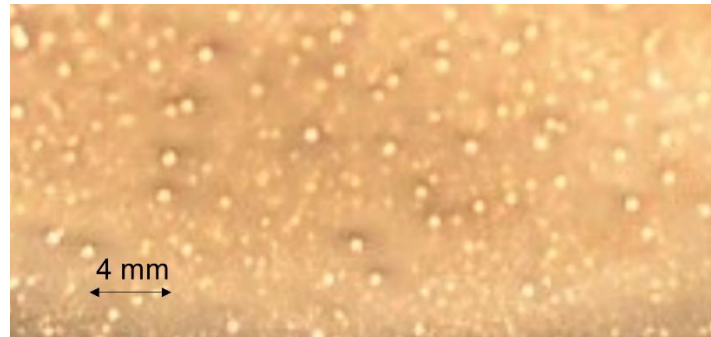


Figure 6.9: Macroscopic soot particles surrounded by a dark halo, effectively highlighting a scavenging of the surrounding smaller soot particles through thermophoresis. Image taken from below the flame sheet.

6.4.2 Chemical structure and adiabatic flame temperature in the soot formation region

In Figure 6.10, the evolution of the main species responsible for soot formation and oxidation, calculated numerically using Cantera, is shown as a function of the distance above the fuel inlet for the four flames considered in this study. These species consist of C_2H_2 , H_2 and O_2 ; the first is responsible for the inception and growth of soot while the second, if dissociated into its radical form H^+ , is a prerequisite for acetylene addition during growth [175]. Other oxidative species are not shown because their molar fractions are negligible, namely in the 10^{-11} range. Similarly, the molar fraction of H^+ is in the 10^{-9} range and has also been omitted from the plots. The lower edge of the visible soot layer (i.e. fuel-rich edge) observed experimentally has been aligned for all flames using flame f_1 as a reference and is indicated by a black dotted line, while the upper edge of the soot layer is given by a color-coded dotted line for each flame. The top edge of the soot layers for flames f_3 and f_4 coincide but the dotted lines have been plotted side by side for clarity.

We observe that for all flames, the production of C_2H_2 begins modestly upstream of the visible soot layer and increases exponentially within it. At the top edge of the soot layer, the molar fraction of C_2H_2 correlates with the freestream fuel equivalence ratio ϕ_∞ except for flame f_4 , which exhibits a molar fraction slightly larger than flame f_1 . For all the flames, the molar fraction of acetylene reaches a peak just downstream of the soot layer, followed by a rapid and complete consumption.

Acetylene is therefore available throughout the entire thickness of the visible soot layer for particle inception and surface growth. The molar fraction of methane is also positively correlated with the freestream equivalence ratio, but it has a decreasing trend as it approaches the soot layer. Again, its complete consumption occurs just downstream of the visible soot layer. Since methane is the source of soot precursor molecules, the increase observed across these flames explains the monotonic rise in primary soot particle diameters.

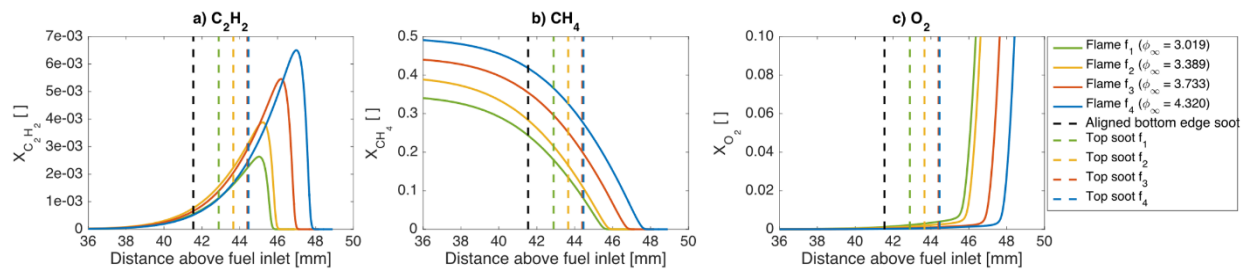


Figure 6.10: Evolution of the molar fraction of a) acetylene, b) methane and c) molecular oxygen as a function of the distance above the fuel inlet for flames f_1 , f_2 , f_3 and f_4

The growth of primary particles and aggregates is also controlled by the diffusion of O_2 into the soot growth region; higher O_2 molar fractions can be observed for flames characterized by lower values of ϕ_∞ , namely f_1 and f_2 . As such, the absence of O_2 penetration into the soot growth region of flames f_3 and f_4 partially explains the relatively larger primary particles.

The evolution of the major species' molar fractions, namely water (H_2O), carbon dioxide (CO_2) along with molecular hydrogen (H_2) with respect to the distance above the fuel inlet for flames f_1 , f_2 , f_3 and f_4 is shown in Figure 6.11. The concentration of water within the soot layer is practically equal for flames f_1 and f_2 but as ϕ_∞ is increased, the concentration decreases for the two richer flames. A peak in water concentration is attained just above the soot layer in all cases, positively correlated with ϕ_∞ . With regards to the molar fraction of carbon dioxide, it also decreases monotonically within the soot layer as ϕ_∞ is increased. Similar to water, the molar fraction of molecular hydrogen increases within the soot layer, attaining a peak just downstream from it,

followed by a rapid consumption. As ϕ_∞ is increased, larger concentrations of molecular hydrogen can be found within the soot layer. It has been previously reported that these three species act as a soot suppressors through thermal, dilutive, and chemical mechanisms [176-179]. We have made a similar observation whereby the relatively lower water and carbon dioxide concentrations in the soot formation region yields larger particles.

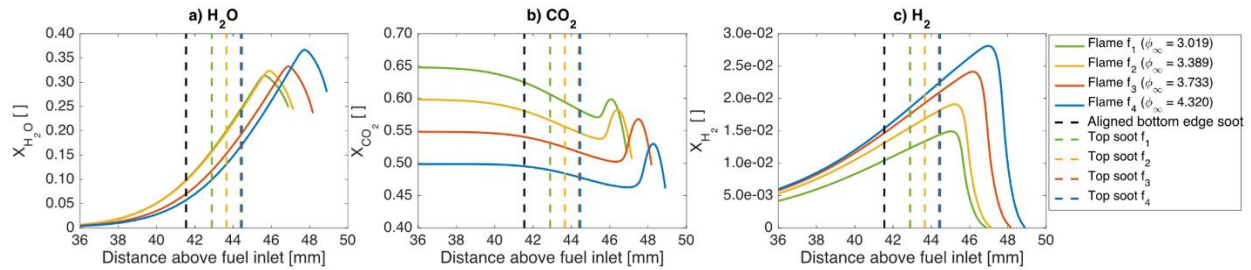


Figure 6.11: Evolution of the molar fraction of a) water, b) carbon dioxide and c) molecular hydrogen as a function of the distance from the fuel inlet for flames f_1 , f_2 , f_3 and f_4

The evolution of the temperature within the combustion domain is given in Figure 6.12. As expected, the temperature attains a peak downstream of the visible soot layer, in increasing order of ϕ_∞ . At the entrance into the visible soot layer and throughout it, the trend is reversed such that the lowest ϕ_∞ yields the highest temperature. Although a minimum adiabatic flame temperature of approximately 1250 K has been previously reported as a requirement for soot formation [44, 180], we observe that none of our flames get close to this value at the upstream edge of the soot layer, while soot was observed for all of them at this location. We reiterate that the numerical model yields an adiabatic flame temperature and does not account for the formation of soot particles or any associated physical phenomena such as heat radiation by soot. In practice, the radiation of heat from the soot particles warms the upstream flow, potentially enhancing soot formation earlier in the combustion domain.

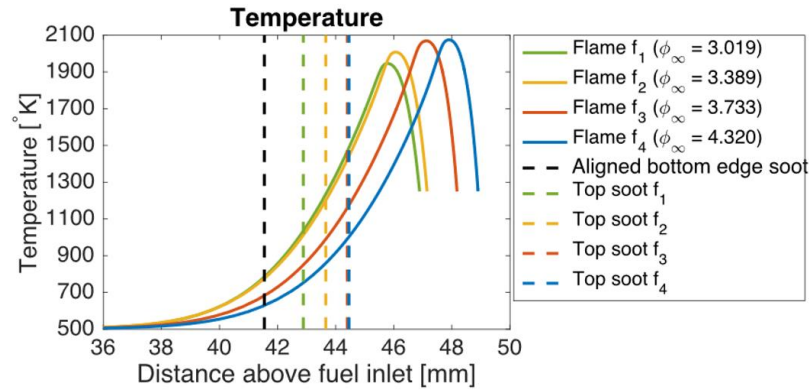


Figure 6.12: Evolution of the temperature as a function of the distance from the fuel inlet for flames f_1 , f_2 , f_3 and f_4

6.4.3 Flame temperature gradient and particle residence time

The temperature gradient in the soot formation region is critical as it controls the particle residence time through the thermophoretic force exerted on them. In Figure 6.13, the temperature gradient is given as a function of the distance from the fuel inlet. Similar to the evolution of temperature within the soot layer, the temperature gradient is inversely related to ϕ_∞ , such that the leanest flame exhibits the largest temperature gradient and vice versa. However, the peak temperature gradient, which occurs downstream of the soot layer, is directly related with the equivalence ratio.

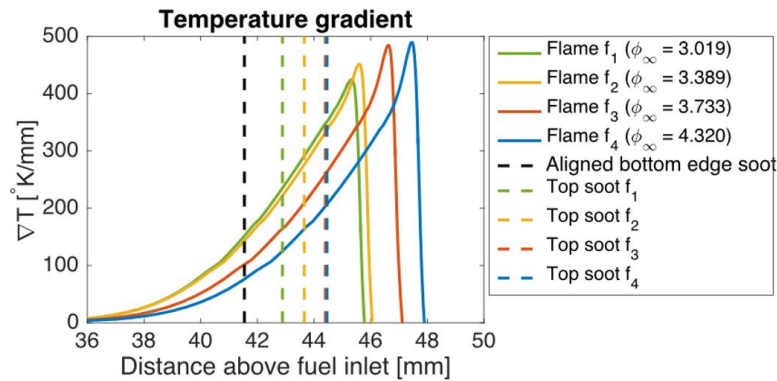


Figure 6.13: Evolution of the temperature gradient as a function of the distance from the fuel inlet for flames f_1 , f_2 , f_3 and f_4

To illustrate the effect of a steep temperature gradient on the particle residence time, three different particle sizes have been considered, namely 50 nm, 500 nm and 5 μm , and their cumulative residence time τ_{res} has been calculated. Given that a monotonic trend was observed for the particle residence time across the four flames, only two extreme cases (i.e. f_1 and f_4) are shown in *Figure 6.14*, for clarity. The transport model assumes a constant spherical shape and size for the particles, that are followed throughout the entire length of the combustion chamber while assuming that the forces acting on them consist of gravity, drag and the thermophoretic force. For particles in the range 50-500 nm, the difference in τ_{res} is negligible, hence the one curve representing the entire size range.

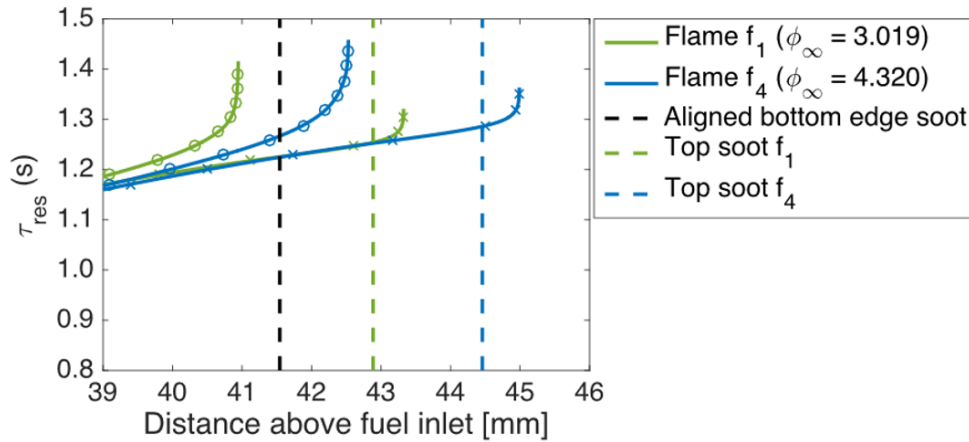


Figure 6.14: Numerical estimation of the cumulative residence time of particles as a function of the distance from the fuel inlet, for the two extreme flames (i.e. f_1 shown in green and f_4 in blue).

Three particle sizes are plotted for each flame, namely 50 - 500 nm indicated by (o) and 5 μm indicated by (x).

As expected, for a given flame, smaller particles (i.e. 50-500 nm) are subjected longer residence times than larger ones (i.e. 5 μm), due to the relative strength of the thermophoretic force compared to the drag force. We can also note that in all flames, the former particles can be held at constant location for roughly 100 milliseconds, conducive to surface growth. Moreover, a threshold particle size of about 5 μm is required for penetration into the visible soot layer for flame f_1 and below 50 nm for flame f_4 . This can seem counterintuitive at first since the temperature gradient of flame f_4

is larger. However, the soot layer is considerably thicker and hence, the temperature gradient at the upstream edge of the soot layer is smaller. Generally, given equal particle sizes, a hotter flame tends to trap particles within the temperature gradient for a longer time than its colder counterpart, hence explaining the large aggregate sizes observed in the former. It is important to reemphasize that the model does not consider particle growth, therefore the residence time of the particles is only calculated until they become stationary due to a balance between the thermophoretic and drag forces. In reality, these particles may never be truly stationary and their residence time in the soot growth region depends on their size evolution and the temperature gradient.

6.4.4 Morphological evolution of the isolated primary particles

Figure 6.15 shows the evolution of the isolated particle's major axis $L_{\text{major axis}}$, the particle surface density SD and the aspect ratio AR as a function of the distance above the fuel inlet. The error bars represent the standard error of the mean (SEM).

For all flames, throughout the entire sampled domain, no clear dependence can be noted with regards to the evolution of the isolated primary particles as a function of the distance from the fuel inlet. Nonetheless, the average size of these particles (i.e. all locations combined) appears to be somewhat positively correlated with the freestream fuel equivalence ratio. Close to the soot layer, an increase in the particle size of flame f_1 can be noted, accompanied by a drastic decrease in the particle surface density deposited on the sampling substrate. Similarly, the decrease in surface density of the heavily sooting flame f_4 upon entering the soot layer is followed by an important increase in particle size.

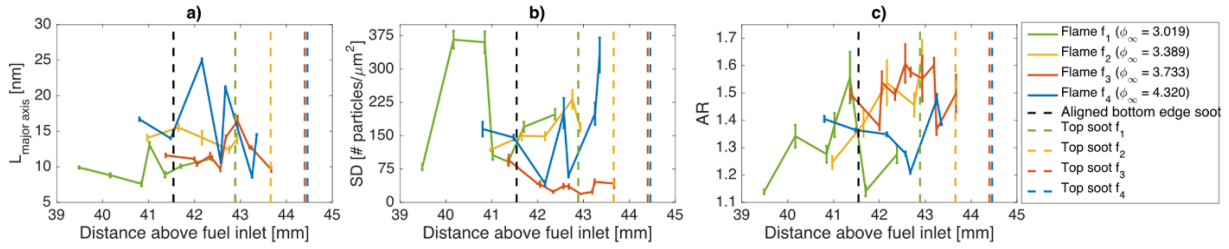


Figure 6.15: Evolution of the inception particle a) the major axis length, b) surface density on the sampling substrate and c) aspect ratio as a function of the distance from the fuel inlet for flames f_1 , f_2 , f_3 and f_4

For the surface density, a positive dependence on the location can be observed within most of the visible soot layer, highlighting a regime of important particle inception, except for flame f_3 . On the contrary, the monotonic decrease in surface density for flame f_3 is associated with an increase in particle size, despite the particles being relatively small compared to the other flames. Moreover, the aspect ratio of these particles is the largest almost throughout the entire visible soot layer, thus enhancing the particle collision efficiency. Globally, it is interesting to observe the same behavior in the three richer flames, namely the increase and convergence of the aspect ratio towards comparable values of about 1.4 - 1.6.

6.4.5 Morphological evolution of aggregates

6.4.5.1 Mean primary particle diameter D_p

In Figure 6.16, the evolution of the mean primary particle diameter is shown as a function of the distance above the fuel inlet for flames f_2 , f_3 and f_4 . The error bars represent the standard error of the mean. As previously, the lower edge of the visible soot layer (i.e. fuel-rich edge) has been aligned for all three flames but using f_2 as the reference since no aggregates have been observed for flame f_1 .

We note that prior to entering the visible soot layer, the mean primary particle diameter is comparable for the three flames, namely around 17 nm, despite the difference in ϕ_∞ between the flames. As the aggregates approach the lower edge of the visible soot layer, the primary particles

of flame f_4 double in diameter f_2 exhibits only a slight increase to under 20 nm and f_1 remains constant. It is also interesting to observe the divergence in the mean primary particle diameter of the different flames as the aggregates travel through the visible soot layer, explained by a combination of increasing particle residence time inside the soot layer but also the relative propensity of the flames to synthesize soot precursors (i.e. molar fraction of C_2H_2 in Figure 6.10a). The peak primary particle diameter is reached within the visible soot layer, at 19 nm, 31 nm, and 38 nm, in order of increasing ϕ_∞ , respectively. Moreover, despite approaching the region characterized by stoichiometric combustion, the mean primary particle diameter maintains its magnitude remarkably well, at a value close to its respective global maximum for each flame.

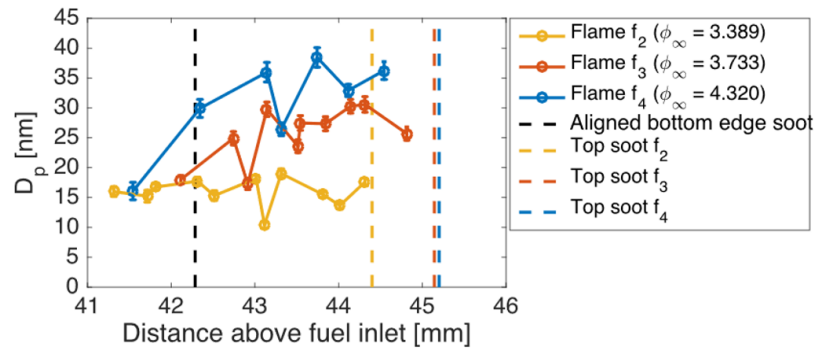


Figure 6.16: Evolution of the aggregate primary particle diameter as a function of the distance from the fuel inlet for flames f_2 , f_3 and f_4

6.4.5.2 Mean number of primary particles per aggregate N_p , aggregate maximum length L_{max} and overlap coefficient C_{ov}

The evolution of the mean number of primary particles per aggregate N_p (semi-logarithmic plot), the aggregate maximum length L_{max} and the two-dimensional overlap coefficient C_{ov} as a function of the distance above the fuel inlet is shown in Figure 6.17. By analyzing the two former parameters simultaneously, one can determine whether the growth of an aggregate (i.e. increase in N_p) occurs preferentially along an axis, thereby increasing L_{max} . For example, if N_p increases while

$L_{\max}$ decreases, it entails that the aggregate loses particles that are along the $L_{\max}$ axis while gaining more particles along an axis orthogonal to $L_{\max}$.

