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The Dynamics of Buoyant Fires and their Suppression with Chemically Enhanced Water Mist

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Declaration

I, Tony Xiao, declare that this thesis is my own work and has not been submitted in any other form for any other degree or diploma at any other university institution or tertiary education. The intellectual content of this thesis is the product of my own work and all the assistance received in preparing this thesis and sources have been acknowledged.

Author: Tony Xiao

Dedication

This thesis is dedicated to my family and my late grandfather, who, throughout my life, provided me with his wisdom, strength and love for this world which he had left behind. I wish I could have said these words to you in person, but thank you for being such a big part of my life.

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Publications

Chapters 3, 4 and 5 resulted in published journal papers where I designed the study, analysed the data and wrote the drafts of the manuscripts. References as listed below:

- T. Xiao, V. Gupta, A. R. Macfarlane, C. Kennedy, M. J. Dunn, A. Kourmatzis, J. L. Torero, and A. R. Masri. On the structure of buoyant fires with varying levels of fuel-turbulence. In: *Combustion and Flame* 257 (2023), p. 112993. [1]
- T. Xiao, V. Gupta, M. J. Dunn, and A. R. Masri. Joint OH-PLIF and Mie scattering imaging of enhanced water mist suppression of buoyant fires. In: *Proceedings of the Combustion Institute* 40 (2024), p. 105331. [2]

Chapters 3, 4 and 5 resulted in conference papers where I designed the study, analysed the data and wrote the drafts of the manuscripts. References as listed below:

- T. Xiao, V. Gupta, M. J. Dunn, A. Kourmatzis, J. L. Torero, A. R. Masri, Some characteristics of buoyant fires with varying levels of turbulence. 13th Asia-Pacific Conference on Combustion. Dec 2021
- T. Xiao, V. Gupta, M. J. Dunn, A. R. Masri, Water Mist Fire Suppression of the Sydney Buoyant Turbulent Fire Burner. Australian Combustion Symposium, November 2023.

Attestation

In addition to the statements above, in cases where I am not the corresponding author of a published item, all references to the sources have been acknowledged.

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As the supervisor for the candidature upon which this thesis is based, I can confirm that the authorship attribution statements above are correct.

Supervisor: Assaad R. Masri

Abstract

This thesis presents experimental results based on the Sydney Fire Burner that produces 10 - 40 kW CNG turbulent buoyant diffusion flames. This thesis focuses on revealing complex fire phenomena, specifically buoyant fires, and the effects of enhanced fuel-turbulence levels and their suppression through chemically enhanced water mist. The novelty of the burner employed is the ability to control fuel-turbulence purely through the inclusion of a perforated plate that is recessed inside the burner.

The burner is characterised through means of LDV, used to obtain exit plane boundary conditions of velocity for the different fuel flow rates, and fuel-turbulence levels. DSLR images and LDV show that the changes observed in flame structure due to enhanced turbulence are achieved purely through the inclusion of the perforated plate and not through the change in HRR. High-speed (250 Hz) simultaneous imaging of OH-PLIF and Mie scattering of soot is applied to all flame cases, where the measurements are used to temporally resolve the evolution of flame structure with increasing fuel-turbulence levels. Classical flame pinch-off instabilities are observed where local quenching creates separate flame pockets. The flames begin to transition from a varicose to sinuous type instability with increasing levels of fuel-turbulence, thereby shifting the mechanism of oxidiser transport into the flame. This also correlates with increased flame wrinkling observed in the upstream region of the flame, which is typically dominated by diffusive forces.

The flame co-flow is then seeded with fine water mist droplets ($d_{32} \approx 50\mu m$) at varying concentrations of alkali metal salts (KHCO_3 and NaHCO_3) to observe the effects of enhanced

suppression through water mist. An unprecedented characterisation of the boundary conditions is measured through PDPA, obtaining droplet size distributions, velocity and flux. Average flame extinction delay times are measured for varying flow rates of water mist and concentrations of inhibitors to produce flame stability maps, comparing suppression efficacy, giving the following inhibitor rankings: $\text{KHCO}_3 > \text{NaHCO}_3 > \text{H}_2\text{O}$. Since enhanced water mist suppression works through gas phase cooling and inhibition of the high temperature reaction zones, high-speed (400 Hz) simultaneous imaging of OH-PLIF and Mie scattering of droplets is performed to temporally and spatially resolve droplet and inhibitor transport in the flame front.

Chemically enhancing water mist has shown promising results for use in real applications. However, this can be further improved by the use of a more powerful flame suppressant such as ferrocene, an additive that is not only more effective than alkali metal salts but is also non-corrosive and non-conductive. Multiple implementations of aqueous dispersion of ferrocene are tested to assess suppression efficacy. Unfortunately, no enhanced suppression was observed, however, the method of host-guest inclusion of ferrocene shows the most promise for further research.

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Nomenclature

Variable	Description	Units
<u>Roman Symbols</u>		
A	Area	(m ²)
$\text{\AA}$	Angstroms	
B_M	Spalding mass transfer number	
B_f	Flame blow-off percentage	
C	Solute concentration	(ppm (mass/mass))
C_d	Drag coefficient	
c_p	Specific heat	(kJ/kg)
D	Burner/pool/droplet diameter	(m or mm)
D_0	Initial droplet diameter	(μm)
D^*	Non-dimensional flame diameter	
d_{10}	Arithmetic mean diameter	(μm)
d_{32}	Sauter mean diameter	(μm)

Da_I	First Damköhler number	
dt	Change in time	
$\frac{du_p}{dt}$	Particle acceleration	(m/s ²)
dx, dy, dz	Grid cell size	
F_{OH}	OH counts	
F_{OH}^-	OH spatial presence	
Fr_f	Buoyancy-momentum flame Froude number	
g	Gravity	(m/s ²)
ΔH_c	Heat of combustion	(MJ/kg)
LOC	Limiting oxygen concentration	
L_f	Flame height	(m)
L_r	Recess distance	(mm)
M	Arbitrary molecule or Molar concentration	(mol/L)
$\dot{m}$	Mass flow rate	(kg/s)
$\dot{m}'_w$	Air entrainment rate	(kg/s)
Nu	Nusselt number	
Pr	Prandtl number	
Q_f	Flame heat release	(kJ)
Q_w	Heat absorbed by water	(kJ)
$\dot{Q}$	Flame heat release rate	(kW)

$\dot{Q}^*$	Non-dimensional heat release rate	
$\dot{Q}_c$	Convective heat release rate	(kW)
r	Radius	(m or mm)
Re	Reynolds number	
Sc	Schmidt number	
Sh	Sherwood number	
Re_D	Reynolds number with characteristic length D	
Re_s	Reynolds number with characteristic length s	
S	Air to fuel mass stoichiometric ratio or strain rate tensor	
t	Time	(s)
T_∞	Ambient/far-field air temperature	(K)
T_o	Ambient air temperature	(K)
$\Delta\bar{T}_{fa}$	Modified mean peak flame temperature rise	(K)
u'	RMS velocity	(m/s)
u_x, u_y	Axial and radial velocity	(m/s)
$\dot{v}$	Volumetric flow rate	(mL/min)
V_c	Grid cell volume	
$\%w/v$	Solute concentration	(g/100mL)
x, y, z	Distance in space or position vector	(m or mm)
$\dot{x}, \dot{y}, \dot{z}$	Derivative of x,y or z	

$\ddot{x}, \ddot{y}, \ddot{z}$ Second derivative of x,y or z

X_α Mole fraction of species α

Y_α Mass fraction of species α

Greek Symbols

κ Curvature (1/mm)

μ_t Local eddy viscosity

∇ Gradient

ϕ General field expression

$\bar{\phi}$ General filtered field expression

τ_{time} Characteristic time scale (s)

τ_{mix} Characteristic mixing/flow scale (s)

τ_f Integral time scale (s)