Once again, we observe that prior to entering the visible soot layer, all flames yield aggregates of comparable dimensions, as highlighted by $L_{\max}$ and N_p . For flames f_2 and f_3 , N_p remains modest, assuming values between 3 and 30 particles, while $L_{\max}$ ranges between 38 and 116 nm. The former flame exhibits a sharp increase in N_p from 8 to 25 particles, but also in C_{ov} from 0 to 0.6 just prior to the downstream edge of the visible soot layer, suggesting that the strong thermophoretic force near the flame promotes particle aggregation but also surface growth/sintering of particles inside the aggregates [181]. In the case of flame f_3 , despite the nearly constant value of N_p and $L_{\max}$ throughout, the value of C_{ov} assumes a peak of approximately 0.45 almost halfway into the visible soot layer followed by a monotonic dip to an overlap coefficient of zero at the farthest point sampled. Flame f_4 shows a similar trend in C_{ov} to that of flame f_3 except for a recovery of the overlap coefficient following the sharp decrease. In all flames, for most sampling intervals, the number of primary particles per aggregate N_p (i.e. its logarithm) correlates well with the aggregate maximum length $L_{\max}$, suggesting that when primary particles coagulate onto (or detach from) an aggregate, the coagulation/detachment generally occurs at the extremities of the $L_{\max}$ axis of the aggregate.

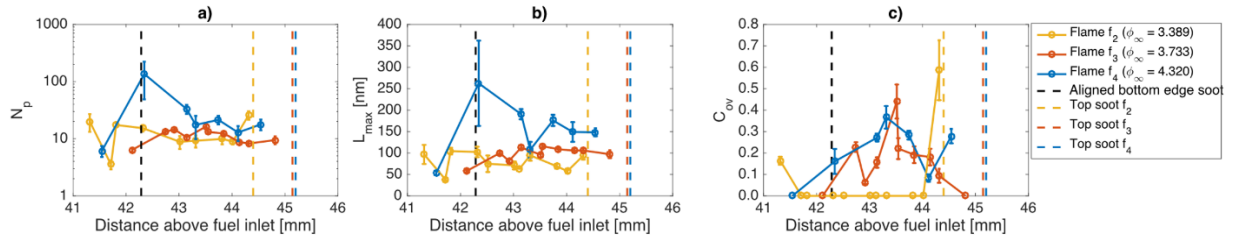


Figure 6.17: Evolution of a) the number of primary particles per aggregate, b) the aggregate maximum length and c) the overlap coefficient as a function of the distance from the fuel inlet for flames f_2 , f_3 and f_4

6.4.5.3 Fractal dimension D_{fL} and fractal pre-factor k_L

In *Figure 6.18a*, the evolution of the fractal dimension D_{fL} as a function of the distance above the fuel inlet is shown for flames f_2 , f_3 and f_4 . Flame f_2 is characterized by a D_{fL} value of approximately 1.6 upstream of the visible soot layer, followed by a sharp drop until the upstream edge of the soot layer and a subsequent increase to a peak value of 1.7 halfway into it. In the case of flame f_3 , D_{fL} increases from 1.2 to 1.6 upon entering the visible soot layer and reaches a plateau characterized by modest oscillations in magnitude. The fractal dimension of flame f_4 begins at a value of 2.2, drops rapidly to 1.8 upon entering the soot layer and remains rather constant within it for most sampling intervals. It is interesting to note that the fractal dimension of the richest flame mostly decreases while passing through the visible soot layer while the other two flames exhibit a more complex fractal evolution. Generally, most of the change in D_{fL} occurs in the region near the upstream edge of the soot layer (i.e. inception region), and to a lesser extent due to oxidation when the aggregates approach the downstream edge of the soot layer. Another interesting observation is the convergence to a narrow D_{fL} range of 1.5 - 1.7 for all three flames as the aggregates approach the oxidation zone. In *Figure 6.18b*, the fractal pre-factor k_L is shown as a function of the distance above the fuel inlet since it complements the fractal dimension in describing the morphology of the aggregates, especially in the low N_p limit where it can distinguish between aggregates formed by the diffusion-limited-aggregation (DLA) mechanism or the diffusion-limited-cluster-aggregation (DLCA) mechanism [182]. The former refers to aggregates formed as a result of particle-cluster collisions while the latter pertains to the aggregation of a cluster with another cluster. The value of k_L is typically larger for DLCA aggregates compared to those formed by DLA, implying that they tend to be composed of a larger number of primary particles given an equal fractal dimension D_{fL} and normalized length (i.e. L_{max}/D_p).

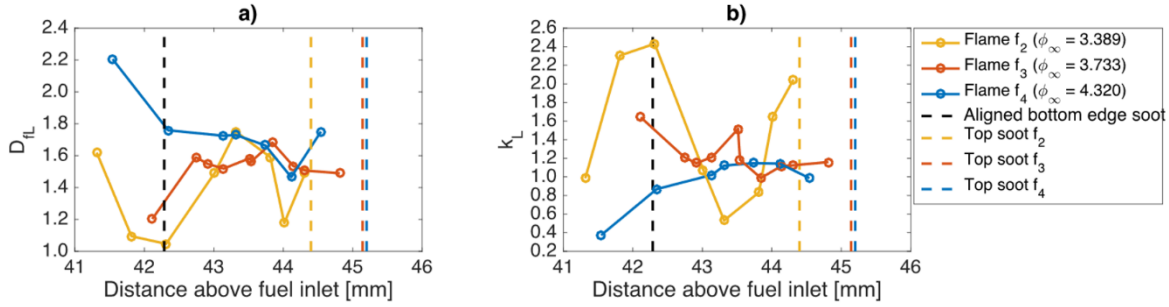


Figure 6.18: Evolution of the fractal dimension and the fractal pre-factor as a function of the non-dimensional location in the burner for flames f_2 , f_3 and f_4

6.5 General discussion

Prior to the appearance of aggregates, isolated primary particles have been observed in all the flames, at all the sampled locations. As these particles approach the visible soot layer, a decrease in size can be noted, likely attributed to their carbonization (i.e. dehydrogenation) due to the absorption of heat from the soot layer. For the leanest flame (i.e. f_1), the surface density of sampled particles is the largest among all the flames, suggesting the highest in-flame soot particle number density. As previously reported, lightly sooting flames exhibit large number concentrations that quickly collapse due to coagulation and/or coalescence [183], as observed here. Given that the concentration decrease is associated with an increase in the isolated particle diameter, and that no aggregates have been observed at this location, we can confidently affirm that this regime is characterized by coalescence. Flame f_4 also reaches a comparable surface density but only halfway through the visible soot layer. However, the ensuing decrease was not associated with a growth of the isolated particles, hence outlining a regime where coalescence has ceased. As these particles travelled through the soot layer, their aspect ratio was noted to converge towards values of 1.4 - 1.6 for the three richer flames, possibly due to a preferential deposition of surface growth species along a specific axis.

In all the investigated flames, the earliest aggregates were composed of primary particles of practically equal diameters (i.e. approximately 17 nm) irrespective of the equivalence ratio of the flames, Given that the surface density of isolated particles close to the upstream edge of the soot

layer was also comparable across all flames, this observation suggests that at this concentration, the critical particle size for efficient particle collision is around 17 nm. Although previous studies reported a critical soot formation temperature of 1250 K [180, 184], in our burner, the upstream edge of the visible soot layer is characterized by lower temperatures, namely between 600 K for flame f_4 and 750 K for flame f_1 . However, the numerical model used for the temperature and flame structure calculation does not account for particle formation, which effectively irradiates heat upstream and promotes early formation of soot. It has previously been shown that the onset of soot can be controlled by decreasing the strain rate, hence increasing the residence time [44, 185]. As a result, the long residence times achievable in this burner through the alignment and opposition of the thermophoretic and drag forces may be responsible for the formation of soot at these low temperatures.

As the aggregates travel through the soot layer, the primary particle diameter grows. Even at the farthest sampled locations, no significant decrease in particle size was observed. This may indicate that the particles were subjected to a strong heat treatment (i.e. annealing) [186] given the long residence times, such that the level of surface porosity and thus the oxidizer penetration is very low, resulting in a slow and mainly surface-based particle oxidation [187]. The primary particle diameter of 40 nm observed in our burner are far larger than those observed in other experimental configurations with methane as fuel [14, 188, 189].

From a morphological standpoint, similar trends have been observed between evolution of the number of primary particles per aggregate and the aggregate maximum length in the burner, suggesting that particles preferentially coagulate along the $L_{\max}$ axis of the aggregate, thereby implying an alignment between this axis and the direction of the temperature gradient. With regards to the evolution of the overlap coefficient of flames f_3 and f_4 , it is characterized by a sharp rise followed by an important decrease, potentially associated with surface growth and oxidation, respectively. The decrease in C_{ov} may also be a consequence of the heat treatment, resulting in a slight rearrangement of primary particles within the aggregates.

The fractal dimension of the youngest aggregates is clearly dependent on the equivalence ratio and thus on the local abundance in soot precursors. Scarcity of such species gives aggregates with a

fractal dimension of ~ 1.6 , which grow subsequently as observed for flame f_2 , whereas the abundance of precursors yields aggregates that fill the projection plane very well (i.e. $D_{fL} \sim 2.2$) but erode as they approach the soot layer, as highlighted by a decreasing trend in D_{fL} throughout the soot layer. Halfway into the soot layer, the aggregates converge towards a comparable fractal dimension of 1.6 - 1.8. In the case of flame f_2 , the relatively lower concentration of precursors results in aggregates whose fractal dimension constantly evolves throughout the entire soot formation region. It is interesting to note that the fractal dimension of the leaner flames (i.e. f_2 and f_3) presents an overall increasing trend while for the opposite is true for the richest flame (i.e. f_4). This observation is likely associated with the steeper temperature gradient of flame f_4 , effectively coagulating particles earlier upstream. Through our spatially resolved study, we have been able to observe aggregates with very small and very large D_{fL} values in distant regions of the flames, namely 1.2 and 2.2, that are uncommon encounters in the literature for experimental flames. Nevertheless, upon aging, the aggregates reach fractal dimensions of 1.6 - 1.8 that agree quite well with reported values [77, 188, 190].

It is important to mention that upon viewing the sampling grids on the TEM, we observed that in the case of flame f_4 , the largest aggregates landed on the metal strips (Figure 6.19), exposing only their extremities to the carbon film portion of the sampling grid (i.e. the ‘transparent’ TEM grid holes). This is due to a larger temperature gradient between the flame environment and the bars of the grid, compared to the naked carbon film. As such, it represents a limitation of the sampling methodology beyond a threshold aggregate size, and an alternative will be investigated in a future work, where the thermal properties of the sampling substrate are homogenous across the sampling area.

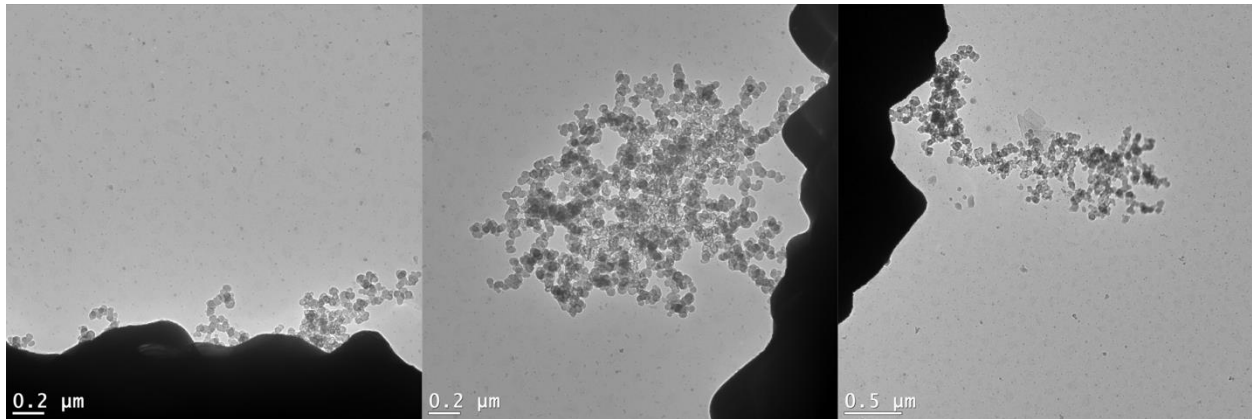


Figure 6.19: TEM micrographs depicting soot aggregates landing preferentially on the metal portion of the sampling substrate. This behavior was observed only for flame Φ_4 where aggregates are considerably larger compared to the other flames

6.6 Conclusion

In this study, we have investigated the morphological evolution of soot in an unstretched and unstrained one-dimensional diffusion burner, where long residence times can be obtained through the alignment and opposition between the thermophoretic force and the drag force exerted on particles. These long residence time result in macroscopic aggregates visible to the naked eye. Four flames characterized by an increasing freestream fuel equivalence ratio ϕ_∞ were analyzed and their chemical structure within the soot formation region was obtained through numerical simulations. We have observed that the morphological complexity of soot is highly correlated with freestream fuel equivalence ratio. As such, for a lean flame, the fractal dimension begins at a low value and increases as the aggregates travel through the combustion domain and vice versa. Upon reaching deep enough inside the soot layer, the fractal dimension converges towards values of around 1.7, irrespective of the flame equivalence ratio. The primary particle diameter found in aggregates scales with the equivalence ratio as well, ranging from 17 nm for the leanest flame in which aggregates have been captured (i.e. f_2) to about 40 nm in the richest flame. Moreover, the coexistence of inception particles with aggregates throughout the entire soot formation region has also been observed in all flames. This unique spatially resolved soot morphology dataset obtained in a simple flame configuration can provide an excellent means for the validation of models

targeting the formation of soot in conditions where complexities induced by the flow field are absent due to the one-dimensional nature of the flow in the reaction zone.

**CHAPTER 7 ARTICLE 3: EFFECT OF CELLULOSE NANOFIBERS,
MELAMINE POLYPHOSPHATE AND ACTIVATED CARBON ON THE
FLAMMABILITY AND PARTICULATE EMISSION OF
THERMOPLASTIC POLYURETHANE**

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ABSTRACT Cellulose, a promising bio-sourced reinforcement, is increasingly used in polymer-matrix composites but its effect on the reaction-to-fire of the resulting composite is uncertain, as it contains oxygen but can also contribute to the formation of insulating char. Here, we investigate the effect of FiloCell® cellulose nanofibers (CNF) addition and interactions between cellulose and two fire retardants; melamine polyphosphate (MPP) and activated carbon (AC) using a 2¹3² full factorial design. Samples are fabricated by compression molding and the reaction-to-fire is evaluated by measuring the heat release rate in a cone calorimeter. In addition to smoke obscuration measurements, particulate matter is analysed in the fire plume using a scanning mobility particle sizer. The results show that the endothermic degradation of the FiloCell® cellulose can contribute a fire-retardant effect and lower the amount of MPP required to limit the total heat of combustion of the composite. However, FiloCell® addition increases smoke production measured through opacity, with size distributions shifted towards larger sizes. MPP decreases the particle size and the smoke opacity. The results therefore reveal that the addition of FiloCell® cellulose fibers in composites can degrade some fire properties but improve others. The careful dosing of fire retardants can mitigate these detrimental effects while maintaining the advantages provided by the FiloCell®; increased mechanical properties and decreased total heat of combustion.

Keywords – Cellulose, FiloCell, composite, fire retardant, reaction-to-fire, particulate matter, smoke, natural fiber, cone calorimetry

7.1 Introduction

The use of plant-derived reinforcement in polymer matrix composites (PMCs) is a promising avenue to decrease the carbon footprint of the polymer industry [191] while producing material systems with desirable mechanical properties [192, 193]. Their lower density compared to traditional fiber reinforcements results in overall lighter composites, contributing to significant fuel savings during their useful life [191]. A prime candidate for bio-sourced reinforcement is cellulose, a polymer of glucose and the main constituent of wood. It is the most abundant naturally occurring biopolymer. It can be harvested from different sources and processed into different forms; nanocrystals, nanofibers, and microfibrils, each having a different morphology, physical and chemical properties [194, 195]. Cellulose is particularly appealing as an engineering material due to its excellent mechanical properties [195]. For instance, the interlaminar shear and flexural strengths of glass reinforced polymer composites are increased by 30% and 43%, respectively, when using cellulose nanocrystals as sizing for glass fibers [196]. Cellulose nanofibers (CNF) can also be used as the main reinforcement in select polymer matrices, yielding PMCs with competitive mechanical properties [197]. These properties arise from the extraordinary high aspect ratio of CNF, their high surface area, and their surface chemistry [192, 195, 196, 198].

However, CNFs are highly flammable and include oxygen in their chemical composition, namely $(C_6H_{10}O_5)_n$, requiring research for applications where the reaction-to-fire is an issue. The thermal degradation of cellulose starts at temperatures of approximately 300 °C, and results in the outgassing of volatile combustible species [199, 200]. Moreover, the presence of oxygen in the molecular structure may lead to a decrease of the limiting oxygen index (LOI), effectively enabling a sustained combustion of the PMC in oxygen-depleted atmospheres [201]. These flammability concerns can partially be offset by fire-suppressing mechanisms observed in pure samples, such as the endothermic dehydration and decomposition [199-202] and the production of insulating char [200, 202, 203], delaying the thermal degradation onset [194] and lowering the rate of pyrolysis in PMCs containing cellulose [193]. These mechanisms are similar to those brought by several

fire-retardants (FR) and therefore fire retardance in cellulose-containing PMCs should carefully consider synergistic effects. For instance, the incorporation of CNF in a polymer could improve mechanical properties while reducing the amount of fire retardants needed to achieve an acceptable reaction-to-fire.