ρ_∞ Ambient/far-field density (kg/m³)

ρ_o Ambient density (kg/m³)

ρ Single-point Eulerian auto-correlation function

σ Cross correlation, inhibitor concentration

ϵ Turbulence intensity (m/s)

Δ LES filter width

Abbreviations

CARS	Coherent Anti-Stokes Raman Spectroscopy
CFD	Computational Fluid Dynamics
CNG	Compressed Natural Gas
DSLR	Digital Single-Lens Reflex
EtOH	Ethanol
FDS	Fire Dynamics Simulator
Fc	Ferrocene
FFT	Fast Fourier Transform
FWHM	Full Width Half Maximum
HRR	Heat Release Rate
ID	Inner Diameter
LII	Laser Induced Incandescence
LDV	Laser Doppler Velocimetry
LES	Large Eddy Simulation
MaCFP	Measurement And Computation Of Fire Phenomena
OH	Hydroxyl Radical
PDF	Probability Density Function
PDA	Phase Doppler Anemometry
PLIF	Planar Laser Induced Fluorescence
PVC	Probe Volume Correction

RMS	Root Mean Square
SHAR	Spray Heat Absorption Ratio
SGS	Sub-Grid Scale
SLM	Standard Litres per Minute
UV	Ultra Violet

Chapter 1

Introduction

1.1 BACKGROUND AND MOTIVATION

Fire has played a critical role in the shaping of human civilisation, with its influence stretching from basic needs such as heat and lighting to transport and large-scale industrial processes. However, when uncontrolled, this becomes a formidable force that demands respect and careful management to mitigate its destructive potential on both human lives and property. Historically, fires have left an ever-lasting impact on cities and societies around the globe, with several infamous historical fire incidents serving as reminders of their destructive potential. Major incidents include but are not limited to, The Great Fire of Rome in 64 AD, which consumed large portions of Rome, reshaping local urban landscapes [3]. The Great Fire of London 1666 destroyed much of the city, resulting in significant advancements in fire safety regulations in the UK [3]. The Great Chicago Fire of 1871, burned through the heart of the city destroying thousands of buildings [4], eventually leading to the establishment of modern fire departments in the United States. These historical fires have not only caused immense destruction to residential and commercial property but have also resulted in extremely high death tolls. This has paved the way for societies to treat the issue of fire safety seriously, introducing the ideas of preventive measures and innovative regulations to

manage the ever-growing list of fire hazards. However, in recent years, building envelopes have evolved dramatically in size and complexity, presenting new challenges for fire safety. These developments have driven further technological advances in various engineering fields, including but not limited to material science, structural engineering, wind engineering, acoustics and many more. Fire safety science saw the first passive fire protection systems being developed in the early 20th century [5] but has however, seen an exponential growth in the complexity of physics required to predict flame spread in modern infrastructure. As a result, modern-day fire-related incidents are unfortunately plentiful in number and high in casualties. The most notable recent high-rise building fires include the Grenfell Tower fire in 2016 [6]. Of particular note, the Grenfell Tower fire has prompted a significant response in the UK, leading to regulatory reforms in the safety of high-rise buildings. These reforms have resulted in the evacuation of an increasing number of buildings deemed unsafe for occupation [7]. These failures in modern buildings underscore the need to expand the current knowledge base with validated and science-based fire engineering solutions.

Current building standards and construction codes related to fire prevention, safety, and suppression are still heavily empirically driven, relying on standardised experiments (prescriptive design) to extrapolate thresholds that define construction standards to achieve life safety objectives [8]. This empirically driven approach becomes hazardous when the data is applied outside its intended scope. The introduction of new open-plan building architecture and emerging hazards such as power storage systems (batteries) has significantly increased the risks associated with fire safety. Modern building envelopes now incorporate a diverse range of materials, including various types of plastics and other environmentally friendly substances. The combination of these complex systems introduces unknown levels of fire risks and hazards, which result in standardised tests being inadequate to capture the dynamics and spread of flames within complex building compartments [9]. Moreover, it is impractical to experimentally test every possible type of building envelope with different contents inside due to the vast variability in construction methods and materials. Consequently, it is essential to advance our knowledge base in fire safety science by adopting a more fundamental approach

to understanding complex fire phenomena using sophisticated experimental datasets. This shift will enable more accurate assessments and improvements in predicting fire behaviour in complex environments.

In this context, Computational Fluid Dynamics (CFD) tools such as FDS and OpenFOAM (FireFoam) are increasingly utilised to evaluate building performance under various flame ignition conditions. However, the efficacy of these models in predicting flame dynamics is highly variable across existing literature, even in the simplest of cases such as pool fires. Therefore, a deeper understanding of flame dynamics is essential. Further development of existing models is critical for accurately predicting flame spread across a wide range of length and time scales. This requires accurate CFD models validated by detailed experimental data that span a range of buoyant flames that are representative of real fire scenarios. Ultimately, the goal is to leverage CFD modelling techniques to achieve performance-based design objectives.

Fire protection comes in two categories: (i), passive, where the physical design of building structures and materials are used to achieve life safety objectives. (ii), active, which is used where passive measures fall short of meeting building design objectives or fail to maintain tenable conditions for evacuation — whether due to the complexity of the problem or economic constraints — active fire suppression methods are employed to meet life safety objectives. Active suppression either extends the margin of safety during fire-related evacuations or, in special cases, is focused on the protection of sensitive property or equipment. The most common and widely used method of fire suppression is water. Water has been, and will continue to be, the universal “go-to” fire suppression medium for the foreseeable future. This is largely due to its high specific heat capacity and latent heat of vaporisation, properties that make it an excellent fire suppressant. Additionally, water’s non-toxic nature and widespread availability in large quantities further solidify its position at the top of the fire suppression hierarchy. The primary delivery method of water-based suppression in buildings is sprinklers [10], with the goal of surface wetting to prevent further production of pyrolysis gases in a high-temperature environment [11]. This ultimately delays or prevents the onset of untenable

conditions, allowing for sufficient evacuation times. Sprinklers are primarily used in areas where water damage to property is not a priority and where mains water pressure and flow rates can sustain their continuous operation. However, since sprinklers require a constant supply of enormous quantities of water, their use and feasibility are only available where existing infrastructure supports these water demands, therefore limiting their applicability to areas without suitable supporting infrastructure.

The limited applicability of traditional water-based suppression systems has driven the development of various alternative fire suppression methods. In the 20th century, initial efforts focused on creating chemical suppressants that could rival or even surpass the effectiveness of water. Halogenated compounds, particularly Halon 1301 (bromotrifluoromethane), were among the first chemical suppressants to be widely used, developed primarily by the United States Army [12]. Halon 1301 demonstrated strong fire inhibition capabilities with relatively low toxicity [13, 14, 15, 16], which led to its widespread implementation in various systems, including portable fire extinguishers for public use, total flooding systems for electronic control rooms and storage facilities for sensitive property. However, it was not until the 1980s that the ozone-depleting potential of many halogenated compounds was identified, which led to the Montreal Protocol in 1987 requiring their total or partial phaseout[17]. This meant that alternative non-ozone-depleting fire suppression systems had to be identified and successfully installed in place of halogenated suppressants.

Currently, a multitude of modern fire suppression methods are used depending on the application. These methods include but are not limited to traditional water sprinklers, water mist systems, inert gas flooding systems, and foam suppression systems, just to name a few. Inert gas flooding systems are extremely limited in application as this requires positive pressure compartmentalisation. Foam suppression systems have attracted a lot of controversy in recent years, with concerns about toxic by-products produced in suppressing larger flames [18]. This includes the contamination via fluoridated surfactants in groundwater near multiple military sites all around the globe, with countries seeing potential phasing out of fluorinated foam suppression systems in the near future [19]. As a result, water

misting suppression systems have seen a surge in interest over the past few decades. Water mist suppression systems are unique in that they use water to target gas-phase combustion, which is significantly different from water sprinklers, where surface wetting and fuel surface cooling are the primary forms of flame suppression [20]. Initially developed for fire safety on aeroplanes and maritime ships, water misting systems have since advanced significantly to safeguard various facilities, including commercial buildings and data centres. Misting systems can be used in a variety of ways, whether to extinguish a fire or to shield a target from one, thus preventing flame spread [21]. By atomising water to produce droplet diameters smaller than 1000 microns [22], droplets no longer pass freely through the flame front but mostly evaporate on contact or within the flame sheet, utilising water's high latent heat of vaporisation to ultimately cool gas-phase temperatures, inhibiting combustion.