Inducing intumescence in a polymer exposed to fire is one of the most common approaches to improve its reaction-to-fire. However, this often requires a large fraction of active agents in the formulation [204, 205], adversely affecting mechanical properties. For instance, melamine polyphosphate (MPP) is typically mixed in large concentrations in polymers to achieve a significant reduction in flammability [206]. It acts by releasing phosphoric acid and a gaseous blowing agent (i.e. melamine); the former enhances the carbonization of the polymer matrix while the latter expands the thermally-degraded layer of the matrix, forming a protective porous char. A synergy between MPP and CNF is likely, as even dilute inorganic acids have been observed to hydrolyze cellulose [207], yielding glucose that can then contribute to char formation [208, 209].

To further accelerate the formation of this protective char layer on the exposed surface of PMCs, activated carbon (AC) can be added to render the material more opaque to infrared radiation [210]. Activated carbon is a mainly amorphous carbon structure that has been chemically treated to yield very large pore volume and internal surface area through the selective gasification of carbon atoms [211, 212]. Again, synergies are expected with the presence of CNF as a result of percolation [195]. AC and thermally degraded CNF result in a network of carbon whose high thermal conductivity can contribute to dissipate the heat crossing the protective char layer. Moreover, these carbon-based materials can also adsorb a considerable quantity of gaseous hydrocarbons [213]. As a result, the rapid carbonization of a thin surface layer shields the virgin matrix below and partially impedes the diffusion of oxygen and the outgassing of combustible species.

The present work investigates these potential synergistic effects between the proposed CNF reinforcement (FiloCell®) and the fire retardants incorporated into a thermoplastic polyurethane (TPU) polymer matrix, through quantitative measurements of flammability metrics, smoke opacity and particulate matter size distributions. As such, when a CNF reinforcement is present in the PMC, it is limited to a single loading level; an approach sufficient to achieve the scope of

identifying the synergies between the reinforcement and the additives. The fire-retardant additives considered are MPP and AC, owing to their complementary mode of action with CNF, as highlighted above. The polymer matrix of the PMCs studied is polyether-based TPU, a choice justified by its processing characteristics compatible for compounding with CNF and its relatively poor flammability performance, despite its ubiquitous use. In polyurethane material systems, mechanical properties [194, 214] and chemical resistance [215] can be tuned to cover a wide range of applications, from the midsoles of running shoes to various automotive components such as engine mounts and seats cushions. Medical devices also use polyurethanes due to their exceptional biocompatibility [194, 215]. However, the combustion of polyurethanes results in a strong flame accompanied by burning drips, thick smoke, with a practically inexistent char yield [204, 216].

Although the main purpose of incorporating cellulosic material in a PMC is the improvement of the mechanical properties, this aspect will not be addressed here as it was previously covered in the literature [192, 194, 217]. For instance, at a loading of 16.5 wt.% in TPU, CNF results in a five-fold and a 30-fold increase in the strength and stiffness of the PMC, respectively [192]. To investigate the interactions between CNF, MPP and AC, flammability response variables derived from the ISO-5660 standard are used. Information on the particulate matter size distributions emitted by the burning composites is also obtained from a scanning mobility particle sizer (SMPS). The significant interactions observed on the response variables are identified through an ANOVA, with the most important effects discussed to highlight underlying mechanisms.

7.2 Experimental

7.2.1 Materials

The raw materials used in the TPU/CNF composite system consist of Laripur 5260EG polyether-based thermoplastic polyurethane supplied in pellet form by COIM and FiloCell® cellulose nanofibers supplied by Kruger Biomaterials. The neat TPU polymer is characterized by a density of 1.15g/cm³ and a melt volume rate (MVR) of 10-20 cm³/10min at a temperature of 210 °C. FiloCell® is characterized by a fiber diameter ranging between 30 and 500 nm, a fiber length between 100 and 2000 µm and a density of 1.45 g/cm³. Additionally, the manufacturing process

of FiloCell® comprises a proprietary surface treatment to enhance the dispersion by preventing filament aggregation [218]. The thermogravimetric data of FiloCell® indicates a degradation onset temperature of 220 °C [219], which suggests that the surface treatment does not significantly affect its thermo-chemical properties in relation to raw cellulose, for which the typical degradation onset temperature is between 200 and 300 °C [199, 200, 220]. The fire-retardant additives melamine polyphosphate (Melapur 200) and activated carbon (NORIT SA 2) were obtained in powder form by BASF and Acros Organics. The particle size of these powders is $D_{98} = 25 \mu\text{m}$ for melamine polyphosphate and $D_{90} = 135 \mu\text{m}$ for activated carbon.

7.2.2 Manufacturing process

The neat TPU pellets were dried at a temperature of 195 °F for 3 hours according to the manufacturer's specification, in an oven under vacuum. The cellulose was dried simultaneously with the TPU pellets. Following the TPU/CNF compounding in the twin-screw extruder using a proprietary compounding methodology (Kruger Biomaterials), the TPU/CNF pellets were stored in sealed bags, in a well-ventilated room, away from sunlight exposure. Prior to compounding the neat TPU and the TPU/CNF pellets with the fire-retardant additives, the pellets were dried again under the conditions described above. The fire retardants, namely MPP and AC, were stored in sealed jars inside cabinets, away from sunlight and have not been dried prior to compounding. The test specimens have been stored in sealed bags. The last heat treatment that the specimens received was during the compression molding process. The specimens were exposed to the laboratory atmosphere for a few hours before the test, during preparation and measurements steps.

The compounding of the TPU pellets with the cellulose filaments was performed in a twin-screw extruder, to achieve a 15 wt.% cellulose loading. The 3.85 mm diameter extrudate was cut into 2.20 mm long pellets. The incorporation of the fire-retardant additives into the material system was performed in a 60 mL batch mixer (Haake Rheomix OS). The mixing temperature and speed were set to 190 °C and 50 rpm, respectively, for a total mixing duration of 7 minutes. The resulting fire-retardant material systems were compression-molded in a hot press using a 200 x 200 x 3 mm stainless-steel mold. To prevent the polymer from sticking to the plates, a 0.5 mm-thick PTFE film was used between the plates and the mold. The compression cycle consisted of 17 minutes at a

temperature of 205 °C under 0.65 MPa of pressure, followed by a 5-minute cooling period at ambient plate temperature and 0.65 MPa of pressure. In Figure 7.1, a sample of five cone calorimeter specimens is shown, adequately representing the color range and surface topology of the entire test set. The ridges on the sample surface are due to deformations in the PTFE films used during compression molding and are less than 1mm high.

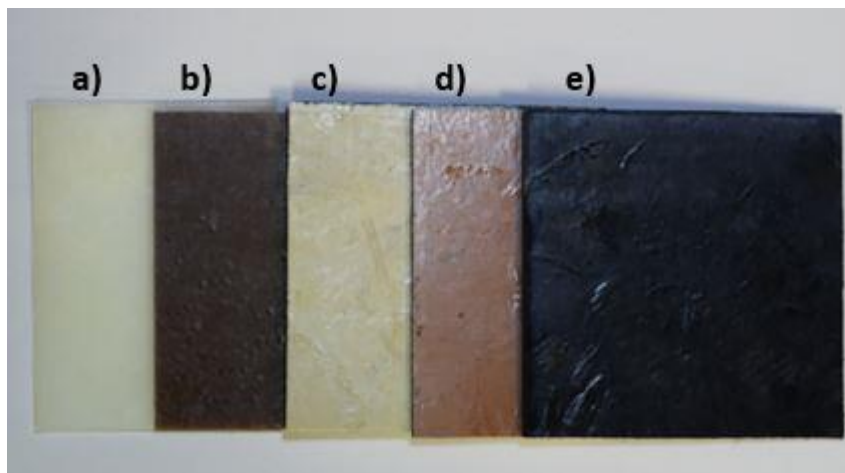


Figure 7.1: Five cone calorimeter sample specimens: a) neat TPU, b) TPU/15CNF, c) TPU/15MPP, d) TPU/15CNF/30MPP, e) TPU/15CNF/10AC

7.2.3 Cone Calorimeter

The flammability tests are performed in a cone calorimeter following the ISO-5660 test standard. The test specimens have nominal dimensions of 100 x 100 x 3 mm and are exposed to a radiant heat flux of 35 kW/m² in the horizontal orientation. The specimens are wrapped in aluminum foil and mounted in the standard specimen holder without any wire mesh. The heat release rate is calculated based only on the measurement of oxygen consumption.

7.2.4 Aerosol Sampling

The size distribution of particulate matter evolving from the burning specimens is measured using a scanning mobility particle sizer (SMPS), composed of an electrostatic classifier (TSI Model

3082) and a condensation particle counter (TSI Model 3775). A schematic representation of the aerosol sampling setup based on [221] is shown in the Figure 7.2 but with a single dilution stage.

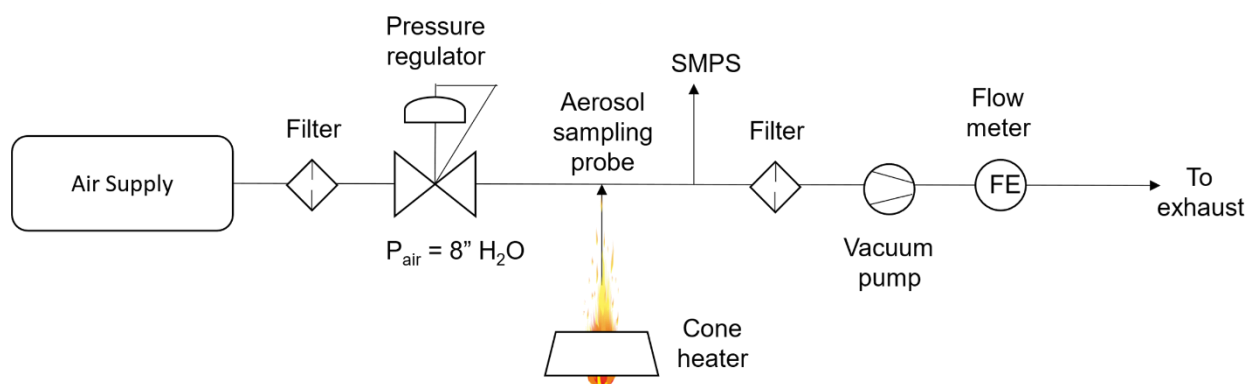


Figure 7.2: Schematic representation of the aerosol sampling system

The sampling of the aerosol is achieved using a probe composed of a 0.4 mm brass 3D printer nozzle mounted on a 1/4" OD steel tube. The probe continuously draws aerosol-ridden gas from the fire plume, 50 mm above the top hole of the cone heater and is connected to a dilution line fed with filtered compressed air. At the other end of the dilution line, a vacuum pump (Welch 2562B-01 B) ensures that the pressure at the sampling probe is below the atmospheric pressure. The aerosol sampling flow rate can be controlled by adjusting the air supply pressure. Given the performance curve of the vacuum pump, the highest dilution ratio for the setup (1:100) is achieved at an air supply pressure of 1990 Pa, which results in an aerosol flow rate of 0.4 liters/min through the sampling probe. The volumetric flow rate at the outlet of the vacuum pump is measured using a mass flow meter (Hastings HFC-203). The SMPS is connected in parallel on the dilution line and is operated with a sheath flow of 15 liters/min and an aerosol flow rate of 0.325 liters/min, resulting in a particle mobility diameter (d_m) spectrum between $6 < d_m < 240$ nm, divided into 150 size channels. For each scan, the SMPS integrates the number of particles at each size channel for a duration of 55 seconds. Including the instrument's purge time, each scan lasts a total of 76 seconds, immediately followed by the next scan. The data acquisition of the SMPS is stopped as soon as the heat release from the material ceases.

7.2.5 Design of experiments

A 2^13^2 full factorial design has been considered. The CNF factor is a two-level factor that captures whether cellulose nanofibers are present in the composite. If present, the CNF mass loading is equal to 15 wt.% with respect to the total mass of the composite (polymer plus fiber reinforcement only). The fire-retardant additives, namely melamine polyphosphate (MPP) and activated charcoal (AC) are present at three levels to capture any potential curvature in the response functions. The three levels for MPP and AC consist of 0, 15 and 30 parts per hundred of resin (phr) and 0, 5, 10 phr, respectively. For additives incorporated in neat polymer, the phr value of each is calculated with respect to the mass of the neat polymer while for the polymers reinforced with CNF, the phr value is calculated with respect to the mass of neat polymer and including CNF. The 2^13^2 full factorial design results in a total of 18 unique material treatment combinations and three replicates are tested for each.

7.3 ANOVA Response Variables

Statistically significant interactions between CNF, MPP and AC on the response variables characterizing flammability and smoke production are identified through an analysis of variance (ANOVA), followed by a general linear model fit. This type of analysis is comprehensive and accounts for the variance between test repetitions and across material treatments to identify significant effects of the additives on the response variables. The ANOVA plots discussed in this work are limited to those that show significant effects and the details pertaining to the ANOVA general linear model are given in the Supplemental Material section at the end of the manuscript. The main effect of each additive (CNF, MPP, AC) and the two-way interactions between any pair of additives, namely CNF x MPP, CNF x AC, MPP x AC) are considered. The details of the ANOVA, including P-values for the normality and equal variances' tests along with the F-value/P-value pair for the model terms, are presented in Table 7.3 and Table 7.4 in the Supplemental Material. In these tables, a summary of the analysis can be found for each response variable, where the terms marked in bold revealed a significant effect. Additionally, if a Box-Cox transformation was used to fulfill the ANOVA validity requirements for a response variable, the λ value is given

in the tables and the response variable is labeled with an asterisk (*). Plots of main and interaction effects show the evolution of response variables following changes in one or two term levels, respectively. Interaction effect plots include two (i.e. number of CNF levels) or three (i.e. number of MPP levels) trend line, each composed of three measurement points. The label of the first point represents the absolute value of the response variable at that point. For the remaining two points, the value labeled is the difference relative to the preceding point, quantitatively representing of the magnitude of the main and interaction effects.

The set of flammability response variables consists of the heat of combustion per unit of specimen area (H_c/A), the peak heat release rate per unit area (PHRR/ A^*) and the smoldering combustion component of the total heat released per unit area ($\%THR/A_{smold}$). The particulate matter response variables consist of the total smoke production in the flaming regime ($S_{A,flm}$), the time until peak smoke production in the flaming regime and in the smoldering combustion, respectively given by $t_{S,max,flm}$ and $t_{S,max,smold}$. Additionally, at the peak smoke production in the flaming and smoldering combustion regimes, the size of particulate matter is also investigated, namely $d_{p,max,burn}^*$ and $d_{p,max,smold}^*$. In Figure 7.3a, a burning specimen is shown under the radiant heater of the cone calorimeter. The raw data used to calculate these response variables consists of the evolution of the heat release rate, shown in Figure 7.3b for the 15CNF/15MPP/5AC material system.

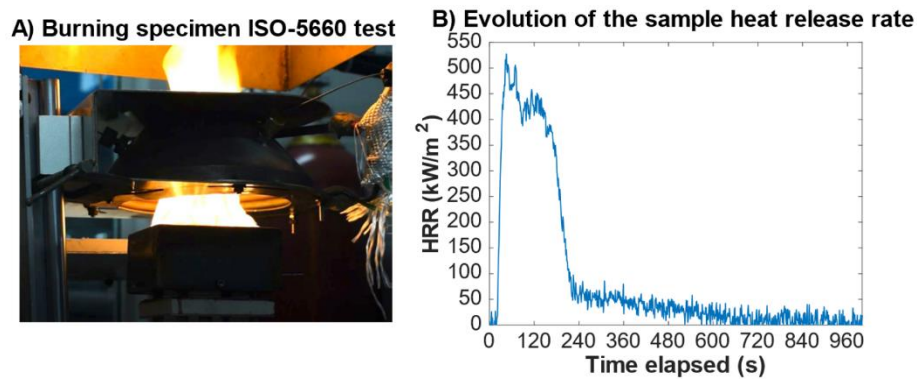


Figure 7.3: A) Photograph of a cone calorimeter test B) evolution of the heat release rate for the 15CNF/15MPP/5AC material system

The raw data pertaining to the smoke production and particulate matter size distributions is obtained from a laser obscuration measurement (i.e. smoke opacity) and a scanning mobility particle sizer, respectively. An example of each of these measurements is shown in Figure 7.4a and b for the 15CNF/15MPP/5AC material system.

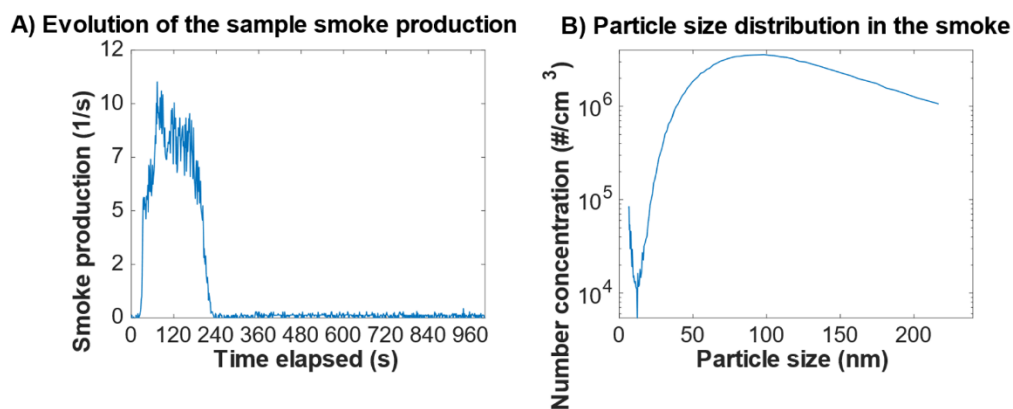


Figure 7.4: A) Smoke production and B) smoke particle size distribution for the 15CNF/15MPP/5AC material system

As an indication of the variability across the three samples tested for each material system, the mean (μ) and the standard deviation (σ) have been calculated for the various parameters measured in the cone calorimeter and are summarized in Table 7.1.