The suppression mechanisms behind water mist are inherently complex in nature given the interactions between water droplets and a fire. Therefore, building accurate predictive models for water mist suppression has proven to be an enormous challenge yet to be overcome. The lack of accurate models necessitates extensive full-scale testing to meet current regulatory code requirements and design standards for water mist fire suppression systems, such as those provided by FM Approvals [23]. This significantly increases the costs of implementing water mist suppression systems, which has hindered their wider adoption. To circumvent this issue, further model development is required to ensure that water mist fire suppression systems can be accurately simulated to predict flame suppression. Achieving this goal requires well-characterised experiments with near-field measurements of flame-droplet interactions and boundary conditions. These are essential for model validation, enabling models to accurately capture suppression effectiveness. Such experimental measurements include but are not limited to, droplet size distributions, velocities, and positions, all relative to the flame sheet. These datasets will facilitate the development of improved sub-models in water mist suppression.

Since water misting systems target gas-phase combustion, their suppression efficacy can be significantly enhanced through the addition of chemical inhibitors dissolved in water. This

includes common chemical inhibitors used in fire extinguishers, such as sodium bicarbonate and potassium bicarbonate. These chemical inhibitors are highly effective [24] and non-toxic, readily dissolving in water to form a stable, homogeneous solution. Due to their simplicity and low cost, alkali metal salts like sodium and potassium bicarbonate have become predominant in chemical fire suppression. However, despite the benefits of enhanced chemical suppression, the challenges associated with the implementation of water misting systems remain significant, such as the corrosive properties of an aqueous base pose many challenges: where not only does it significantly increase the initial costs of installing a corrosion-resistant suppression system, but the logistics of immediate cleanup of the suppression area after a fire is also crucial to prevent further corrosive damage to property. In response to this limitation, efforts are being made to gather more experimental data on enhanced water mist fire suppression giving engineers a better understanding of the potential benefits of chemical suppressing additives. Further efforts have recently also explored new water mist fire suppressing additives such as ferrocene [25]. These alternatives aim not only to match, but potentially surpass the effectiveness of alkali metal salts while also offering additional benefits, such as being non-corrosive and non-conductive.

To address the many challenges in modelling fire dynamics and enhanced water mist fire suppression, it is essential to conduct carefully designed experiments with well-defined boundary conditions, accompanied by high-fidelity near-field measurements of both flame structure and flame-droplet interactions. This necessity has motivated the works presented in this thesis, with the primary objective of improving aspects of our understanding of the physics underlying both complex fire phenomena and water mist fire suppression.

1.2 RESEARCH AIMS

This research aims to unravel the complex near-field structures of turbulent buoyant fires and provide a sophisticated data set of flame structure with varying levels of fuel turbulence. A water mist fire suppression experimental set-up with the same flame is also studied to look at the suppression efficacy of different chemical additives such as KHCO_3 and NaHCO_3 ,

alongside an attempt to develop methods of using ferrocene as a water mist additive. This is presented through the Sydney buoyant fire burner, which all the work in this thesis is based on. The primary objectives are as follows:

- Characterise the Sydney fire burner using PDA (Phase Doppler Anemometry) for exit plane boundary conditions and simultaneous high-speed OH-PLIF (Planar laser Induced Fluorescence) and Mie scattering of soot for flame structures with varying levels of fuel-turbulence.
- Develop a water mist fire suppression system looking at enhanced suppression through chemical additives (alkali metal salts). Characterise the boundary conditions through PDA, and create flame stability maps quantifying suppression efficacy of varying concentrations of different inhibitors.
- Apply simultaneous high-speed OH-PLIF and Mie scattering of droplets to observe flame-droplet dynamics, gaining a deeper understanding of droplet evaporation and inhibitor transport in the flame front.
- Attempts to develop new methods to deploy ferrocene as an additive in water mist fire suppression and to assess its suppression efficacy.

1.3 THESIS OUTLINE

Chapter 2 looks at previous work in the literature, on how numerical modelling in fire has been developed using empirical correlations from a variety of canonical experiments. Then it examines the recent collective push in developing experimental databases to validate various sub-models that have been developed from empirical correlations. Additionally, this chapter will also look at the current progress in chemically enhanced water mist fire suppression, focusing on how numerical modelling is applied in this context and reviewing the state-of-the-art experimental results related to chemically enhanced water mist suppression.

Chapter 3 introduces the burner used for most of this thesis work, alongside the fuel and co-flow conditions. A characterisation of the burner is performed using LDV to obtain exit plane boundary conditions.

Chapter 4 presents the experiments performed on flames with varying levels of fuel-turbulence. This includes observations of the evolution of flame structure with increasing fuel-turbulence. This is performed through the simultaneous high-speed imaging of OH-PLIF and Mie scattering of soot.

Chapter 4 presents a novel canonical laboratory-scale water mist fire suppression experiment, using the same fire burner introduced in this thesis. Fire suppression efficacy is investigated by varying the mass flow rate of the water mist, which is enhanced with alkali metal salts. Flame stability maps are generated to compare the suppression performance of different alkali metal salts at various concentrations. PDI is used to fully characterise the boundary conditions, while the high-speed simultaneous imaging of OH-PLIF and Mie scattering of droplets is used to study flame droplet interactions.

Chapter 5 extends upon Chapter 4 by increasing both the temporal and spatial resolution of the high-speed OH-PLIF and Mie scattering of droplets to obtain time-resolved chemical inhibition, observing individual droplets as they traverse the high-temperature reaction zones.

Chapter 6 illustrates an attempt to develop novel methods of implementing ferrocene as a chemical additive for water mist fire suppression. Flame stability limits of the different solutions of aqueous dispersion of ferrocene are obtained, evaluating the suppression efficacy of the various implementation methods of ferrocene in water.

Chapter 7 presents the thesis conclusion, outlining the major findings and results within this thesis. Recommendations for future work are also discussed.

Chapter 2

Literature Review

This chapter provides a concise overview of existing experimental and numerical research on turbulent buoyant fire phenomena and chemically enhanced water mist fire suppression. The review begins by examining fire dynamics and the various empirical correlations used in modern computational models for both implementation and validation. It then explores water mist fire suppression and chemically enhanced water mist fire suppression, with a focus on understanding the complex mechanisms behind flame extinction through water mist. A literature review is conducted to assess the state-of-the-art datasets used for model validation in both flame dynamics and water mist fire suppression, showcasing the challenges they face. This highlights the breadth of applications and the need for advanced laser diagnostics to probe and resolve the structures of fires. The final section of this chapter presents a brief description of the more advanced laser diagnostic techniques that are used herein, applicable to both turbulent buoyant fires and water mist suppression. Exploiting these techniques commonly used in combustion science may unveil a more fundamental understanding of both flame and droplet dynamics.

2.1 TURBULENT BUOYANT FIRE DYNAMICS

The structure and heat transfer mechanisms that govern the burning behaviour of buoyant turbulent fires are the result of multifaceted, complex, and coupled interactions between energy release (Heat Release Rate, HRR) and the fire-induced turbulent flow fields driven by buoyancy forces [26]. Fundamentally, fires are an uncontrolled combustion process that can involve gaseous, liquid, or solid fuels. At realistic length scales, fire dynamics are defined by a complex three-dimensional interaction of turbulent mixing, mass transport, flame radiation, gas-phase chemistry, and soot formation and oxidation processes that operate in a volume with length scales that can be in the order of a few centimetres to several meters [27]. Initially, at small scales, this combustion process is often dominated by gas phase diffusion, and as the fire develops, the process transitions into a more complex regime characterised by the fire-induced turbulent mixing of fuel and oxidiser, which significantly influences the overall flame dynamics [28, 29]. The scale of fire growth can be illustrated through design fires, such as a compartment fire as shown in Figure 2.1. Typically, fires initially follow a t-squared law [30] where the size of the flame in terms of HRR follows an exponential growth curve with respect to time, known as a “growth period”. In most cases, these flames reach a phase of steady-state burning (constant HRR), where the rate of production of pyrolysis gases is at its maximum (or combustion is limited due to under-ventilation), resulting in a post-flash-over fully developed fire. This is eventually followed by a “decay period” with a constantly decreasing HRR once the consumption of fuel outpaces the production of pyrolysis gases. The wide range of HRRs presented in classical design fires illustrates the difficulty of resolving near-field flame structures as such measurements become experimentally challenging due to limitations such as spatial resolution and optical accessibility. Given the wide spectrum of length scales involved in a single fire event or scenario, experimental testing also becomes prohibitively expensive and logistically challenging when attempting to assess building/structural performance [31]. As a result, computational models are often employed to prescribe fires across these varying scales. However, despite their utility, these models face significant challenges, particularly in accurately resolving near-field flame structures. The

lack of knowledge of detailed phenomena and the need to cover large computational domains (compromising between resolution and computational cost), severely limiting our capability in predicting near-field fire behaviour.

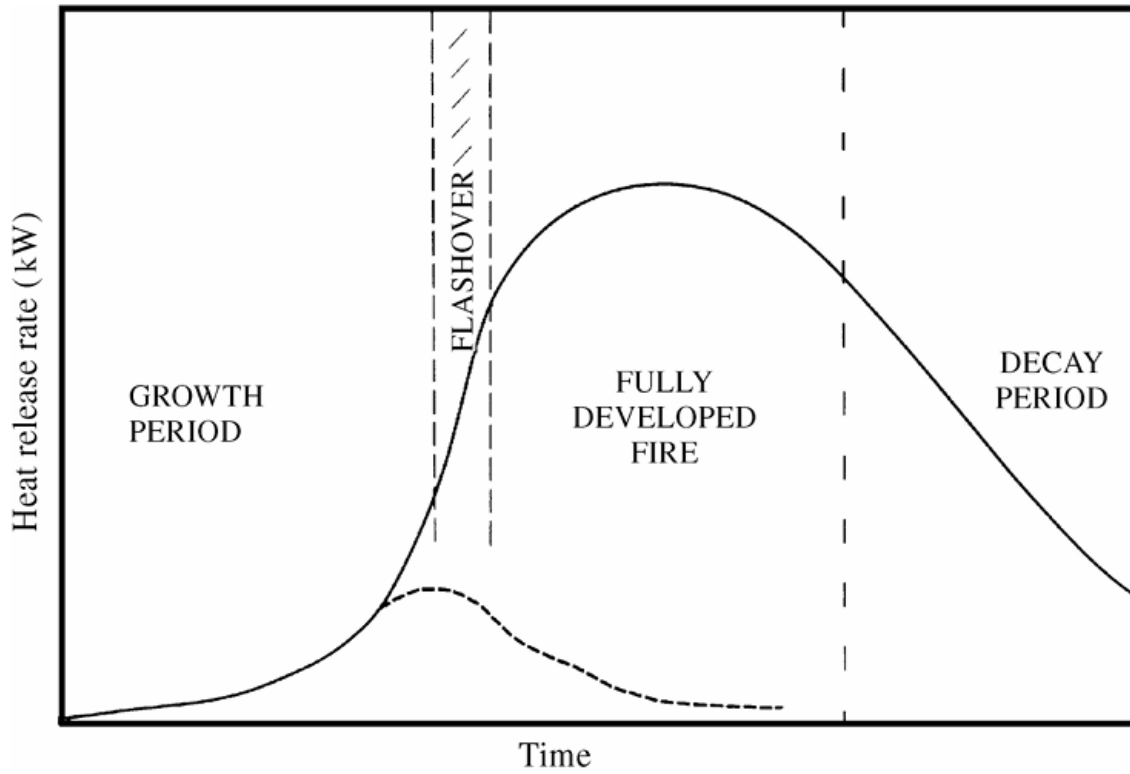


Figure 2.1: A simple design fire curve extracted from Drysdale [32].

2.1.1 Empirical correlations of fires

To address these challenges, empirical correlations offer a valuable tool for interpreting the complex coupling processes within a fire without resolving the fine near-field flame structures. These correlations, derived from extensive experimentation, provide generalised relationships for macroscopic fire features. These include but are not limited to experimental correlations such as Equation 2.1 for flame height (height L_f normalised by the pool/burner diameter D) with respect to a non-dimensional HRR $\dot{Q}^*$ [32, 27], Equation 2.2 for entrainment rates ($\dot{m}$, where z is the axial height and $\dot{Q}_c$ is the convective HRR) [33], centerline temperatures [34],

thermal feedback [35], Equation 2.3 for burning rates (m'_w) [36], global radiative fractions [37], and soot volume fractions [35, 37], all of which typically serve as integral inputs/outputs of computational predictive models [38], or are used as model validation tools.

$$\frac{L_f}{D} = 3.7\dot{Q}^{*\frac{2}{5}} - 1.02 \quad (2.1)$$

$$\dot{m} = 0.071\dot{Q}_c^{\frac{1}{3}}z^{\frac{5}{3}}(1 + 0.026\dot{Q}_c^{\frac{2}{3}}z^{-\frac{5}{3}}) \quad (2.2)$$

$$L_f = 400m'_w{}^{\frac{2}{3}} \quad (2.3)$$

The majority of existing literature has these macroscopic features characterised for very specific experimental conditions, resulting in a heavily empirically driven database used in computational modelling. This has been beneficial due to the economic viability of fast computations of fire behaviour over a broad range of mesh sizes [39, 40, 41, 42] that is amenable to resolving fire problems in traditional building structures in a variety of fire scenarios.

2.1.2 CFD and modelling approaches

Common tools for modelling buoyant fire phenomena include the likes of FDS (Fire Dynamics Simulator) and the FM Global open source FireFOAM solver. Since fire scenarios generally require large computational domains, the lack of resolution in the computational grid means that small scale structures within a flame are not resolved. Typically to address some of these challenges, large Eddy Simulation (LES) is commonly used with infinitely fast chemistry, which models the larger turbulent structures directly while relying on sub-grid scale models to represent the smaller scales. The LES equations are derived by applying a low-pass filter of width Δ to the Navier-Stokes equations. Equation 2.4 shows a general expression for a filtered field $\bar{\phi}$, where V_c is the cell volume, $\mathbf{x}$, $\mathbf{y}$ and $\mathbf{z}$ are position vectors and $d\mathbf{x}$, $d\mathbf{y}$ and $d\mathbf{z}$

are the cell sizes in the direction of their respective vectors. This low pass filter allows for only the large-scale (low-frequency) structures in the turbulent flow field to pass through, while smoothing out the small scale turbulent fluctuations, where the filter width Δ is the cube root of the cell volume V_c .

$$\bar{\phi}(x, y, z, t) \equiv \frac{1}{V_c} \int_{x-\delta x/2}^{x+\delta x/2} \int_{y-\delta y/2}^{y+\delta y/2} \int_{z-\delta z/2}^{z+\delta z/2} \phi(x', y', z', t) dx' dy' dz' \quad (2.4)$$