Table 7.1: Variability of the measured parameters in the cone calorimeter illustrated by calculating the mean (μ) and the standard deviation (σ) over 3 samples for each material system

Material system	Peak heat release rate μ (kW/m ²)	σ (kW/m ²)	Peak smoke prod. μ (1/s)	σ (1/s)	Percent residual mass μ (%)	σ (%)	Time to ignition μ (s)	σ (s)	Time to extinction μ (s)	σ (s)
OCNF/OMPP/OAC	700	117	10.8	0.7	6.00	1.84	49.0	3.3	290.8	38.4
OCNF/OMPP/5AC	912	77	13.0	2.2	0.91	0.90	35.1	4.7	293.8	1.3
OCNF/OMPP/10AC	1103	67	10.4	0.4	1.05	0.76	32.5	6.8	239.2	4.7
OCNF/15MPP/OAC	808	47	11.8	0.8	3.14	1.59	42.5	4.0	283.0	18.2
OCNF/15MPP/5AC	688	62	10.2	1.4	2.08	0.27	32.5	3.4	261.3	17.6
OCNF/15MPP/10AC	645	29	10.0	0.9	2.21	0.53	26.9	2.0	214.9	13.7
OCNF/30MPP/OAC	480	10	7.9	0.5	3.80	1.39	39.9	2.7	286.4	5.3
OCNF/30MPP/5AC	468	13	8.6	0.7	2.35	1.58	29.5	4.9	278.2	30.4
OCNF/30MPP/10AC	473	42	8.0	0.3	4.27	6.38	26.9	2.7	259.1	10.4
15CNF/OMPP/OAC	606	15	11.3	1.0	0.52	0.90	42.0	2.0	263.5	21.1
15CNF/OMPP/5AC	617	22	10.7	0.9	0.00	0.00	32.9	3.0	263.9	37.5
15CNF/OMPP/10AC	563	38	8.6	0.2	0.00	0.00	36.4	2.3	307.2	10.5
15CNF/15MPP/OAC	496	36	10.6	1.8	2.23	2.63	36.8	9.2	338.4	28.5
15CNF/15MPP/5AC	510	52	10.1	0.4	1.07	0.93	27.7	6.5	536.9	117.2
15CNF/15MPP/10AC	496	30	13.4	6.0	1.44	1.11	33.4	2.7	466.3	121.7
15CNF/30MPP/OAC	453	32	8.5	1.2	1.59	1.69	32.9	3.8	278.6	8.5
15CNF/30MPP/5AC	436	4	6.1	0.1	0.69	0.60	29.9	2.3	298.1	6.7
15CNF/30MPP/10AC	444	27	5.8	0.1	4.00	2.77	29.9	3.9	270.4	14.7

7.4 Effects on Flammability

The flammability of the investigated material systems in the cone calorimeter is illustrated by the Petrella plot [222] shown in Figure 7.5. It simultaneously illustrates the fire load through the total heat evolved (THE) until the end of the test and the flame spread through the quotient of the peak heat release rate and the time to ignition (PHRR/ t_{ign}).

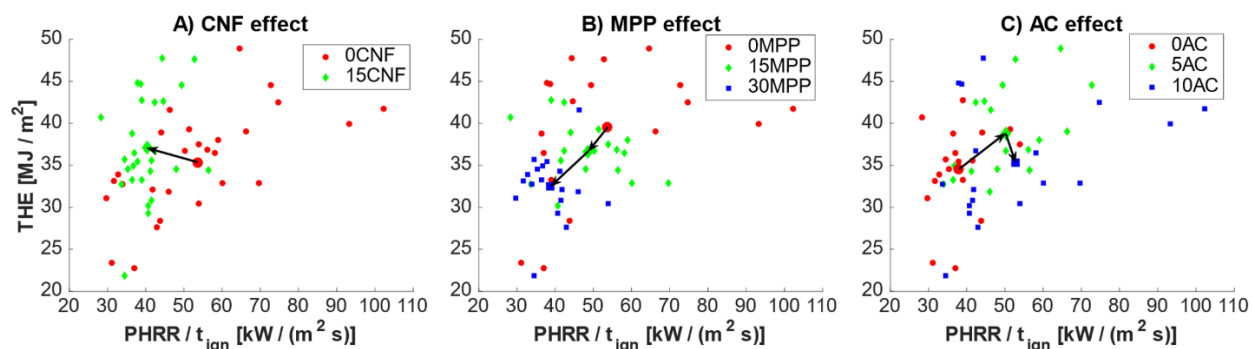


Figure 7.5: Petrella plot illustrating the fire load and flame spread effects of a) CNF reinforcement, b) MPP and c) AC additives when incorporated into TPU

Although a slight increase can be observed in the total heat evolved (i.e. +5%), the incorporation of CNF into the neat TPU results in a 31% decrease in the flame spread metric (i.e. $\text{PHRR}/t_{\text{ign}}$), as shown in Figure 7.5a. The efficiency of MPP as a flame retardant is illustrated in Figure 7.5b, where both the total heat evolved, and the flame spread are significantly reduced. The decrease is even more pronounced upon increasing the loading level of MPP from 15 wt% to 30 wt%, indicating a non-linear behavior with respect to the concentration of this fire retardant. The addition of AC is detrimental to both the total heat evolved and the flame spread. Nonetheless, at 10 wt% AC, a total heat evolved comparable to the untreated material can be obtained.

To assess whether the effect of the reinforcement and additives on the flammability occurs in the condensed phase or in the gas phase, the percent residual mass (%RM) is plotted against the total heat evolved, as shown in Figure 7.6.

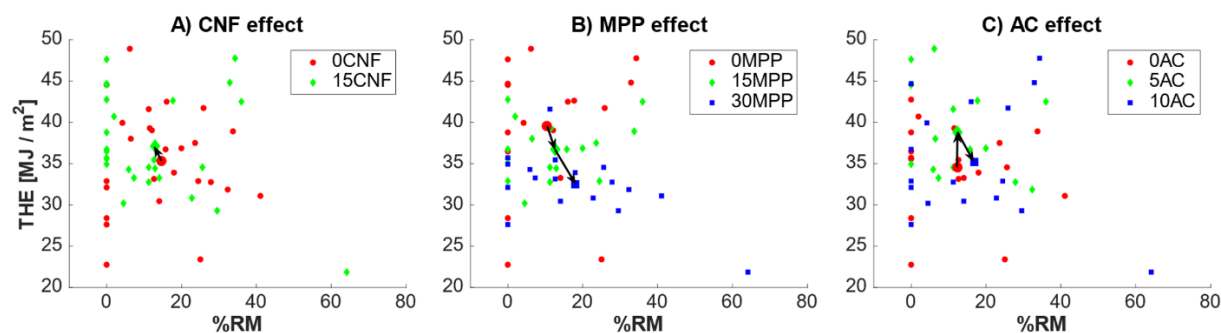


Figure 7.6: Plot illustrating simultaneously the total heat evolved and percent residual mass, allowing to determine whether the fire-retardant effect of a) CNF reinforcement, b) MPP and c) AC additives occurs in the gas phase or in the condensed phase.

For the CNF-reinforced material systems, the total heat evolved is higher than that of non-reinforced TPU while the residual mass is lower, indicating a better conversion of the specimen mass into heat. The presence of MPP monotonically enhances the residual mass and reduces the total heat evolved, clearly indicating a fire-retardant effect in the condensed phase. It is interesting to note that the incorporation of CNF yields on average less residual mass (Figure 7.6a) even though MPP enhances the production of char, suggesting an antagonistic effect between CNF and MPP with regards to char production. The addition of 5 wt% AC only enhances the total heat evolved without any significant effect on the residual mass, suggesting that the additive is fully converted into heat. At a loading of 10 wt%, the total heat evolved is restored to a value similar to that without AC while the residual mass is increased by approximately 4%, highlighting a condensed-phase action of the additive.

The effects on the heat of combustion (i.e. H_c/A), shown in Figure 7.7a and Figure 7.7b, reveal that when independently combined with CNF, melamine polyphosphate and activated carbon exhibit synergies that reduce H_c/A up to loading levels of 15 wt.% and 5 wt.%, respectively. In the absence of CNF, the addition of AC results in an overall increase in the heat of combustion. The complex MPP/AC interaction shown in Figure 7.7c reveals that an optimal MPP/AC weight ratio of 3 tends to decrease H_c/A .

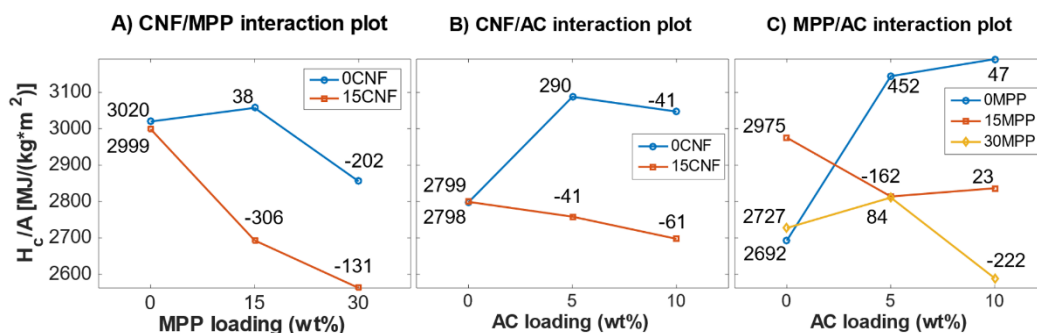


Figure 7.7: Interaction effects on the H_c/A response variable

The performance of MPP in the neat TPU polymer is poor below a loading level of about 15 wt.% as the additive is incapable of curbing the thermal degradation. Instead, it promotes the outgassing of combustible species, possibly through an acid-driven hydrolysis of the TPU polymer matrix [223]. To further understand how the heat release is affected by the incorporation of these additives, we refer to the component of the total heat that is released during smoldering combustion, namely $\%THR/A_{smold}$ shown in Figure 7.8. This metric indicates whether material degradation is steered towards char formation early in the test, thereby shifting a portion of the heat release from the flaming to the smoldering combustion regime.

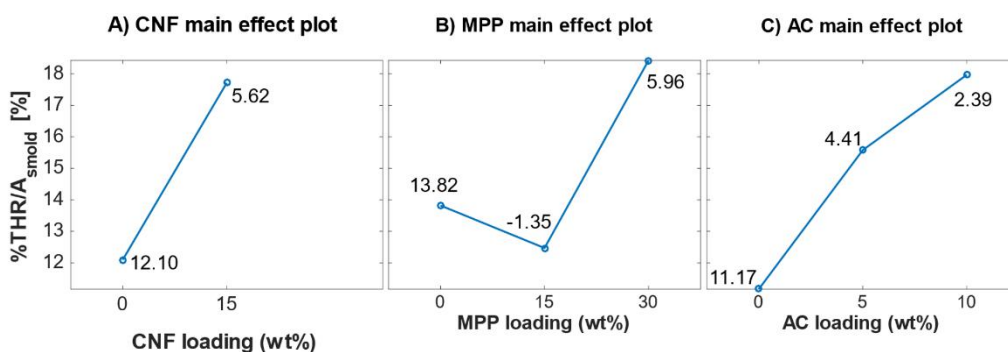


Figure 7.8: Main effects on the $\%THR/A_{smold}$ response variable

We note that all additives contribute to an overall increase in the smoldering component of the total heat released, indicating the promotion of primary char formation. The decrease associated

with an MPP loading of 15 wt.% is consistent with the acid-driven hydrolysis hypothesis formulated above.

The char remaining after the test is shown in Figure 7.9 for the material systems which exhibit somewhat observable differences. The residual mass from the neat TPU and the TPU/15CNF systems is composed only of ash and is not shown here.

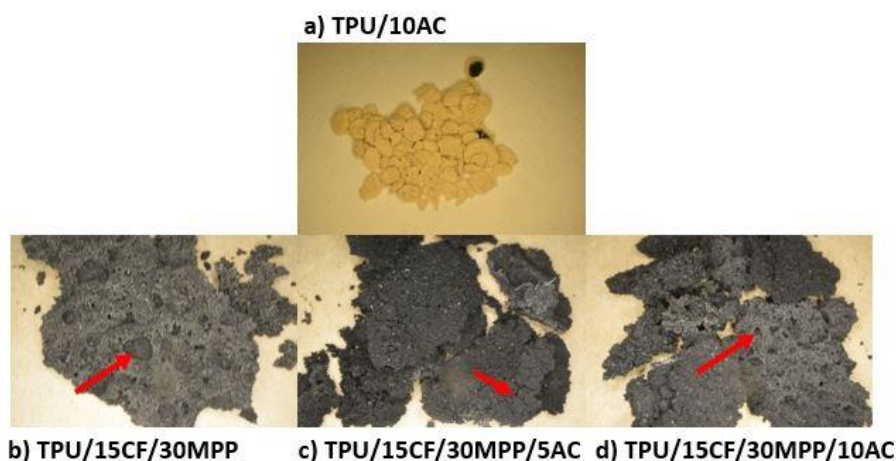


Figure 7.9: Images of the chars produced by various material systems

The addition of AC to any non-MPP material system results in a beige residual powder aggregated into small porous lumps, as shown in Figure 7.9a. To obtain char, MPP is always required in the investigated material compositions. Figure 7.9b and Figure 7.9d depict the chars from the systems yielding the largest residual mass; these are characterized by large holes, indicated by red arrows. At a loading of 5 wt.%, AC seems to influence the size of these holes, whereby the char exhibits smaller porosities and a few cracks, as shown in Figure 7.9c. As a general observation, all the chars obtained were very friable.

7.5 Effects on Smoke and Particulate Matter Size and Concentration

We first illustrate the relationship between the rate of heat release and the smoke production by plotting these parameters in Figure 7.10 for the 18 unique materials systems investigated. We can note that the production of smoke is closely related to the rate of heat release in terms of magnitude

but also its evolution in time. Moreover, the addition of MPP lowers the smoke production monotonically.

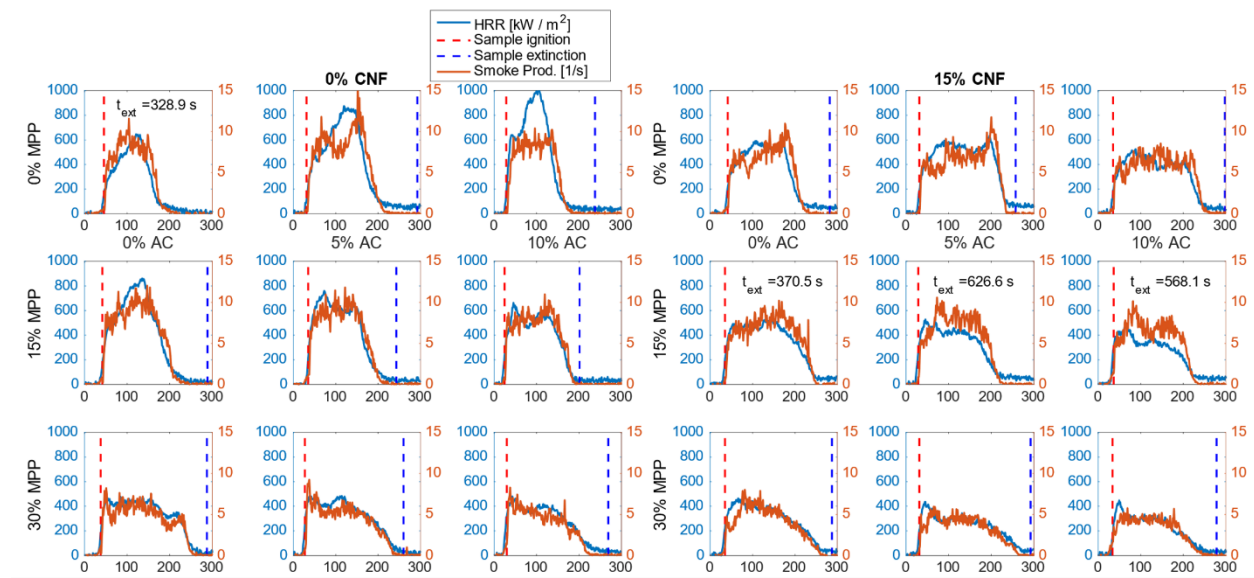


Figure 7.10: List of plots illustrating the evolution of the heat release rate (blue) and the smoke production (brown) for the 18 unique material systems investigated.

We proceed to investigate the effects of CNF, MPP and AC on the total smoke production in the flaming regime (i.e. $S_{A,flm}$) response variable to determine whether an improvement can be achieved relative to the smoke produced by the neat polymer. The main effects of the additives are visible in the interaction plots of Figure 7.11.

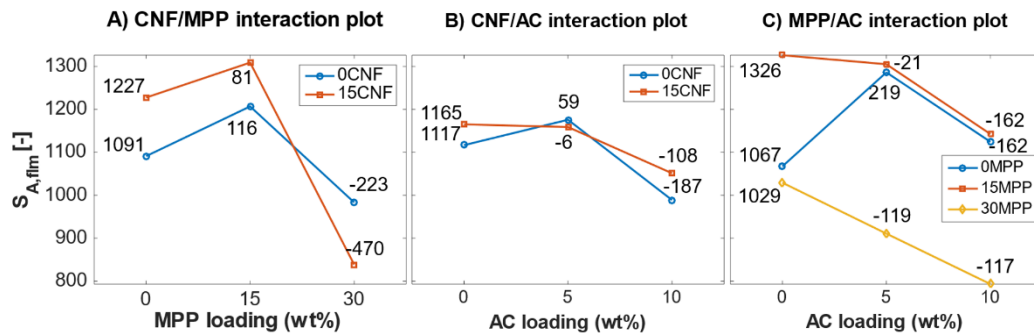


Figure 7.11: Interaction effects on the $S_{A,flm}$ response variable

In Figure 7.11a, we observe that the addition of CNF into neat TPU has a promoting effect on the production of smoke, but this behavior can be drastically offset through a CNF/MPP synergy by introducing 30 wt.% MPP. The addition of AC can also offset the detrimental effect of CNF (Figure 7.11b). Moreover, as indicated in Figure 7.11c, AC exhibits a strong synergy with MPP towards reduction of smoke, but only up to a loading of 5 wt.%.

Additional insight on the smoke production can be obtained by monitoring the effect of the additives on the time until peak smoke production in the flaming ($t_{S,max,flm}$) and in the smoldering ($t_{S,max,smold}^*$) regimes, shown in Figure 7.12a. We note that the addition of CNF increases the time to peak smoke production in the flaming regime by 30.5 seconds, as expected from the initial endothermic thermal degradation of CNF, providing a cooling effect, and lowering the rate of pyrolysis.

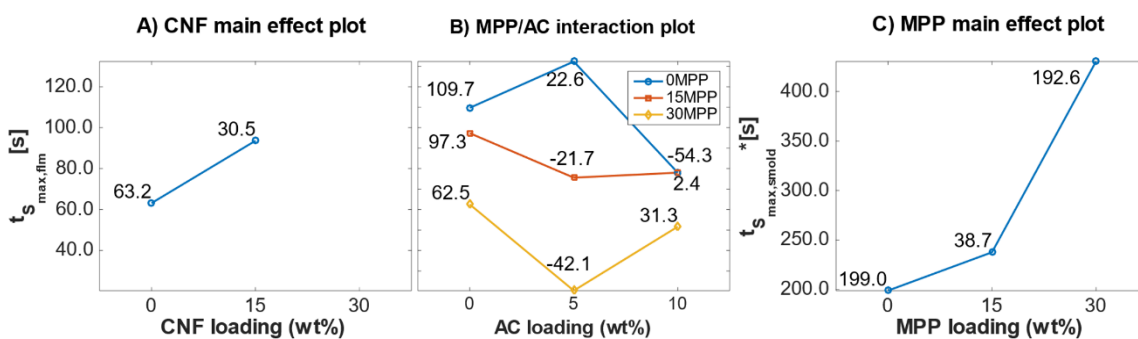


Figure 7.12: A) Main effects and B) interaction effects on $t_{S,max,flm}$ and C) main effects on $t_{S,max,smold}^*$ response variables

The MPP/AC interaction shown in Figure 7.12b outlines a synergetic effect towards an early attainment of the peak smoke production except for the neat TPU system, for which the peak is delayed. In the smoldering regime, the presence of MPP delays the time to peak smoke production (Figure 7.12c), outlining a char that is thermally more stable compared to non-MPP systems.

To further complement the smoke obscuration data, the effects of the additives on the particle size measured at the smoke concentration peaks are shown in Figure 7.13a and b, for the flaming regime and the smoldering regime, respectively.

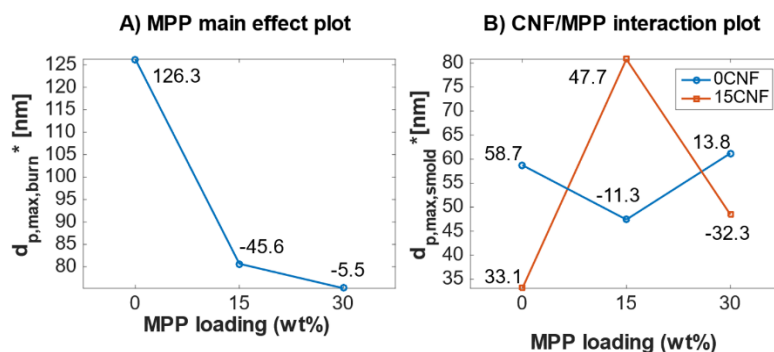


Figure 7.13: A) Main effects on $d_{p,max,burn}^*$ and B) interaction effects on $d_{p,max,smold}^*$ response variables

In the flaming regime, the addition of MPP lowers particle sizes, perhaps through a combination of solid phase and gas phase phenomena, namely a low rate of pyrolysis, char promotion and gaseous dilution. In the smoldering regime, the interaction between CNF and MPP results in increased particles sizes, especially at a loading of 15 wt.% MPP, highlighting the poor thermal stability of the resulting char.

7.5.1 Evolution of the particle size over time

Each SMPS scan provides a particle concentration for each of the 150 size channels, namely from 6 to 240 nm. The evolution of the particle size distribution as measured by the SMPS is shown in Figure 7.14 on a semi-log scale for the TPU/5AC material system. Each plot represents one scan and the red marker indicates the centroid of the distribution. The latter is averaged over two test repetitions and is plotted in subsequent figures to capture the evolution in mean particle size and mean particle concentration.

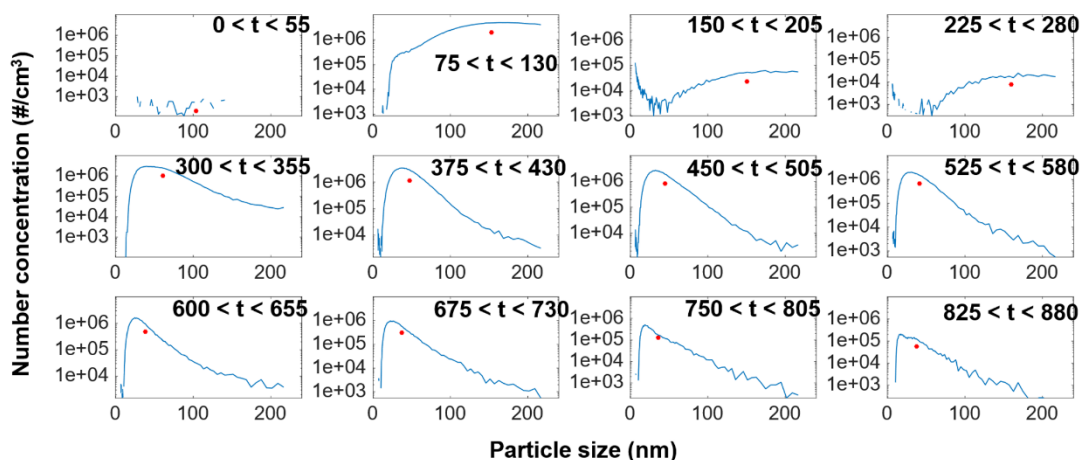


Figure 7.14: Evolution of the particle size distribution for the TPU/5AC material system; time labels indicate data acquisition interval for each SMPS scan in seconds and the red dot indicates the centroid of the distribution

We may observe that early in the test (i.e. first row of plots), the main mode of the distributions shifts towards large particles (i.e. > 150 nm), as a result of the important rate of pyrolysis and particle aggregation in the flaming regime, enhanced by flame turbulence and large thermal gradients. In the smoldering combustion regime, the mode returns to values below 100 nm as the rate of pyrolysis drops and the combustion is more efficient due to an enhanced ventilation of the smoldering material.

7.5.1.1 Non-CNF treatments

In Figure 7.15a, the effect of MPP addition on the mean particle size evolution is shown. The addition of up to 15 wt.% MPP results in a decrease in the mean particle size with respect to the neat polymer; a further loading to 30 wt.% decreases the particle size slightly in the smoldering combustion regime, namely after the 300-second mark. At a fixed MPP loading, larger particles are emitted in the flaming regime (i.e. the first 300 seconds of the test, on average) compared to the smoldering regime. In the latter stage, the low gasification rate of the thermally stable char yields smaller particles compared to the flaming regime where the pyrolysis and particle agglomeration rates are high. The addition of AC into the neat TPU also lowers the particle size,

as seen in Figure 7.15b and a loading of 10 wt.% yields an average particle size evolution comparable to that obtained from a MPP loading of 15-30 wt.%.

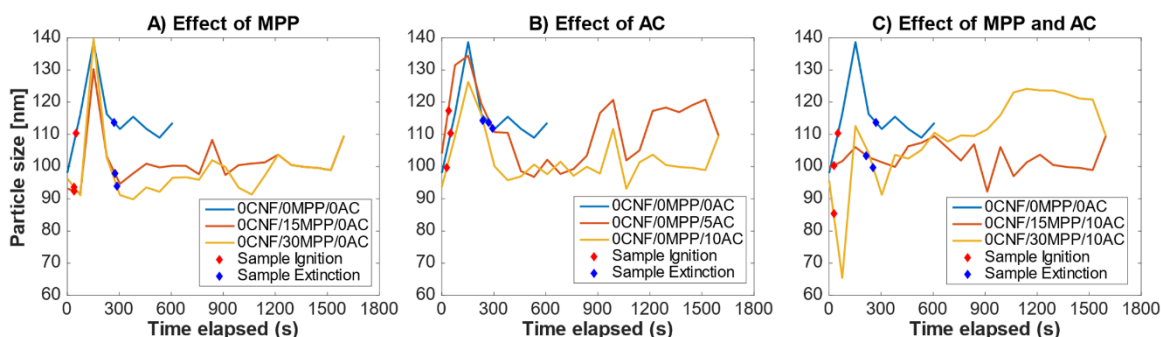


Figure 7.15: Effect of A) MPP, B) AC and C) MPP and AC on the particle size evolution for the non-CNF material systems

The most notable observation from the incorporation of both MPP and AC into the polymer matrix is the elimination of the large peak observed in the flaming combustion regime, as seen in Figure 7.15c at an MPP/AC loading ratio of 15/10 wt.%. Somewhat counter-intuitively, a further increase in the MPP loading to 30 wt.% while keeping AC at 10 wt.%, the average particle size increases significantly. This transition from a very low rate of pyrolysis to a significantly higher one is associated with a significant shift of the heat release towards the smoldering regime, as observed in Figure 7.8b and c.

7.5.1.2 CNF-reinforced composites

The incorporation of CNF into TPU results in the emission of larger particles compared to the neat polymer in the flaming regime and small particles of approximately 40-60 nm after extinction until around the 1200-second mark. For the remainder of the test, the particle size emitted by CNF-

reinforced TPU is similar to that from the AC-treated polymer. This similarity may arise from a comparable char degradation mechanism between the two material systems.

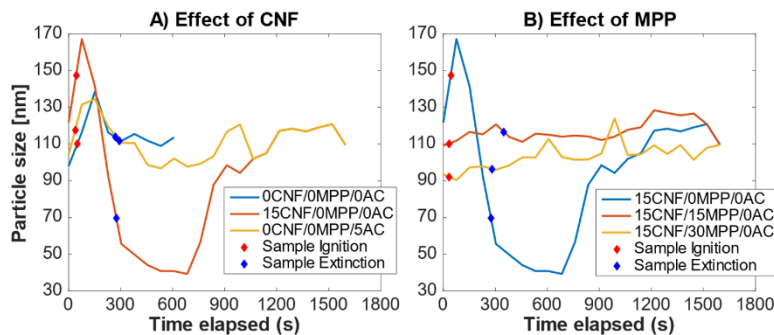


Figure 7.16: Effect of A) CNF and B) MPP on the particle size evolution for the CNF-reinforced material systems

In Figure 7.16b, we observe that the incremental addition of MPP into CNF-reinforced TPU reduces the average particle size in the flaming regime but this trend reverses for the smoldering portion of the thermal degradation, outlining a regime of inefficient combustion, as indicated also by the heat of combustion (Figure 7.7a). A more pronounced reduction of the average particle size may be obtained from the incremental addition of AC into the CNF-reinforced polymer, as shown in Figure 7.17a. The CNF/AC interaction has shown that AC monotonically reduces the heat of combustion (Figure 7.7b) but less than MPP in the CNF/MPP material (Figure 7.7a), hence a more efficient combustion yielding smaller particles.

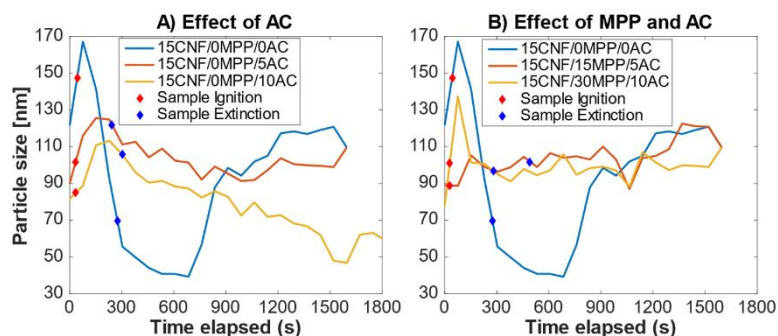


Figure 7.17: Effect of A) AC and B) MPP and AC on the particle size evolution for the CNF-reinforced material systems

The combined effect of MPP and AC follows from the independent effect of MPP and AC on the CNF-reinforced TPU discussed above, namely a reduction in the average particle size, as shown in Figure 7.17b. The MPP/AC interaction on the heat of combustion (Figure 7.7c) is indicative of a less efficient thus sootier combustion.

7.5.2 Evolution of the concentration of particulate matter over time

The evolution of the particle concentration over the duration of the test is shown on semi-log plots, with the magnitude representing the diluted (1:100) stream sent to the SMPS.

7.5.2.1 Non-CNF treatments

The addition of 15 wt.% MPP into the neat TPU does not exhibit a significant effect but a further increase to a loading of 30 wt.% translates into a larger concentration relative to the neat TPU, as depicted in Figure 7.18a. For the same treatments, the average particle size was observed to follow an opposite behavior (Figure 7.15a). This indicates that the inert dilution provided by MPP does not necessarily imply a curbing of particulate matter inception but rather, it prevents the aggregation of particles, resulting in smaller particles and larger concentrations. Moreover, larger particles present in a smaller concentration (TPU/15MPP) result in a stronger smoke production signal (Figure 7.11a) compared to the opposite case occurring for the TPU/30MPP material combination.

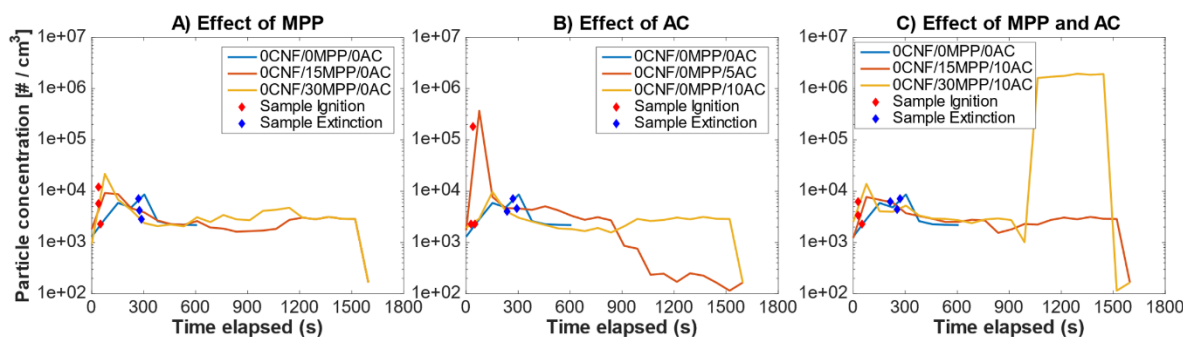


Figure 7.18: Effect of A) MPP and B) AC and C) MPP and AC on the evolution of the particle concentration for the non-CNF material systems

The incremental addition of AC into neat TPU results in a behavior opposite to that of MPP, increasing the average particle concentration at 5 wt.% but reduces it slightly upon a further increase to 10 wt.% relative to the neat TPU. The effect of AC on the total smoke production shown in Figure 7.11b follows a similar trend. The overall decrease in both the size and particle concentration upon addition of AC confirms a lower rate of pyrolysis, postulated earlier as an expected effect.

The simultaneous increase in MPP and AC to 30 wt% and 10 wt%, respectively, reveals a drastic increase in the average particle concentration but only late in the smoldering combustion regime, as shown in Figure 7.18c. In this case, both the particle size and the particle concentration increase while the heat of combustion decreases (Figure 7.7c), pointing towards a less efficient combustion.

7.5.2.2 CNF-reinforced treatments

The similarity of the particle size evolution late in the smoldering combustion regime between the TPU with 5 wt.% AC and the CNF-reinforced TPU evoked previously also applies to the evolution of the particle concentration, as shown in Figure 7.19a. However, in the CNF-reinforced case, the peak particle concentration is smaller than in the AC-treated material in the flaming regime, potentially associated with the high coagulation due to the increased propensity of cellulose to produce soot upon thermal degradation. The large number of inception particles result in particle growth and coagulation, thus reducing the aerosol particle concentration.

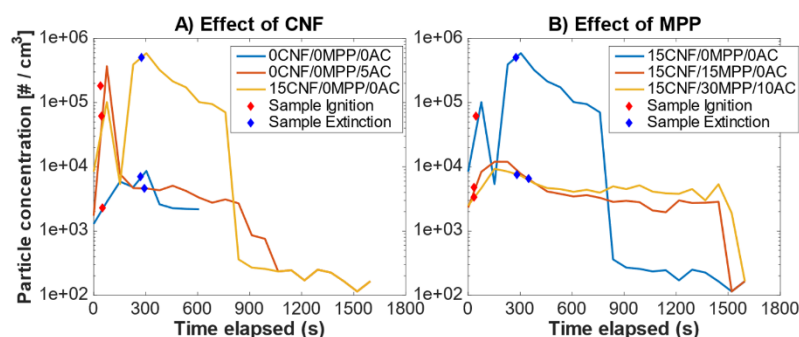


Figure 7.19: Effect of A) CNF and B) MPP on the evolution of the particle concentration for the CNF-reinforced material systems

In the presence of CNF, the addition of 15 wt.% MPP decreases the particle concentration for the first half of the test duration, as shown in Figure 7.19b; no significant effect can be seen after a further increase to 30 wt.%. This observation is linked to an insufficient MPP loading level at 15 wt.%, effectively catalyzing the degradation of the material, contributing to particle growth (Figure 7.16b) at the expense of the particle concentration.

The addition of AC into the CNF-reinforced TPU leads to an overall decrease in the average particle concentration, as shown in Figure 7.20a and is also accompanied by a decrease in the average particle size (see Figure 7.17a). These observations hint at a reduction in the inception rate and in the yield of soot growth molecules. The inception rate has been shown to impact particle growth through coalescence [183], whereby a high inception rate increases the likelihood of coalescent particle collisions, contributing to particle growth, and vice versa. The average particle concentration at 5 wt.% AC is somewhat lower than at 10 wt.% but in the latter case, the particle concentration is constant throughout the test duration.

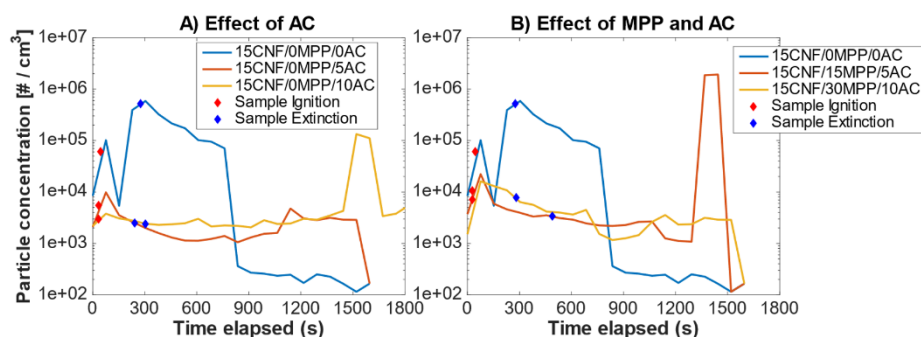


Figure 7.20: Effect of A) AC and B) MPP and AC on the evolution of the particle concentration for the CNF-reinforced material systems

The simultaneous incorporation of both MPP and AC, namely from neat TPU/CNF to a 15/5 wt.% MPP/AC loading, decreased the average particle concentration for the first half of the test duration and decreased it for the second half relative to the untreated CNF-reinforced TPU, as shown in Figure 7.20b. A further simultaneous increase to 30/10 wt.% MPP/AC does not exhibit a significant effect. The same trend was observed for the average particle size across these loading levels (refer to Figure 7.17) for the first half of the test duration. As outlined for the effect of AC above, a

simultaneous increase in the particle size and particle concentration may result from enhanced inception and coalescence/aggregation mechanisms, ultimately fueled by a high rate of pyrolysis and vice versa.