Since the small scale turbulent structures are filtered out (smoothed), a sub-grid scale (SGS) turbulence model is employed to close both the SGS momentum and scalar flux terms. A number of SGS models are currently implemented (user selected) in both FireFOAM and FDS, these include the Deardorff's model, constant coefficient Smagorinsky or dynamic Smagorinsky, Vreman's and WALE (Wall-Adapting local Eddy-viscosity) models. For example, the constant Smagorinsky model uses Equation 2.5 to solve for the magnitude $|S|$ of the strain rate tensor S . This uses the resolved flow of cell indices i and j , and ∇u , the gradient of the velocity vector. The local eddy viscosity μ_t is solved using Equation 2.6, which is ultimately used to close the LES by modelling the sub-grid scale stress tensor. Where C_s is the Smagorinsky constant obtained from varying methods of verification [43]. Further details on these implementations are presented in the FDS technical guide [43].

$$|S| = \left(2S_{ij}S_{ij} - \frac{2}{3}(\nabla \cdot \mathbf{u})^2 \right)^{\frac{1}{2}} \quad (2.5)$$

$$\mu_t = \rho(C_s\Delta)^2|S| \quad (2.6)$$

However, even with LES, the resolution of near-field flame structures is still fundamentally limited by the grid size and the accuracy of the sub-grid scale models. [44, 45]. To understand the scaling relationship between the numerical domain and the size of a flame, a general guideline is proposed in the FDS user guide, using a mesh scaling relationship with the non-dimensional flame diameter D^* [46] (Equation 2.7). Where $\dot{Q}$ is the total HRR of the fire (kW), ρ_∞ is the ambient air density (kg/m³), c_p is the air specific heat (kJ/kg K), g is the

gravitational acceleration and T_∞ is the ambient air temperature (K). Generally, in this case, a constant D^*/dx of 10 - 20 is maintained where dx is the size of the computational grid. Since the computation grid scales with the size of the flame ($\dot{Q}$), the smallest grid spacing (dx) is generally quite large when compared to the near field flame structures, where the flame reaction zones are typically in the millimetre scale.

$$D^* = \left(\frac{\dot{Q}}{\rho_\infty c_p T_\infty \sqrt{g}} \right)^{2/5} \quad (2.7)$$

As a result, with the rapidly increasing complexity of materials used in building construction, coupled with unique modern structural designs and emerging hazards (e.g. battery fires), the predictive capabilities of current modelling techniques are increasingly challenged. The single major drawback to the empirical nature of modern computational fire models is that they are often scenario specific (such as ideal pool fires), hence limiting the ability of such models to generalise [47]. This means that empirically driven modelling may no longer be sufficient in accurately predicting fire behaviour. To enhance the accuracy of fire models, it is crucial to better resolve the various processes at a local level. Achieving this requires carefully designed experiments with well-defined boundary conditions and detailed, quantifiable outputs. This limitation highlights the need for alternative approaches to capture the broader characteristics of fire dynamics.

2.1.3 Recent experimental data

Over the past few decades, there has been a systematic push to generate datasets that can be used to validate the sub-models of modern computational fluid dynamics codes through the development of statistically resolved databases that are amenable to validating turbulent flows [48], gas-phase temperature fields [48, 49, 50], radiative emissions [35, 51] and soot formation [50, 52, 53]. These databases provide valuable temporal and spatially resolved profiles of key quantities such as the simultaneous LII/CARS (Laser Induced Incandescence and Coherent anti-Stokes Raman Spectroscopy) measurements by Frederickson et al. [54] and

Kearney et al. [55], which deliver joint statistical data on gas-phase temperature and soot volume fraction. These kinds of databases have facilitated an improved phenomenological understanding of buoyant turbulent fires.

More recently, with the introduction of the MaCFP Working Group (Measurement and Computation of Fire Phenomena) in 2017 [56], which is endorsed and supported by the International Association for Fire Safety Science (IAFSS), establishes a common framework for a joint effort between experimentalists and modellers to target specific knowledge gaps and areas of interest. MaCFP consists of three sub-groups, one looking at condensed phase phenomena, specifically that of thermal decomposition and pyrolysis [57]. One looking at radiation and the last of particular interest for this thesis looks at the gas phase Measurement and Computation of Fire Phenomena (MacFP). The community has presented target flames/fires that have been introduced as experimental databases deemed suitable for the validation of fire models as shown in Table 2.1. These include the validation of buoyant plumes through the Sandia FLAME facility’s helium plume, flame extinction at reduced oxygen concentrations with porous sintered bronze burners, single and parallel PMMA panels for fire growth, a suite of gaseous and liquid pool fires, and a porous wall burner for wall fires. These sets of experiments provide an extensive list of experimental measurements on canonical buoyant turbulent flames in various configurations. These are also complementary to an existing list of validation data provided in the FDS validation guide.

Table 2.1: List of MaCFP target flames for model validation

Phenomena	Group	Burner/Flames	Reference
Buoyant Plumes	Sandia (FLAME facility)	Helium Plume	Sandia [58, 59]
Flame Extinction (reduced oxygen concentration environment)	FM (Factory Mutual) and UMD (University of Maryland)	FM's Ethylene Burner and UMD Line Burner	FM [52, 60, 61], UMD [62, 63]
Fire Growth	NIST (National Institute of Standards and Technology) and UMD	Parallel Panels (PMMA) and UMD SBI (Single Burning Item, PMMA)	NIST [64, 65], UMD [66]
Gaseous Pool Fires	Sandia (FLAME facility) and National Bureau of Standards	Sandia's Circular Plume and McCaffry's Porous Burner	Sandia [67, 68], McCaffery [69]
Liquid Pool Fires	NIST	Pool fires	NIST [70, 71, 48]
Wall Fires	FM	Porous Wall Burner	FM [72, 73]

Though the list of experimental measurements and configurations is quite extensive, some of the canonical scale experiments create complexities and couplings at the fuel surface that are difficult to model and require either the resolution of species transport in a porous media (sand and sintered bronze burners) or quantification of the surface energy balance (pool fires). The latter is particularly challenging as the flame-to-surface thermal feedback requires a detailed resolution of convective and radiative transport across very small length scales, which is often not amenable for validation studies due to limitations in the available data as sophisticated near-wall diagnostics are required [56]. Instead of modelling mass transport at the surface, empirical wall functions developed for non-reacting flows are usually employed, carrying significant limitations and uncertainties when extrapolated to fire scenarios [38]. Thus, the surface boundary condition that describes the local mass transport of fuel from such fire sources is poorly conditioned to validate the complex sub-models needed to scale up fire processes [74]. Also, high-fidelity measurements characterising both the spatial and temporal flame structure of buoyancy-driven flames at the scales of fires are not readily available in the literature [75] (Table 2.1). This is largely owing to the sensitivity of a buoyant turbulent flow that forms above the condensed fuel surface to the fuel boundary conditions and other parameters. An example of this complexity is demonstrated by flow visualisation measurements for the piloted ignition of an oil slick by Wu et al. [76]. These experiments show a distinct increase in the turbulence levels above the condensed fuel upon the inclusion of a flush floor surrounding the heated fuel tray, as observed by the absence of symmetric eddy structures for an isolated fuel tray. Such observations are emblematic of realistic fire scenarios at larger scales and demonstrate the importance of developing experiments at a canonical scale that have well-defined boundary conditions yet can generate controlled turbulence levels that are typical of large-scale fires. This is because the turbulence level is difficult to parameterise since turbulence is constrained to the air-side strain rate, which is governed by the fuel size, mass transfer number, and the boundary conditions for condensed fuels, or the fuel injection rate for gaseous fuels. In both cases, turbulence is generated by the buoyancy forces acting along the air entrainment region axis and is therefore not particularly amenable to being controlled and parameterised experimentally.

This has been identified as a major gap in the literature [75] and has therefore motivated the development of the burner presented here in this thesis, which stabilises buoyant turbulent diffusion flames, with a simple mechanism for introducing and controlling the level of fuel-turbulence. Boundary condition and flame structure characterisation are carried out using various advanced laser diagnostic techniques, which are described in the final section of this chapter.