7.6 Discussion

The cone calorimetry and particle size distribution data indicate that overall, the incorporation of 15 wt.% FiloCell® CNF into fire retarded TPU improves the fire performance of the resulting PMC. The heat of combustion is strongly suppressed, mainly because of the synergistic reaction of MPP with CNF. An equal reduction would perhaps be possible at a loading level higher than 30 wt.% if only MPP is used into the neat polymer; a composition that is detrimental to the mechanical properties [216]. Additionally, despite increasing the fire load, CNF shifts a portion of the heat release into the smoldering combustion regime, thereby also decreasing the peak heat release rate, effectively reducing the risk of fire propagation [224]. Incorporated into the PMC alone, AC can provide a slightly better increase in the smoldering component of the total heat release than CNF, at a loading of only 10 wt.%. Despite reducing the heat of combustion and increasing the smoldering component of the total heat release, the presence of CNF has a detrimental effect on the action of MPP with regards to the residual mass (i.e. char) remaining at the end of the test. Nevertheless, this effect can be offset by introducing AC into the mix at a mass loading above 5 wt.%, triggering an enhanced residual mass. Due to its low thermal decomposition temperature, CNF compounded alone into TPU enhances the total production of smoke in the flaming regime. However, another synergistic reaction with MPP occurring at a mass loading of 30 wt.% results in a better smoke performance than its non-CNF counterpart; further smoke reduction can be achieved by adding AC. Additionally, the endothermic degradation of CNF delays the time until peak smoke production in the flaming regime and by exploiting the interaction between MPP and AC, it can be increased additionally. This is an important finding as the time elapsed until peak smoke production is a crucial parameter to account for evacuation requirements in fire safety. To preserve an acceptable level of visibility, low particulate matter concentrations are desired, if an accidental fire was to take place. We have observed that the incorporation of AC

into the CNF-reinforced TPU minimized the size as well as the concentration of particulate matter, both in the flaming regime and the smoldering regime.

It is important to re-emphasize that the scope of this study is to identify synergistic effects between the proposed material systems, namely TPU, Filocell® CNF and fire-retardant treatments consisting of various loading combinations of MPP and AC. Other types of CNFs should be investigated to determine whether the findings reported herein generally apply to all CNFs, irrespective of fiber morphology and surface treatments. With regards to the effect observed on smoke and particulate matter, FiloCell® CNF is expected to volatilize readily compared to larger cellulose fibers due to its high specific surface area. As a result, this study with FiloCell® CNF is expected to tackle the worst-case scenario with respect to particulate matter yield, considering equal loading levels of cellulose.

7.7 Conclusion

In this study, we have investigated the interactions between the FiloCell® cellulose nanofiber reinforcement, and fire-retardant additives, namely melamine polyphosphate and activated carbon, with regards to flammability and smoke production in a TPU polymer matrix composite. Additionally, we have shown that the implementation of SMPS measurements can provide information complementary to the smoke obscuration measurement of the cone calorimeter. We demonstrated that the incorporation of 15 wt.% FiloCell® CNF along with the various mass loading combinations of FR additives allows the fine tuning of the fire performance and particulate matter response variables, effectively broadening the range of potential applications of the CNF-reinforced TPU. Two-way synergies have been identified between CNF and the fire retardants on many of the response variables considered. Overall, the CNF-reinforced TPU treated with MPP, and AC shows a fire performance that is considerably enhanced compared to the neat TPU polymer.

In our future work, we propose to investigate a further replacement of MPP with AC to determine whether higher loadings of the latter can imitate the fire-retardant effect of MPP. Although the addition of 10 wt.% AC enhanced the flame spread, the total heat evolved was comparable to that

without AC, while a portion of the heat release was shifted to the smoldering regime and the heat of combustion was reduced. From a particulate matter standpoint, AC effectively decreased the concentration and size of particles for most of the material systems considered herein.

7.8 Supplemental Material

7.8.1 ANOVA

The material treatments investigated in this study are summarized in Table 7.2.

Table 7.2: List of the investigated material systems

Treatment #	CNF Level ID (wt.%)	MPP Level ID (wt.%)	AC Level ID (wt.%)
1	1 (0%)	1 (0%)	1 (0%)
2	1 (0%)	1 (0%)	2 (5%)
3	1 (0%)	1 (0%)	3 (10%)
4	1 (0%)	2 (15%)	1 (0%)
5	1 (0%)	2 (15%)	2 (5%)
6	1 (0%)	2 (15%)	3 (10%)
7	1 (0%)	3 (30%)	1 (0%)
8	1 (0%)	3 (30%)	2 (5%)

9	1 (0%)	3 (30%)	3 (10%)
10	2 (15%)	1 (0%)	1 (0%)
11	2 (15%)	1 (0%)	2 (5%)
12	2 (15%)	1 (0%)	3 (10%)
13	2 (15%)	2 (15%)	1 (0%)
14	2 (15%)	2 (15%)	2 (5%)
15	2 (15%)	2 (15%)	3 (10%)
16	2 (15%)	3 (30%)	1 (0%)
17	2 (15%)	3 (30%)	2 (5%)
18	2 (15%)	3 (30%)	3 (10%)

The ANOVA analysis relies on two assumptions which must be verified for every response variable: 1) the normality assumption and 2) the equal variances assumption. The former is tested using the Anderson-Darling normality test, where the null hypothesis H_0 states that the data follows a normal distribution, and the significance level is set at $\alpha = 0.05$. If the data follows a normal distribution (i.e. $p\text{-value} > \alpha$), Bartlett's test may then be used to verify the equal variances' assumption, given the normally distributed data. For the equal variances' test, the null hypothesis H_0 states that the variances in the data are all equal and the significance level is also set at $\alpha = 0.05$.

To determine the main effects and the interaction effects of the three factors, namely CNF, MPP and AC on each of the response variables, an ANOVA general linear model is used to fit the response variable data. The general linear model is composed of the terms representing each of the three factors (i.e. main effects) and the terms representing all the two-factor combinations (i.e. interaction effects) and tests for the significance of each of the terms on a response variable of interest. The null hypothesis H_0 of the general linear model states that the means of the response data are equal among all the levels of a factor (or term). Similar to the normality and equal variances tests, the general linear model outputs a p-value for each term in the model, indicating whether varying the level of that term has a significant effect on the response variable. Since a significant effect implies that the means of the response variable at different factor levels are not equal (H_0 is not confirmed), a p-value that is less than the significance level of $\alpha = 0.05$ is expected. The general linear model is tuned by successively eliminating the terms for which the p-value is larger than the significance level, until only the significant terms remain.

In the tables below, the response variables which fulfill the normality, and the equal variances assumptions are shown, along with their respective p-values for both tests. Additionally, the f-value/p-value pair for the significant terms of the ANOVA general linear model fit is given. Because the existence of significant interaction effects outlines a dependence between the terms involved in the interaction, the main effects of those terms will not be discussed. Only the significant main effects of the terms that are not involved in significant interactions will be discussed. For example, the H_c/A response variable is a function of the CNF, MPP and AC terms (i.e. main effects) and of the two-way interaction terms (i.e. interaction effects), namely CNFxMPP, CNFxAC and MPPxAC. Since each of the factors are involved in interactions with the remaining factors, the main effects of the factors will be dismissed. On the other hand, the $t_{S,max, flm}$ response variable is significantly affected by the CNF term and the MPPxAC term. Because the main effect of CNF is significant and is not involved in an interaction, it will be discussed but the main effects of MPP and AC, despite being significant, will not be discussed independently but only as part of the MPPxAC interaction effect. For each response variable, the effects that will be discussed are marked as bold.

Table 7.3: ANOVA analysis of the flammability response variables

Response Variable		H_c/A	%THR/A_{smold}	PHRR/A*
P-Value for Normality Test (Anderson-Darling)		0.589	0.301	0.075
P-Value for Equal Variances Test (Bartlett's)		0.51	0.106	0.097
λ of Box-Cox Transformation (if applicable)		N/A	N/A	-2
Main Effects F-Value/P-Value	CNF	3.94/0.054	11.45/0.001	2.30/0.138
	MPP	8.13/0.001	4.72/0.013	29.43/0.000
	AC	21.54/0.000	5.76/0.006	6.24/0.005
Interaction Effects F-Value/P-Value	CNF x MPP	5.06/0.011	N/A	8.87/0.001
	CNF x AC	5.98/0.005	N/A	5.36/0.009
	MPP x AC	8.66/0.000	N/A	4.56/0.004
	CNF x MPP x AC	N/A	N/A	3.24/0.023

When the data of a response variable is not normally distributed, and the equal variances assumption is not met, a Box-Cox transformation is performed, and the normality and equal variances' tests are subsequently applied on the transformed data. If the transformed data fulfills the normality and equal variances assumptions, this data is fitted with the general linear model and the trends of the significant effects are compared to those of the original data. If the trends between the original data and the transformed data are similar, the effects of the significant terms are discussed using the trends of the original data. It is important to note that when a data transformation is required, the trends of the significant effects are only discussed qualitatively. As an example, the peak heat release rate (PHRR) response variable was transformed using a Box-Cox transformation with $\lambda = -2$ to fulfill the normality and equal variances' assumptions of the ANOVA. Note that the percent residual mass (% RM) response variable represents a unique case where the normality assumption is refuted but the equal variances assumption is fulfilled and no value of λ for the Box-Cox transformation normalizes the distribution. We have decided to include this response variable in the analysis as it is widely accepted that ANOVA is robust to deviations from the normality assumption. The transformed response variables are marked with an asterisk (*) and the λ -value of the Box-Cox transformation is indicated in the table, if applicable.

Table 7.4: ANOVA analysis of the smoke and particulate matter response variables

Response Variable		$d_{p,max, burn}^*$	$d_{p,max, smold}^*$	$t_{s,max, flm}$	$t_{s,max, smold}^*$	$S_{A, flm}$
P-Value for Normality Test (Anderson-Darling)		0.05	0.834	0.276	0.095	0.158
P-Value for Equal Variances Test (Bartlett's)		0.185	0.154	0.02	0.48	0.083

λ of Box-Cox Transformation (if applicable)		0	-0.5	N/A	0.5	N/A
Main Effects F-Value/P-Value	CNF	0.02/0.880	7.52/0.009	11.19/0.002	0.61/0.437	24.25/0.000
	MPP	4.30/0.019	0.77/0.471	3.20/0.050	6.20/0.004	25.99/0.000
	AC	1.86/0.167	3.13/0.056	3.98/0.026	0.34/0.711	27.07/0.000
Interaction Effects F-Value/P-Value	CNF x MPP	N/A	6.25/0.005	N/A	N/A	14.68/0.000
	CNF x AC	N/A	1.87/0.169	N/A	N/A	8.67/0.001
	MPP x AC	N/A	1.76/0.159	2.76/0.039	N/A	13.92/0.000
	CNF x MPP x AC	N/A	1.52/0.216	N/A	N/A	4.05/0.008

CHAPTER 8 GENERAL DISCUSSION

The work presented here addressed the topic of soot formation in configurations that span a wide range of complexity, from a simple one-dimensional flow field in the reaction zone to highly complex, turbulent flames over solid fuels. Given the need for characterizing the morphology of soot aggregates, which is a tedious and potentially subjective task when performed manually, the first objective consisted of developing an automated primary soot particle detection algorithm for TEM micrographs of soot. This algorithm would then serve to achieve the second objective, which is to morphologically characterize the soot acquired in the one-dimensional unstrained diffusion burner. Since the morphology of soot is highly dependent on the conditions in which it was produced, a good performance of the algorithm can only be obtained if a broad range of soot morphologies are used for its development. For this purpose, the third objective consisted of acquiring soot samples from a configuration representative of accidental combustion, namely the cone calorimeter.

8.1 Image processing of soot aggregates

In the first article presented in Chapter 5, the image processing algorithm tackling the automated primary particle detection was discussed. Similar to algorithms based on the circular Hough transform method, the algorithm is highly sensitive to the lower bound of the detectable diameter, especially to the 0 – 10 nm range. However, the algorithm is only mildly sensitive to changes in the upper bound of the diameter range. Compared to manual measurements, the algorithm detects many more particles and despite a good fit between the input edge map and the detected circles, the algorithm underestimates the mode of the particle size distribution. The detected distribution is log-normal while the manually measured distribution is normal. Through the definition of a metric comparing location of the manually measured circles with that of the automatically detected ones, we were able to demonstrate that the underestimation is only partly attributed to the lower bound of the imposed diameter range. As such, it arises also because the edge map of the aggregate only includes particles located around the periphery of the aggregate, which are younger and therefore, smaller. On the contrary, manual measurement focuses more on particles in the core of

aggregates, probably due to these particles being larger and more readily distinguishable. To extend the detection of particles to the core of the aggregate, edges that are inside the aggregate must be detected. This can be done by performing a multi-level thresholding operation on the region represented by the aggregate, yielding a more complete edge map to be used as an input for the algorithm. With this edge map, the detection of circles is not limited to the particles present on the periphery of the aggregates but rather, the entire aggregate region is considered. Until now, the manual measurement of primary particles in aggregates is considered the benchmark for the morphological quantification of soot. As a result, given the discrepancy observed between the particle size distributions obtained by the manual and automated methods, we have resorted to performing the morphological analysis of soot by the former method.

8.2 Morphological characterization of soot in the 1d burner

The spatially resolved morphological characterization of soot from the one-dimensional diffusion flame has been performed manually, as presented in Chapter 6. Our unique experimental configuration permitted the observation of isolated inception particles coexisting with mature soot aggregates throughout most of the visible soot layer. A detailed analysis of the inception particles revealed that they are considerably smaller (i.e. almost half the size) compared to the primary particles found in aggregates from the same flame. Their size distribution follows a log-normal shape, and their aspect ratio ranges between 1.4 and 1.6. The number of isolated particle per unit surface of the sampling grid (i.e. surface density) has been quantified to provide a proxy for the in-flame soot volume fraction. We have been able to observe that lightly sooting flames and heavily sooting flames typically exhibit the highest number of inception particles. For both the leanest and the richest flames, namely f_1 and f_4 ($\phi_{\infty, f1} = 3.019$ and $\phi_{\infty, f4} = 4.320$), the decrease in the surface density in the inception region was associated with an increase in the particle size, outlining a region of coalescence. The detailed quantification of inception particles from TEM images is valuable as typical in-situ laser diagnostics are not sensitive to partially solidified soot [225]. The size distribution of aggregate primary particles follows a normal shape, and the primary particle diameter increases with the freestream fuel equivalence ratio. With regards to the fractal dimension in the inception region, it is also directly linked to the freestream fuel equivalence ratio.

Moreover, for the lean flames, the fractal dimension tended to increase as the aggregates travelled through the combustion domain while for the rich flame, it decreased. Deep inside the soot layer, the fractal dimension of aggregates converged towards values of 1.5 - 1.7 irrespective of the freestream equivalence ratio. Numerical simulations have shown the presence of methane and acetylene within the entire soot layer of the investigated flames along with increasing flame temperatures, positively correlated with the freestream fuel equivalence ratio along with minimal molecular oxygen penetration inside the soot layer. Moreover, the particle residence time was noted to be largest for the particles between 50 and 500 nm in flame $f_4 = 4.320$ due to its larger temperature gradient. Given their size, these particles have been shown to be temporarily trapped in the soot growth region of the flame due to the alignment and opposition between the thermophoretic force and the drag force.

8.3 Flammability and particulate matter emission of burning polymers

Despite having validated the soot sampling methodology over burning polymers prior to the test campaign, soot could not be observed in the scanning electron microscope (SEM), potentially due to a reaction compromising the mirror finish of the disks, or to the deposition of a thick layer of tar resulting in a poor contrast level with the soot particles. Upon performing a visual inspection of the disks, a ‘smoky’ deposit could be seen to the naked eye, but in the SEM, the entire observation area was blurry, and no features could be distinguished. To remedy this, it is suggested that the sampling of soot be performed farther above the top face of the specimen, where soot is more mature, and the concentration of tar is reduced. Nevertheless, the SMPS allowed us to gather data regarding the particulate matter yield that permitted to draw conclusions with respect to the effect of the three additives on the evolution of the yield and size distributions of particulate matter as a function of time throughout the duration of the test. In fact, we noted that the addition of cellulose shifts the particle size distribution towards larger sizes and increases the production of smoke; an effect that can be offset by the incorporation of MPP. However, cellulose delays the time to peak smoke production in the flaming regime; an interesting behavior from a fire safety standpoint. In terms of flammability, the endothermic degradation of cellulose can contribute to a

fire-retardant effect and minimize the loading of MPP needed to obtain a performance comparable to TPU treated with MPP only, thus resulting in a more environmentally friendly material and without the compromise on mechanical properties resulting from high loadings of inorganic flame retardant.

8.4 General impact

The work presented here has permitted to draw important conclusions with respect to the formation of particulate matter in flames. Although the automated primary particle detection algorithm yielded underestimated particle size distributions compared to manual measurements, we have been able to demonstrate that this was partially a result of the algorithm focusing exclusively on particles present around the periphery of the aggregates. These particles follow a log-normal distribution, similar to the isolated primary particles characterized in detail using samples from the one-dimensional unstrained diffusion flame. In fact, the peripheral particles present were isolated primary particles that only recently coagulated with the aggregates, hence the log-normal size distribution determined by the algorithm. Given that the particle size distribution is different between the core and the edge of an aggregate, both regions need to be considered for an accurate measurement of the mean particle size. Currently, we have been able to identify only two algorithms [111, 130] that use primary particle edges that are not limited to the periphery of the aggregates, but their performance is poor due to their unrefined and noisy edge detection. Moreover, the use of a soot dataset from burning polymers has enabled the observation of a shift towards larger primary particles in aggregates compared to soot from the methane diffusion flame, most likely arising as a result of enhanced soot precursor concentration. We have also proposed an intuitive quality parameter that informs the user on the quality of fit between the detected circle and the input edge map, therefore giving more credibility to the output of the algorithm. Image processing algorithms such as the one described herein are necessary for a rapid and unbiased quantification of soot morphology and are useful in generating large datasets required for the validation of numerical models aimed at predicting soot morphology, which are currently scarce. Nevertheless, further work is required to obtain a performance of the automated primary particle detection algorithm that is comparable with that obtained by manual measurements.