2.2 FIRE SUPPRESSION

Where passive engineering alone cannot provide the required fire protection objectives, active fire suppression systems are used to supplement passive protection systems. Active fire suppression systems are ubiquitous in modern buildings and industrial infrastructure due to emerging fire hazards such as mass timber construction, combustible cladding systems [77], battery systems [78] and hydrogen storage. In light of the growing list of hazards, water mist suppression systems are emerging as a viable alternative to conventional fire protection methods [79][78], such as commonly used sprinklers and gaseous suppressants in industrial settings. In the United States, the relevant standard is NFPA 750, which defines water mist as “a water spray for which the flow-weighted cumulative volumetric distribution of water droplets is less than $1000\text{ }\mu\text{m}$ within the nozzle operating pressure range” [22]. Figure 2.2 shows where water “mist” droplets lie on a distribution of droplet sizes.

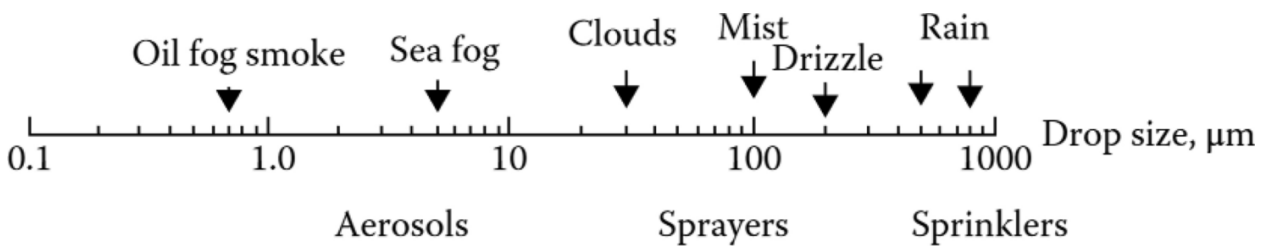


Figure 2.2: A spectrum of water droplet terminologies as a function of droplet sizes [80].

Water mist fire suppression has seen significant growth in interest over the last few decades, particularly in areas of property protection [81]. However, the increased interest has not

been reflected in application, as this is primarily due to the constraints set by regulatory bodies requiring full-scale testing to develop water mist fire protection systems [81, 23]. This leads to a dramatic increase in costs for both development and certification, impeding the advancement and use of water mist fire protection systems. Attempts to reduce the cost overhead include developing scaling relationships to downscale the size of testing facilities [82, 83, 84, 85]. However, this requires an extensive database from experiments that cover a wide range of scales and parameters such as varying fuels, levels of air vitiation, and ventilation [85]. Such a demand requires massive expenditure of time and resources but is essential if realistic design tools are to be developed. Numerical modelling of water mist fire suppression systems on the other hand would significantly reduce the costs of development and certification by eliminating or reducing the need for testing facilities.

2.2.1 Physical and thermal suppression

Water mist fire suppression follows a far more complex pathway for flame inhibition in comparison to standard water sprinklers, primarily due to the differences in both size and residence times of the droplets in the flame front. Flame extinction through water mist is typically achieved through three main physical driving phenomena with different contributions to flame inhibition [86]. The main suppression mechanisms are as follows:

- Gas phase cooling
- Fuel and oxidiser dilution
- Gas phase displacement

Gas phase cooling is the direct loss of sensible enthalpy through heat transfer between the flame sheet and water mist droplets. Water, having an extremely high latent heat of vaporisation ($\approx 2260 \text{ kJ/kg}$), effectively absorbs a large amount of energy from the flame due to droplet evaporation, leading to significant cooling of the gas phase. If the flame temperature falls below a critical threshold needed to maintain combustion as a result of

reaction zone cooling, the flame will extinguish. This is known as the quenching temperature. For diffusion flames, this limiting temperature is around 1600 K [32], and it is similar for premixed methane-air flames under certain conditions [87]. Quenching of the flame through gas phase cooling only occurs when a large number of droplets evaporate in the flame front. However, due to the small size of the water mist droplets, significant evaporation also occurs prior to the flame front due to high surrounding air temperatures and flame radiation. This allows for only a portion of the droplets to penetrate into the high temperature reaction zones, which is known as a cooling efficiency. The cooling efficiency of water spray can be represented by a “spray heat absorption ratio” known as SHAR [88], a ratio between the heat absorbed by the water droplets and the flames heat release as shown in Equation 2.8. Where Q_w is the heat absorbed by the water and Q_f is the heat release of the flame. SHAR calculations have shown that instant flame extinguishment is achieved when $SHAR \geq 0.6$, while SHAR values of $\simeq 0.1 - 0.3$ only showed flame “suppression” but not extinguishment [89]. However, SHAR is only a qualitative descriptor of suppression performance and is not suitable for direct application in numerical modelling. Significant advancements in numerical modelling techniques have since been made.

$$SHAR = \frac{Q_w}{Q_f} \quad (2.8)$$

Gas phase dilution is also a major contributor to flame extinction. Water droplets upon vaporisation expand to a volume two orders of magnitude greater than their liquid state [90]. Therefore, locally, where the droplet once was, is a region of a dilute mixture of fuel and oxidiser. One example model for flame extinction looks at the limiting oxygen concentration (LOC), whereby if the following inequality is satisfied $X_{O_2} < X_{O_2,lim}$, extinction is assumed. Typical values for LOC in hydrocarbon diffusion flames are approximately 13 % [91, 32], with more recent experiments having also looked at canonical flames in reduced oxygen concentration environments [92] showing local extinction occurring below 16 %. More complex extinction models, such as the one in FDS that considers the dilution effects of both fuel and oxygen, can be found in the FDS technical guide [43]. The last major contributor to

flame extinction is gas phase displacement. This is purely a kinematic effect, in addition to gas phase cooling and dilution, whereby high droplet momentum physically disrupts the local flow field [20]. In such situations, inhibition in the flame front is either caused by a “blow-off” effect [93] or excessive strain in the reaction layer. Other flame suppression mechanisms are also further discussed by Mawhinney et al. [20], but contribute far less to flame extinction.

Current progresses in experimental data needed for model validation include a plethora of small to medium scale suppression of pool fires [94, 95, 96, 97, 98], small scale laminar diffusion flames [99, 100, 101, 102, 103, 104, 105] and large scale fire suppression experiments [106, 107, 108]. The studies mentioned primarily provide broad-scale metrics, including gas phase temperatures near the flame, extinction delay times (time until flame extinction upon water mist activation), smoke concentrations, and radiant heat fluxes. While large-scale experiments offer valuable statistics that can aid in engineering design for specific scenarios, they are, however, not ideal for model validation due to experimental complexities and the lack of detailed near-field data. Conversely, small-scale experiments offer better insights into suppression performance and near field phenomena, but still often lack detailed characterisations of the boundary conditions while also not being representative of real fires.

In light of the gaps in near field measurements, some recent studies have focused on the fundamental aspects of water mist suppression. Specifically looking at boundary conditions, where they show significant variations in water mist suppression performance due to changes in spray characteristics, such as droplet diameters [102], nozzle cone angles and mass flux [109]. This indicates that suppression performance is highly sensitive to the type of experimental configuration [110, 111] and experimental boundary conditions. It is therefore crucial to provide a comprehensive characterisation of the suppression performance of water mist in a canonical experiment with well-posed boundary conditions to resolve the complex near field flame droplet interactions. The UMD (University of Maryland) turbulent line fire burner [62] is a recent water mist suppression experiment that has experimental data on both the standalone flame [112] with water mist suppression [110]. This is a key example of a canonical flame co-flow setup, where the flame is representative of a real fire. However, it’s important

to note that the estimated water mist droplet sizes of “ $6.6\mu m$ ” in this study are significantly smaller than those typically used in practical applications, and the boundary conditions are also not well characterised.