The detailed morphological quantification of soot from the one-dimensional diffusion flame has also enabled the observation of the coexistence between isolated primary particles and aggregates throughout the entire soot layer. These particles are considerably smaller in diameter compared to those found in mature aggregates and in the inception region of the flames, they are present in high concentrations, which collapse subsequently in favor of an increase in the size of particles, outlining a regime of coalescence. In the flame of highest freestream equivalence ratio, aggregates visible to the naked eye could be observed and these were surrounded by a halo of darkness. Given the radiative heat transfer from these large aggregates, they become colder than the surrounding gas, permitting the condensation of soot precursor species on their surface but also drawing nascent particles to collide with them as a result of the temperature gradient within this halo. The evolution of particle size in the cone calorimeter validates this hypothesis. Indeed, large aggregates are observed almost exclusively in the flaming regime where heat radiation by aggregates, and thus thermophoresis, is important. In the smoldering combustion regime, a considerable decrease in the particle size can be noted, associated with the presence of soot precursors and the formation of inception particles but the inability of these particles to coagulate towards the formation of aggregates. It is interesting to highlight that the size of particles in the smoldering combustion regime of accidental polymer combustion is also characterized by a log-normal distribution.

CHAPTER 9 CONCLUSION AND RECOMMENDATIONS

In this chapter, the objectives of the dissertation are recalled, and their achievement is assessed by considering the main results obtained in the three papers presented earlier. In addition, the shortcomings of the implemented methodology are discussed to provide a way forward for future investigations while avoiding the duplication of unfruitful methods.

9.1 Image processing algorithm for automated primary particle detection

The first objective pertained to the development of an image processing routine capable of assisting the morphological characterization of soot by an automated detection of primary particles in images derived from TEM micrographs. Through the careful formulation and refinement of a score used to select the final circular candidates, the proposed algorithm could choose the circles that best fit the edge map of the aggregate with limited bias with respect to their size and with a reduced sensitivity to the imposed upper diameter bound. Moreover, it was able to detect a shift in the particle size distribution toward larger particles when aggregates from flames of increasing fuel freestream concentration are considered. Through the formulation of pertinent metrics, the detailed data analysis and comparison with manual measurements has revealed that a representative particle size distribution cannot be obtained by only detecting primary particles around the periphery of aggregates. In addition, it has shown that manual measurements typically consider primary particles within the core of the aggregate, suggesting a potential bias of the manual method as well. Despite the discrepancy between manually measured and automatically detected particle size distributions, one could assess the level of confidence in the output of the algorithm by referring to the proposed quality parameter, which quantifies the fit between each detected circle and the edge map on which the given circle sits, effectively measuring how much of the detected circle's circumference is confirmed by the edge pixels of the aggregates.

Nevertheless, prior to the algorithm being fully relied upon to replace the manual measurement method, some improvements must be achieved. Firstly, given the current underestimation of the

primary particle size distribution by the algorithm due to its focus exclusively on particles present around the edges of the aggregates, it is suggested that aggregate edge maps including inner aggregate edges be supplied to the algorithm, and its performance be re-assessed in relation to manual measurements. Moreover, the aggregate segmentation step should be automated to reduce the operator time and any potential operator bias. Lastly, a detailed comparison with existing techniques for the automated detection of primary particles in aggregates should be performed to establish the relative performance of the proposed algorithm with the state of the art.

9.2 Morphological study of soot in the 1d burner

The second objective was to sample and perform a spatially resolved characterization of the morphology of soot collected in the one-dimensional unstrained diffusion burner. The thermophoretically-acquired dataset permitted the observation and the detailed morphological characterization of isolated primary particles found in four flames of increasing freestream fuel equivalence ratio; these particles represent the building blocks of soot aggregates but typically go unnoticed to common in-situ diagnostics. Moreover, the morphology of aggregates found in the three richer flames has also been characterized in terms of mean primary particle diameter, number of particles per aggregate, aggregate maximum length, overlap coefficient and fractal dimension as a function of the sampling location. Numerical simulations of chemical species, temperature and particle residence time complemented the morphological dataset, enabling the understanding of the relative magnitude of the different mechanisms responsible for the observed morphology. The fulfillment of this objective was conditional to the development of a highly optimized substrate holder design for TEM grids, allowing for a smooth and fast sampling procedure while minimizing any unwanted motion of the assembly and maximizing the temperature gradient between the assembly and the gaseous environment. The physical limitations arising from the geometry of the burner were overcome and a repeatable procedure for soot collection has been proposed, facilitating future studies that require soot sampling in this burner, when using other fuels, for instance. The one-dimensional flow field in the reaction zone of our distinctive burner eliminates an important component of complexity in the soot formation process and makes the proposed dataset attractive for the validation of analytical numerical models of soot formation.

These models are highly sought in industries concerned with particulate matter emissions given the evermore stringent requirements to mitigate particulate matter yield. In addition, toxicological studies necessitate a detailed knowledge of the morphology of particles as it governs the transfer of carcinogenic molecules from the particles into the biological tissues.

Nevertheless, a sampling limitation for the large aggregates present in the richest flame has been observed. These aggregates landed preferentially on the metal strips of the transmission electron microscope grids, exposing only their extremities to the observable region of the grids. It is suggested that a sampling substrate with uniform thermal properties across the area be implemented to avoid the sampling bias, such as mirror-polished disks of austenitic stainless steel that can be imaged on the scanning electron microscope. Moreover, only a limited number of flames has been investigated and an extension of this dataset to flames involving gaseous additives, such as hydrogen for instance, can provide additional insights on the soot formation mechanism given the unique experimental configuration available. Lastly, the spatial resolution of the study can also be improved to obtain a more accurate quantification of the evolution of the morphological parameters as a function of the position.

9.3 Soot collection from polymer matrix composites

The third and final objective focused on the collection of a soot dataset from an experimental configuration representative of an accidental fire. The implementation of a scanning mobility particle sizer in the cone calorimeter has permitted to study the evolution of particulate matter throughout the duration of the test, allowing to observe a shift from large to small particles between the flaming regime and the smoldering combustion regime. Moreover, the effect of various additives on the resulting particulate matter could be observed, therefore highlighting the added-value of implementing such an instrument in the standard configuration of the cone calorimeter. Thermophoretic sampling from burning polymers has also been achieved on a mirror-finished austenitic stainless-steel plate that is more homogeneous than the TEM grids from a thermal conductivity standpoint. Although this method was successful in the FAA cabinet, its extension to the cone calorimeter was unfruitful for the sampling of soot from the cellulose-reinforced thermoplastic polyurethane, potentially due to a sampling performed too close the polymer

resulting in the deposition of large amounts of tar that hindered the observation of aggregates in the scanning electron microscope. Nonetheless, using the proposed experimental setup, soot samples have been successfully obtained in the cone calorimeter on transmission electron microscope grids from epoxy and phenolic carbon-fiber-reinforced composites.

In future works, it is recommended that a soot sampling method for electron microscope imaging be developed that is effective irrespective of the material system considered. To achieve this, materials that volatilize readily should be considered because they pose a challenge due to the tar emitted during pyrolysis. Using these materials, different locations along the travel path of the combustion products must be investigated to determine the optimal one. However, for thermophoretic sampling, this location must be in the luminous region of the flame, which constrains it to be either below the cone heater or slightly above it. With regards to the material systems, a survey of various polymeric materials should be investigated as it would reveal the broad range of microstructures produced during their combustion in conditions similar to those encountered in accidental combustion scenarios.

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CHAPTER 11 APPENDIX

11.1 Formation and oxidation of soot

The soot formation process is complex and exhibits dependencies on many variables encountered in experimental configurations. Moreover, the mutual dependence between these variables makes it difficult to quantify the contribution of each to the overall formation process. To present a clearer picture, the parameters of importance in the three lifecycle stages of soot, namely inception, growth and oxidation are presented in the following subsections.

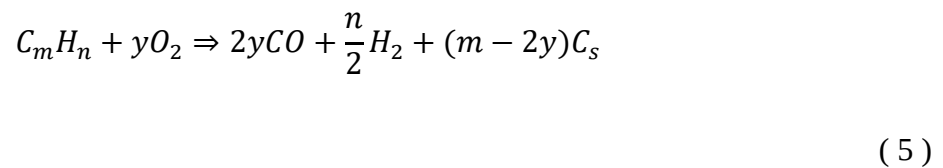
11.1.1 Inception of soot

The inception of soot, also commonly known as soot nucleation, is the process whereby condensation of gaseous hydrocarbon species occurs, thus forming individual spherical particles. The nascent particles exhibit a liquid-like consistency and form translucent images when viewed on the transmission electron microscope (TEM) [226, 227]. These particles are mainly composed of carbon and hydrogen with a hydrogen-to-carbon atom ratio H/C of 0.5, along with negligible oxygen content. In experimental studies, inception is typically determined by the onset of soot luminosity [44, 228]; the particles formed emit visible yellow light, characteristic of the radiation emitted by a black body. This inception criterion is rather inadequate because it represents a later stage of the formation process where particles have solidified through dehydrogenation, resulting in an H/C ratio of about 0.2 [229]. In fact, liquids do not emit much radiation in the visible spectrum since evaporation would occur long before they achieve the required temperature to emit yellow light. Even though this inception criterion is strictly speaking incorrect, it remains a suitable benchmark when more complex diagnostics are unavailable.

A gas phase chemical mechanism capturing the nucleation of soot has been proposed by Frenklach and Wang [230], termed the hydrogen-abstraction- C_2H_2 -addition mechanism (HACA). This mechanism relies on the abundance of key chemical species, namely atomic hydrogen (H) and acetylene (C_2H_2), to sustain the condensation of gas phase molecules leading to soot particle nucleation. In addition to these species, an aromatic molecule serves as a condensation nucleus to

sustain the inception of a soot particle. The formation of the first aromatic molecule may occur through different chemical pathways consisting of odd-carbon atom and even-carbon atom molecules but may also be bypassed altogether by the formation of multi-ring aromatic molecules. The formation of the substrate represents the first step in the soot nucleation process. The growth of the substrate is then promoted by the addition of acetylene to its surface. Before acetylene can adsorb to the surface of the aromatic molecule, free hydrogen radicals must activate it by evicting hydrogen atoms bound to the periphery of the aromatic ring. The HACA sequence is repeatedly stimulated by the deviation it induces on the thermal equilibrium and the growth of the substrate ensues until the depletion of chemical species required by the process or until the surface becomes inactivated. The interested reader is referred to Appendix 1 for a detailed description of the HACA mechanism.

As hinted by the species required in the HACA mechanism, the onset of soot formation begins in pyrolytic (i.e. fuel-rich) environments of the combustion domain. These environments are characterized by important hydrocarbon concentrations, scarce levels of oxidizing species and an observed critical temperature of about $1250K$ [44, 180]. In addition to the observed critical temperature, a critical soot inception carbon-to-oxygen atom ratio C/O of unity has been theoretically derived based on thermodynamics [29]. The following chemical equation has been considered for this derivation:



This equation assumes that the decomposition of the hydrocarbon fuel in pyrolytic environments with low oxygen concentration yields carbon monoxide (CO) and dihydrogen gas (H_2); if the C/O ratio exceeds unity, such that $m > 2y$, solid carbon (C_s) may be formed. In practice, soot inception has been observed at C/O ratios much lower than unity. Indeed, most flames produce soot at C/O ratios starting around 0.5 [231].

At inception, the number density of soot particles represents a large quantity, typically of the order of 10^{11} to 10^{12} particles/cm³ and quickly decreases as a result of coalescence and coagulation as the particles travel further [183]. However, the soot mass loading remains negligible until later stages of the formation process where surface growth dominates in the process of carbon mass addition to incipient particles [29, 175]. Numerical simulations performed by Kennedy et al. [100] indicate that coalescence quickly reduces the number of nascent particles, hence making any dependence between number density and total soot loading highly unlikely. For premixed flames however, a model by Colket and Hall [232] predicted that a linear dependence exists between the formation rate of incipient particles and the total soot loading only for lightly sooting flames and vanished as the mixture richness increased.

To gain an in-depth understanding of the soot formation mechanism, researchers often explore the effect of different experimental variables on the latter. These variables consist of parameters such as the mixture fraction, the flame temperature but also those related to the flow field in the reaction zone, such as the strain rate and the residence time. Additionally, gaseous additives are used to determine whether they exhibit a catalytic or a suppressive effect on the formation of soot.

11.1.1.1 Mixture fraction Z

The stoichiometric mixture fraction Z_{st} is known to have an effect on the sooting capability of flames in various configurations [44]. In the case of normal co-flow ethylene-air/diluted-ethylene-oxygen diffusion flames with a constant flame height, it has been observed that as the stoichiometric mixture fraction is increased, the inlet fuel mass fraction required for soot inception decreases [233]. The same trend has also been observed for the inverse co-flow flames with a constant flame height. In addition, the inlet mass fractions of fuel and oxidizer between the normal and inverse co-flow configurations at the sooting limits are almost identical for the stoichiometric mixture fraction range of $0.2 < Z_{st} < 0.4$, after which they diverge [233]. In counter-flow diffusion flames of constant flame temperature, it has been noted that a low Z_{st} flame promotes soot formation through an enhanced precursor formation while a high Z_{st} flame limits the formation of soot due to the penetration of oxidizing species in the fuel rich region [44]. In the latter flame, a competition between oxidizing and soot promoting species was outlined by the presence of a more

pronounced hydrogen radical concentration; a species known to promote soot formation. Nevertheless, an overall soot inhibiting behavior was observed upon increasing the stoichiometric mixture fraction. The suppression of soot with increasing mixture fraction has not only been observed for different experimental configurations but also across various fuels, namely methane, ethane, propane, ethylene and acetylene [228].

11.1.1.2 Temperature

The activation of any chemical mechanism depends on the satisfaction of a critical temperature condition. The soot inception mechanism is no exception to this requirement. In fact, as mentioned earlier, a critical soot inception temperature of roughly 1250K has been repeatedly reported in the literature [44, 180].

In a study performed by Kumfer et al. [233] on normal and inverse co-flow diffusion flames of ethylene/air, the adiabatic flame temperature at the sooting limits was found to increase linearly with the stoichiometric mixture fraction for both normal and inverse configurations. Despite a lower flame temperature for the inverse co-flow flame at an equal value of Z_{st} , the slope of the curves of the adiabatic flame temperature (T_{ad}) versus the stoichiometric mixture fraction for both configurations is identical. This linear dependence of the flame temperature on the stoichiometric mixture fraction has also been observed for spherical microgravity diffusion flames [234]. This relationship serves as a boundary between the permanently blue regime and the sooting regime and accurately captures the experimental observations of various normal gravity flames available in the literature. The least squares regression of T_{ad} as a function of Z_{st} for experimentally determined sooting limits in normal-gravity flames yields a linear relationship from which result an experimental critical temperature and C/O ratio of 1838K and 0.59, respectively. The linear relationship between the adiabatic flame temperature and the stoichiometric mixture fraction is exhibited not only across different experimental configurations using the same fuel, but also across different fuels, namely methane, ethane, propane, ethylene and acetylene [228]. With regards to the critical temperature required for soot inception across different fuels, at a fixed stoichiometric mixture fraction, methane requires the highest temperature, followed by ethane, propane, ethylene

and acetylene [228, 235]. This observation applies to co-flow diffusion flames but it is also confirmed for premixed flames [236].

11.1.1.3 Flow field (i.e. strain rate & residence time)

The effect of the flow field on the soot inception mechanism is often investigated by considering the residence time or the strain rate, depending on the experimental configuration. The residence time is inversely proportional to the velocity of the reactant streams in the flame [233]. However, most studies focus on the strain rate of the flow field to implicitly capture the effect of the residence time on soot formation [185, 237]. The strain rate represents the velocity gradient with respect to the spatial coordinates, therefore, an increase in the strain rate translates into a decrease in the residence time. Besides the effect of the stream velocity on the residence time, in co-flow diffusion configurations, a strain rate component also results from the buoyancy force [233]. In counterflow diffusion flames, buoyancy is negligible because the flame forms in a domain of the flow field characterized by forced convection, whereas for microgravity diffusion flames, the buoyancy effect is cancelled by the absence of gravitational force [234].

A comparison between the fuel mole fraction of microgravity and normal-gravity diffusion flames at their sooting limits [34, 35] shows that, at an equal mole fraction of oxygen, the latter require a higher mole fraction of fuel to produce soot. Additionally, the effect of convection direction was negligible on the sooting limits of spherical microgravity diffusion flames [234]. In counter-flow diffusion flames at their sooting limits, as the stoichiometric mixture fraction increases, the strain rate required for soot suppression decreases. In other words, as the fuel stream is progressively diluted, the rate of soot particle inception decreases, thus requiring a lower strain rate for suppression. This observation is valid for a large spectrum of Z_{st} values, namely $0.06 < Z_{st} < 0.66$. For normal co-flow diffusion flames, the effect of stoichiometric mixture fraction on the sooting limits is studied based on the height at which soot becomes luminous [44]. This height effectively indicates the characteristic time required for soot inception; a slow inception mechanism results in soot being observed high above the rim of the burner and vice versa. The results show that the sooting limit flame height is relatively constant for a stoichiometric mixture fraction in the range of $0.3 < Z_{st} < 0.6$. Theoretically, an increase in the sooting limit height should be observed in this

range but the noted behaviour is associated with experimental limitations, namely heat loss to the burner rim. As the stoichiometric mixture fraction is progressively increased toward $Z_{st} = 0.7$, the sooting limit flame height exhibits an exponential behaviour. In fact, at a mixture fraction of $Z_{st} = 0.72$, the sooting limit height tends toward infinity.

11.1.1.4 Inert and active gaseous additives

It is intuitive to expect that the dilution of reactants by inert gases will influence soot formation. For example, the introduction of water vapor (H_2O) in the reactant stream will lower the flame temperature, thus lowering the soot yield. The same observation can be made for other inert species with large heat capacities such as nitrogen (N_2) or characterized by high molecular diffusion rates such as helium (He). Chemically active species exhibit soot inhibiting effects through chemical activity but also through thermal and dilution effects; such species consist of molecular hydrogen (H_2) carbon monoxide (CO) and carbon dioxide (CO_2). Therefore, to understand the soot inception phenomenon, it is important to understand the effects of different inert and chemically active species on the formation mechanism. The addition of gaseous species, whether inert or chemically active, has been investigated in various flame configurations.