This thesis aims to provide new insights into the lack of near-field data in water mist fire suppression, utilising an experimental configuration similar to that of White et al. [110], with the focus on a canonical laboratory scale turbulent buoyant flame in a water mist-laden co-flow. The study will include unprecedented boundary condition characterisation and high-fidelity, temporally resolved imaging showing interactions between water droplets and the flame sheet, investigated through the use of advanced laser diagnostic techniques discussed at the end of this chapter.

2.2.2 Water mist suppression modelling

Modern computational models use a two-phase coupled approach to simulate the interactions of droplets with a flame [113]. When a numerical grid cannot resolve small liquid droplets, Lagrangian particles are used to represent multi-phase flows with suspended droplets and/or particles. For example, the Fire Dynamics Simulator (FDS) and Firefoam, both employ a form of the Navier-Stokes equations suitable for low-speed, thermally-driven flow to model mass and species transport in the gas phase (LES as described in Section 2.1.2), coupled with a Lagrangian approach for droplets and particles. An example of this is illustrated in Equation 2.9, which solves for particle acceleration ($\frac{du_p}{dt}$) and momentum transfer to/from the gas phase. Where C_d is the particle drag coefficient, ρ is gas density, $A_{p,c}$ is particle cross-sectional area, m_p is particle mass, u is gas phase velocity and u_p is particle velocity.

$$\frac{du_p}{dt} = g - \frac{1}{2} \frac{\rho C_d A_{p,c}}{m_p} (u_p - u) |u_p - u| \quad (2.9)$$

A water mist spray/droplet field is characterised by the droplet Lagrangian statistics such as velocity, position and also droplet size. In typical modelling tools, droplet sizes are generally randomly generated from a given input, typically a Sauter mean diameter (D_{32})

[114, 115, 43], where the droplet distribution follows a combination of a Rosin-Rammler and log-normal function [116]. A plethora of measurements have been made on droplet size distributions across various misting nozzle types, demonstrating that most spray nozzles produce droplets that are distributed between a Rosin-Rammler and log-normal function [117, 118, 119]. It has been recognised that pressure swirl nozzles are the most efficient method of generating a fine spray, whether it's solid-cone or hollow-cone at a given pressure [120], and is the primary nozzle design choice for fire suppression applications [121].

Given the critical role of droplet dynamics in flame inhibition, particularly the significance of droplet evaporation in the flame front, it becomes essential to accurately resolve both droplet dynamics and evaporation processes. Droplet evaporation is typically modelled through a Sherwood and Nusselt correlation, which represents the mass and heat transfer between the liquid and gas phases respectively. Equation 2.10 shows the implementation of the mass transfer coefficient (h_m) [43], where B_M is the Spalding mass transfer number, Sh is the Sherwood number with blowing, D_{lg} is the diffusion coefficient between the liquid and surrounding gas, L is the droplet diameter and Y is the mass fraction of species α . The full implementation of the mass transfer rate can be found in the FDS technical guide [43].

$$h_m = \frac{Sh D_{lg}}{L} \frac{B_M}{Y_{\alpha,l} - Y_{\alpha,g}} \quad (2.10)$$

$$B_M = \frac{Y_{\alpha,l} - Y_{\alpha,g}}{1 - Y_{\alpha,l}} \quad (2.11)$$

$$Sh = \frac{\ln(1 + B_M)}{B_M} Sh_0 \quad (2.12)$$

A set of wind tunnel experiments with droplets suspended in a tube estimates Sh_0 , which led to the following correlation for an airborne droplet as shown in Equation 2.13 [122]. Where Re_D is the Reynolds number of the droplet, Sc is the Schmidt number. Similar correlations are found for the droplet heat transfer coefficient (h_g) which is detailed in Equation 2.14 as a Nusselt correlation (Nu_0) where Pr is the Prandtl number. The full implementation is available once again in the FDS technical reference guide [43]. Computationally, droplet

transport in the flame front can be resolved at extremely small length scales; however, from an experimental standpoint, this becomes very difficult, particularly when dealing with water mist fire suppression. To resolve flame droplet dynamics, near field measurements of both droplets and the flame front are required to produce model validation data for droplet evaporation. In recent years, more sophisticated droplet evaporation models have been proposed by Kourmatzis et al. [123, 124], primarily in the field of spray combustion. These models have been extensively validated but are computationally expensive to implement in large numerical domains.

$$Sh_0 = 2 + 0.6Re_D^{1/2}Sc^{1/3} \quad (2.13)$$

$$Nu_0 = 2 + 0.6Re_D^{1/2}Pr^{1/3} \quad (2.14)$$

2.2.3 Chemical gas phase suppression

Chemical inhibition of fires was first introduced in the 20th century with the invention of halogenated gaseous fire suppressants such as Halon 1301 (CF_3Br) [12]. Gas phase chemical inhibition in a flame is the result of a catalytic cycle that depletes the pool of intermediary combustion radicals. For CF_3Br , this begins with a thermal decomposition process at elevated temperatures forming the key stable inhibition molecule HBr [13]. The main reactions involving the recombination of free radicals into a stable compound and further radical depleting compounds are shown in Equations 2.15 - 2.18. Where the net effect is the recombination of free hydrogen into a stable hydrogen molecule.



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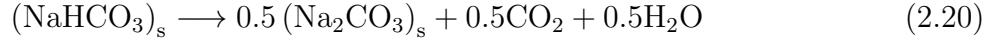


Chemical inhibition of a flame can be characterised by means of the first Damköhler number (Equation 2.19). The depletion of the pool of free radicals increases the chemical reaction time τ_{chem} (flame chemistry time under the effect of catalytic reactions), assuming that the mixing fields (τ_{mix}) are fixed, a critical Damköhler number for flame extinction is established, below which the flame will be extinguished [125, 126]. The other timescale of interest is the mixing time, τ_{mix} of the fuel, oxidiser and inhibiting species within the reaction zone, where decreases in flow timescales (increase in strain rates) will also lead to flame extinction given a long enough chemical time scale [127, 128]. Gaseous chemical inhibitors such as halogenated chlorofluorocarbon (CFC) and hydrochlorofluorocarbon (HCFC) agents are prime examples of flame inhibiting compounds that work on the principle of increasing chemical time scales through radical pool depletion.

$$Da_I = \frac{\tau_{mix}}{\tau_{chem}} \quad (2.19)$$

Modern chemical inhibitors include alkali metal salts such as $KHCO_3$ and $NaHCO_3$. Typically used in fire extinguishers, these inhibitors are highly effective, safe and environmentally friendly. Alkali metal salts work on a similar principle to their halogenated counterparts (CFC and HCFC), where upon thermal decomposition into an atomic hydroxide ($NaOH$ or KOH) [129, 130], it then enters into a catalytic cycle of recombining with intermediary combustion radicals forming stable compounds and further radical depleting compounds terminating key chain branching reactions [131]. The thermal decomposition process of alkali

metal salts can be complex with a multitude of pathways to form the final stable gaseous suppressing agent, KOH or NaOH [132, 133, 129]. An example decomposition process of NaHCO_3 is shown as follows. The first stage of decomposition is proposed by Hu et al. [134] and Wu et al. [135] with a temperature range of 370-543K following Equation 2.20, forming sodium carbonate (Na_2CO_3).



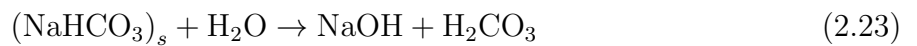
At elevated temperatures, further decomposition steps have been proposed by Chelliah et al. where above temperatures of 1123K, sodium oxide is formed [136] as shown in Equation 2.21.



Sodium oxide reacts heterogeneously with water vapour in the air, forming the final gaseous inhibitor NaOH (Equation 2.22). This is either a single-step or two-step process involving a phase change [137] from liquid to gas.