Du et al. [237], Gu et al. [36], Pandey et al. [40], Gulder et al. [38] and Guo et al. [39] report a suppressive effect on soot yield upon addition of H_2 . The suppressive effect is materialized mainly through a dilutive mechanism due to the preferential diffusion of H_2 , but a chemical effect of a lesser magnitude could also be observed. The effect vanishes for aliphatic hydrocarbons heavier than ethylene [38], possibly due the high amounts of atomic and molecular hydrogen produced by these fuels upon pyrolysis. With regards to CO_2 addition, Gu et al. [36] and Oh et al. [37] observed a combined chemical and dilutive effect of CO_2 on soot suppression, with the latter being much more important in magnitude. A similar observation was made when the additive consisted of CO [35]. Leusden et al. [238] studied the effect of oxygen addition on soot yield and noted that when oxygen is added to the fuel stream, an increase in the temperature, soot volume fraction and concentration of heavier aliphatic hydrocarbons could be observed. Soot volume fraction also increased when oxygen was added to the oxidizer stream. The authors conclude that the overall effect of oxygen addition on soot formation is of thermal nature.

11.1.2 Growth of soot

The growth of soot particles and aggregates can occur through various mechanisms depending on the domains of the flow field considered; these mechanisms can either be chemical or physical in nature. The chemical mechanisms dominate in high temperature environments where radicals and stable species associated with soot growth are abundant. The physical mechanisms consist of coalescence and coagulation; their occurrence and behavior is rather poorly understood [175]. These chemical and physical processes may also operate concurrently [239].

When discussing soot growth, we refer to both the growth of primary particles and that of aggregates. The growth of primary particles typically occurs by coalescence, whereby two or more incipient particles - in a viscous liquid state - collide and merge to form a larger spherical particle. By extension of the particle inception HACA mechanism to surface growth, the primary particles may also grow concurrently by accommodating hydrocarbon species such as acetylene and PAHs on their surface. However, due to the depletion of active sites on the surface, growth by surface addition does not proceed indefinitely and seems to be controlled by the abundance of active sites generated upon inception. In fact, the number of active sites is not a function of the surface area of soot but rather of the thermochemical history during inception. With regards to the growth of aggregates, it occurs by coagulation, which requires the primary particles to have solidified through dehydrogenation. Coagulation is responsible for the fractal morphology observed in soot aggregates. In the following, the most important processes characterizing soot growth will be briefly summarized.

11.1.1.5 Surface HACA

The surface hydrogen-abstraction- C_2H_2 -addition mechanism (i.e. surface HACA) is thought to be the dominant mechanism responsible for carbon addition to incipient soot particles. For instance, in co-flow diffusion flames, 92 % of soot mass is attributed to surface growth [240]. The extension of the HACA inception mechanism to surface growth is a result of the chemical similarity hypothesis [230, 241]. This hypothesis supposes that the surface of incipient soot particles behaves like a PAH molecule such that the elementary chemical reactions occurring on nascent soot

particles may be assumed to also occur during surface growth. As such, the edges of a young soot particle are thought to be composed of an aromatic hydrocarbon, that is, hydrogen atoms bound to a cyclic carbon structure. Even though the surface HACA mechanism is essentially composed of the same steps as the gas-phase HACA mechanism responsible for inception, some details are debated. This debate stems from numerical simulations that outline a temperature dependence of the surface growth mechanism in laminar premixed flames [230]. The main point of difference between the two HACA mechanisms is that the acetylene addition step in the surface HACA mechanism is postulated as being an irreversible step. To reconcile the surface HACA model with the numerical findings, a correction factor α was introduced, which captures the temperature dependence of the soot surface growth mechanism but also the particle size dependence.

The HACA mechanism of surface growth operates as a propagating front of radical sites which allow the addition of aliphatic compounds, mainly acetylene, to the surface of young particles; the five-member aromatic compounds present on the surface are readily converted into six-member aromatics. Any imperfections potentially developing on the surface of the growing particles may inhibit further growth; such defects may occur as a result of collisions of surrounding solid particles with this front [242].

11.1.1.6 Contribution of PAHs to growth

The initial understanding of the surface growth phenomenon did not consider the contribution of PAHs to surface growth under the assumption that PAH concentrations are negligible. A study on laminar premixed ethylene-air flames showed that the concentrations of PAHs in the growth region were important enough to be considered [243]. Additionally, a large proportion of the identified PAHs consists of the highly reactive five-member rings on their periphery [243]. The updated surface growth mechanism consists of acetylene addition to PAHs, acetylene addition to soot and PAH addition to soot. Moreover, the collision efficiency of PAHs with soot is 5000 times larger than that of acetylene with soot. In fact, the contribution of PAH to soot growth is of the order of 95%, as mentioned by the authors. The collision efficiency, for both PAHs and soot, is somewhat proportional to the H/C ratio and decreases with the height above the burner, as observed in

premixed flames. Indeed, as the PAHs grow, their H/C ratio decreases from 1.0 to 0.4 whereas for nascent soot, it decreases from 0.5 to 0.1.

11.1.1.7 Atomic hydrogen concentration

We recall that atomic hydrogen is responsible for the activation of soot particles for acetylene and PAH addition. In numerical simulations, the H-atom concentration was often assumed to be in thermodynamic equilibrium [244]. To verify this assumption, H-atom concentration measurements have been performed in the soot growth region of laminar premixed methane-oxygen flames. It was found that the concentration of H-atom was in thermodynamic equilibrium despite the major product species concentrations being in a transient thermodynamic state [245]. Additionally, observations show that the H-atom concentrations increase with the fuel equivalence ratio as well as with temperature.

11.1.1.8 Surface aging

The state of chemical inactivity of the surface of soot particles is termed surface aging. Two explanations of the surface aging mechanism have been proposed; the first involving the abundance of free hydrogen atoms while the second pertains to a reduction in the number of active sites where hydrocarbon addition can take place. The first cause of growth stagnation is triggered by a low concentration or a super-equilibrium of free hydrogen atoms as well as a decrease in the number of active sites at the soot particle surface. The decrease in active sites on the particle surface was correlated with a decrease in the H/C ratio of the particle as a result of dehydrogenation and annealing [243]. The second cause for surface growth stagnation is the development of surface defects [175]. If the surface of a soot particle is assumed to be composed of aromatic edges and that growth occurs peripherally, there may be occurrences where voids form due to the inability of the particle to accommodate the growth molecule on its surface.

11.1.1.9 Growth dependence on the surface area of soot

Surface growth was initially thought to be proportional to the surface area of the soot particles [246]. An investigation of the surface growth rate in laminar premixed ethylene-air flames later showed that the surface area of soot does not change substantially with the residence time in the flame. The relatively constant surface area observed through extinction methods is a result of a balance between the coagulation of soot particles, which reduces the surface area and surface growth, which increases it. Haynes et al. [183] introduced metal additives (Caesium: Cs) to reduce the amount of coagulation and thus, increase the surface area of soot particles. The surface growth rate was not enhanced by increasing the surface area available for carbon addition. Thus, no dependence of the surface growth mechanism exists with respect to surface area. Woods and Haynes [247] used measurements of the particle size, number density, species concentrations and surface growth rates from five ethylene-air flames to determine the effective soot radical site density as a function of residence time. By assuming that acetylene represents the growth species, they have shown that the radical site density decreases with increasing residence time. They demonstrated that the surface growth rate depends strongly on the number of active sites present on the particle surface at inception, which in turn depends on the flame environment. In addition, the number of active sites also possesses a strong dependence on temperature; they are assumed to become inactivated solely due to thermal processes, which are time dependent.

11.1.1.10 Coagulation

The physical aggregation of primary particles to yield elongated chains is another aspect of soot formation which needs further investigation. The current understanding of the soot growth mechanisms does not allow to pinpoint the exact stage at which individual particles cease chemical growth and begin physical aggregation, i.e. the transition from coalescent to fractal growth [175]. Such a stage may not even exist because coagulation may occur concurrently with surface growth. In laminar premixed methane/oxygen flames, a short residence time was determined to be responsible for a low degree of soot aggregation, when compared to soot aggregates acquired in similar flames with higher residence times [245].

In order to avoid confusion, it is important to reiterate the difference between the terms coalescence and coagulation; the former refers to the merging of two spherical particles to form a larger spherical particle while the latter results in the two spherical particles being joined, sharing a region of contact while preserving their individual spherical shape [248]. Soot aggregates are composed of spheroidal primary particles coagulated together to form elongated chains. Numerical simulations of aggregate growth where surface growth and coagulation occur concurrently show that two variables affect the level of sphericity of the primary particles in an aggregate: the first is a sufficient growth rate while the second is the size of the colliding particles [101, 249]. If the growth rate is sufficient, the smaller particles aggregated at the edges of larger ones will be readily buried but as the size of the colliding particles grows, their individual nature is preserved in the aggregate due to the inability of the surface growth rate to bury them. These numerical observations agree very well with the observed geometries of soot aggregates therefore, particle aggregation and surface growth may not be temporally separated events.

11.1.3 Oxidation of soot

Most studies on the oxidation mechanisms of soot are often performed in reactors instead of the flame environment in which they have been produced. Since flame environments are difficult to characterize in terms of temperature, flow field and species concentrations, it is preferable to have controlled conditions to accurately quantify the contribution of the different parameters involved in oxidation mechanisms. For the above reasons, oxidation of soot is studied in reactors operating in two ranges of temperatures, namely between 300 and 700°C and above 800°C [101]. The former range represents oxidation conditions in post-flame gases, such as soot oxidation apparatuses in diesel engine exhaust systems. The latter range is typically encountered in flame environments, whether very near the reaction sheet or immediately downstream.

11.1.1.11 Particle-size-dependent oxidation regimes

When discussing the oxidation of solid carbon, particles are divided into categories based on their size [187]. The "agglomerate" category consists of particles with sizes between 1 and 100 μm , consolidated by the forces between the material adsorbed on their surface. The "particle" category spans dimensions between 0.1 and 1 μm . The agglomerates and particles exhibit high porosity levels, which increase the

surface available for oxidation reactions. The "spherule" category represents sizes between 10 and 50 nm and individual spherules are joined by means of carbon deposition at their interface. In addition, spherules are characterized by a denser packing resulting in oxidation occurring almost exclusively at the outer surface. Across all domains, the surface of soot exhibits wrinkling due to the presence of 5 and 7-member aromatic rings and dislocations. Various studies found that a sufficiently long residence time for soot particles in high temperature locations ($> 1000^{\circ}\text{C}$) increases the order in the structure and results in more compact particles [10].

The chemical oxidation mechanism of soot consists of a large number of steps, involving adsorption, rearrangement and desorption [101]. The adsorption step represents the addition of a gaseous atom, a radical or a molecule to the surface of the soot particles, thus yielding a surface complex. The surface complex may rearrange itself due to other complexes or functional groups present in its immediate vicinity. Following the potential complex rearrangement is the desorption step, whereby a gaseous molecule vaporizes from the surface of the soot particle.

Based on the porosity of the different size domains enumerated above, three oxidation regimes are assumed to exist when discussing oxidation in a per surface basis [187]. *Regime I* consists of the oxidant being able to penetrate the porosities and thus, internal surfaces are reacting. In this regime, diffusion of the oxidant to the inner surfaces is thought to occur faster than the rate of oxidant consumption, hence the rate of oxidation is controlled by the reaction rate. *Regime II* is similar to *Regime I* however, the diffusion rate of oxidant to the exposed surfaces is slower than the reaction rate; the oxidation rate is therefore diffusion limited. *Regime III* consists of reactions occurring exclusively on the outer surface due to the inability of the oxidant to penetrate the core of the primary particles; spherule oxidation belongs to this regime as a result of the lack of porosities or their dimensions [101, 102]. The effectiveness of porous solid combustion, commonly known as the Thiele modulus, combines all the parameters thought to affect the combustion of porous solids. Among these is a parameter which captures whether the regime of surface oxidation is diffusion-limited or whether it is limited by the oxidation reaction rate. As a result of the discussion above, the diffusion phenomenon is a parameter of fundamental importance in the oxidation of soot.

11.1.1.12 Low temperature oxidation ($< 800^{\circ}\text{C}$)

Low temperature oxidation is typically investigated in isothermal environments but also in temperature-ramping experiments. The isothermal experiments consist of fixed beds of soot aggregates mixed with other

inert solid particles such as quartz, kaolin, silicone carbide or aluminum oxide [250, 251]. The dilution of the soot is performed to ensure that the thermal inertia of the bed is large, such that the isothermal condition is fulfilled throughout the duration of the experiment, especially when exothermic reactions involving soot oxidation occur. The temperature-ramping experiments consist of temperature-programmed oxidation (TPO) and thermogravimetric analysis (TGA). In TPO experiments, the temperature is slowly increased, and the products of combustion are continuously monitored to identify the reactions at play and their onset temperature. Using TGA, it is possible to measure the quantity of adsorbed material as a function of temperature by continuously weighing the sample. The low temperature oxidation can yield insight with regards to the intrinsic kinetic rates. It has been found that soot oxidation can efficiently take place in post flame gases provided that oxygen is abundant [252]. The chemistry of carbon oxidation involves different oxidizing species, namely molecular oxygen (O_2), atomic oxygen (O) as well as the hydroxyl radical (OH). All these species participate in the oxidation of carbon to different extents, however, OH is more potent [253, 254]. In low temperature environments, hydrogen peroxide (H_2O_2) was found to also participate in oxidation reactions [255]. In fact, increasing the flow rate of hydrogen peroxide (H_2O_2) in a diesel engine exhaust system resulted in increased levels of CO and CO_2 , thus making apparent the potential of hydrogen peroxide to oxidize soot in low temperature applications. For temperatures between 150 and 450°C, molecular oxygen (O_2) was observed to adsorb to Spherocharb (carbon substrate) and result in a metastable complex which desorbs only after a time delay or an increase in temperature; the main product of this reaction is carbon monoxide (CO) [252]. To determine the limiting step in the mechanism of soot oxidation, the relative kinetic rates of the different steps must be quantified. For this purpose, Soete et al.[250] used a bed of hydrocarbon-derived soot diluted in quartz beads operated in a transient temperature mode between 350 and 700°C. The steps of interest in the mechanism consist of the adsorption of O_2 and CO and the desorption of CO_2 . In ascending order of magnitude, the kinetic rates consist of the adsorption of O_2 , desorption of CO and desorption of CO_2 . This sequence indicates that the oxidation mechanism, and thus the gaseous yield, is controlled by the ability of the oxygen to be adsorbed on the surface of soot particles, at least for the temperature range considered. The primary products of soot oxidation consist of CO and CO_2 and their relative yield depends on the temperature and oxygen abundance. In low temperature environments with oxygen excess, most experimentally-determined CO/CO_2 concentration ratios are unity however, values as low as 0.12 have been reported for the catalytic combustion of soot using metal oxides [256]. Upon addition of water vapor, the water-gas shift reaction favours formation of CO_2 instead of CO . As the temperature increases, CO production increases but when the temperature approaches 800°C, conversion of CO to CO_2 occurs readily.

11.1.1.13 High temperature oxidation (> 800 °C)

High temperature oxidation is representative of temperatures encountered in flame environments and are performed in laminar burners and shock tubes. Shock tubes are especially efficient at producing high temperatures (up to around 3500 K) in controlled environments. In addition, the shock waves help achieve a homogeneous distribution of soot aggregates along the cross-section perpendicular to the direction of travel of the shock. As a result, the oxidation is more efficient since the local particle density is smaller and thus, oxidizer starvation is less likely to occur locally due to oxidant consumption.

At higher temperatures, representative of gasification environments (larger than 800 °C), important complexes form and include, in order of increasing stability, carbonyl, semiquinone and pyrone [257]. Even though these complexes may cover a large portion of the surface of soot, only a fraction of them participate in gasification reactions. An investigation on the reaction mechanism of oxidants such as O₂, H₂O, CO₂, NO, NO₂, N₂O shows that the mechanism is composed of two global steps [101]. The first step involves the adsorption of an O-atom and formation of a complex while the second step results in the decomposition of the complex and the desorption of a C-atom. The gaseous yield of this sequence is carbon monoxide, produced with an efficiency that depends heavily on the oxygen occupancy at the surface of soot, which correlates with the type of oxidant used. The occupancy depends on the ability of the oxidizer molecule to dissociate; a process with an activation energy dependent on the oxidant used.

The study of soot oxidation performed in flame environments relies on correlations between the concentration profiles of available species across the reaction front. Hwang et al. [45] investigated such concentration profiles in numerical simulations of counter-flow ethylene flames in the soot formation (SF) and soot-formation-oxidation (SFO) configurations. They have found that peak PAH profiles in the SFO configuration are an order of magnitude smaller than in the SF configuration. In addition, the PAH profile exhibits a bimodal distribution with a local maximum on the fuel side of the flame and a global maximum on the oxidizer side. The researchers postulated that the larger PAH peak may be due to soot oxidation, thereby releasing some of the aromatic structures found in soot. Chung et al. [258] performed a numerical analysis on counter-flow propane flames to study the effect of oxidation on particle growth. In the SFO configuration, the investigators found that the number of carbon atoms per particle decreases due to particle fragmentation. This observation was made where the soot particles crossed the stagnation plane and coincided with important concentrations of atomic oxygen (O) and hydroxyl radicals (OH). Using an identical configuration with ethylene and air as the reactants, Du et al. [44] investigated the effect of varying

the oxidant concentration in the oxidizer stream. When the oxidizer stream is undiluted (i.e. 100% O₂), the profiles of O and OH penetrated deeper into the fuel side of the flame, readily attacking soot precursors. With the magnitude of the OH profile being larger than the magnitude of the atomic oxygen, the former is thought to be the dominant species responsible for soot oxidation. In a review paper by Kennedy [100], it is mentioned that the species responsible for oxidation consist of O₂ and OH but other oxygenated species such as H₂O, CO₂ may also participate in oxidation reactions. In addition, his review of the available literature confirms that the limiting step in the oxidation mechanism is the adsorption of oxygen on the surface, stating that the diffusion of oxygen to the surface does not limit the rate of oxidation considering the small size of the soot particles. A study by Vander Wal and Tomasek [102] investigated the effect of the nanostructure of soot from different fuels on the oxidation behavior. Soot generated in a tube furnace from ethanol, benzene and acetylene was seeded into an oxygen-rich methane flame ($\phi < 1$) of a McKenna burner. The observations indicate that for all types of soot, the oxidation increases with the oxygen content of the post-flame gases. The soot synthesized from acetylene required a higher oxygen concentration to exhibit the same level of burnout as the soot from the other fuels. This behavior is attributed to the highly crystalline structure of acetylene soot, as compared to the other types of soot. In fact, the soot from benzene and ethanol displays small and curved graphene segments, respectively, whereas the soot from acetylene exhibits long and concentric segments. A highly disordered soot structure consists of a large amount of edge carbon atoms with unpaired electrons which readily form bonds with adsorbed oxygen.