The kinetic parameters for the aforementioned reaction mechanisms are poorly characterised, due to the large uncertainty of the second stage decomposition. It is common to apply a simplified two-step global decomposition reaction, as described in Equations 2.23 and 2.24 by Babushok et al [130].



NaOH is the key stable molecule that undergoes a radical recombination process. A list of the key reaction processes responsible for radical pool depletion is detailed in Equations 2.25 - 2.27, with a number of existing gas-phase kinetic models for NaOH radical scavenging presented by Babushok et al. and Zamansky et al, where the net effect is recombining OH and H into H₂O [130, 138]. Potassium bicarbonate (KHCO₃), the other alkali metal salt follows a very similar thermal decomposition pathway to that of sodium bicarbonate but at lower temperatures [139]. The catalytic recombination process of KOH is also similar to that of NaOH (Equation 2.25), and there also exists a number of gas-phase kinetic models for the radical recombination of KOH [129].



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Figure 2.3 displays a ranking scheme for various chemical inhibitors, normalised by atomic weight using Halon 1301 as a benchmark. Notably, potassium bicarbonate has consistently demonstrated high effectiveness and reliability in both experiment and practical fire suppression applications. The rankings highlight that alkali metal salts provide an order-of-magnitude improvement in extinguishing performance compared to gaseous halogenated agents [140], although some rankings are derived from experiments on premixed combustion systems. Both alkali metal salts and transitional metals are well-known, recognised inhibitors that have been effectively used in fire extinguishers for decades.

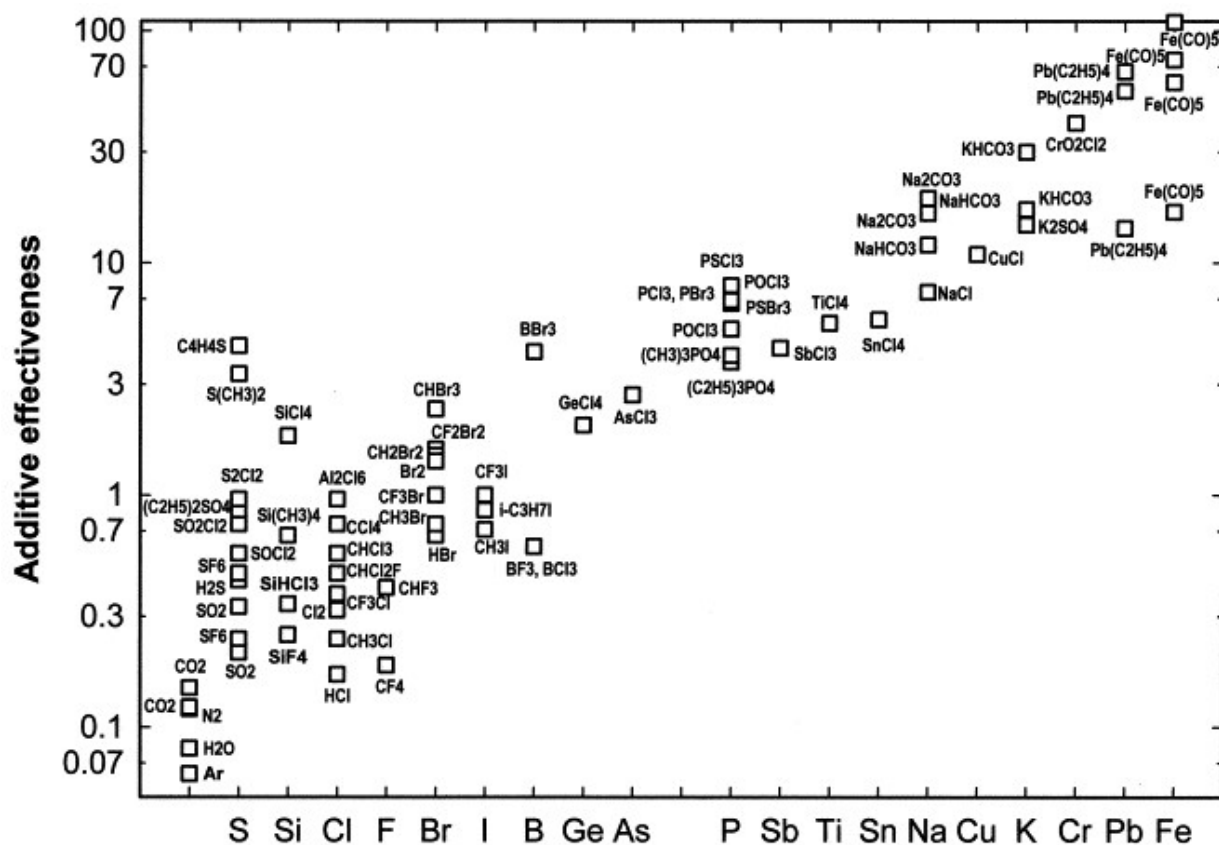


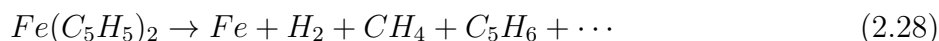
Figure 2.3: Inhibitor effectiveness relative to Halon 1301 for premixed flames. Figure extracted from Babushok and Tsang [140].

To identify any new potential additives that are non-corrosive with suppression capabilities greater than alkali metal salts, a screening of various inhibiting compounds is performed. Figure 2.3 shows that atomic iron is ranked the highest in terms of inhibition effectiveness relative to CF_3Br . Iron pentacarbonyl is the most predominately studied inhibition compound that utilises atomic iron, and it has shown impressive flame inhibition capabilities [141, 142, 143]. However, it is well known that iron pentacarbonyl is highly toxic [144], therefore its use as a fire suppressant is not practical.

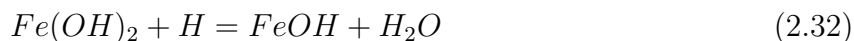
A relatively non-toxic, non-corrosive and non-conductive iron compound that has shown flame inhibiting characteristics is ferrocene. Ferrocene is an extremely stable iron compound known as a metallocene, that presents itself as a single iron atom sandwiched between two

cyclopentadienyl rings. Ferrocene, though commonly known as a good burn rate modifier for solid rocket propulsion [145], at certain relatively low concentrations, ferrocene is seen to dramatically reduce laminar flame speeds resulting in flame inhibiting properties [146]. The limited studies that exist on powdered ferrocene’s application in fire suppression and explosion mitigation have also shown promising results [147, 148, 149].

Flame inhibition through ferrocene (Fc) follows a process of thermal decomposition into the primary long term inhibition molecule FeO, where it then undergoes a catalytic cycle of radical scavenging. Above temperatures of 353 K, pure Fc sublimates into gaseous Fc [150, 151]. At higher temperatures, ferrocene decomposes into atomic iron following a single heterogeneous decomposition step described by Equation 2.28 [152]. The release of atomic iron is a fundamental driver for flame inhibition where the long term molecule FeO is produced.



Homogeneous reaction mechanisms for the iron-catalysed radical recombination cycle have been presented by Rumminger et al. [153]. These mechanisms include a detailed gas-phase decomposition scheme for $Fe(CO)_5$ (iron pentacarbonyl), which has been shown to also apply to ferrocene ($Fe(C_5H_5)_2$) [141]. This decomposition process is significant for various experiments conducted at NIST, where $Fe(CO)_5$ and $Fe(C_5H_5)_2$ are sublimed into a gaseous state using an evaporator and then introduced into a nitrogen stream via multi-stage saturator baths [150]. The main chemical reactions that contribute to the radical recombination process which terminates key chain branching reactions in the combustion process are shown in Equations 2.30 - 2.33, resulting in the net effect of combining atomic hydrogen into a hydrogen molecule.[146, 143, 154, 150].





2.2.4 Chemically enhanced water mist suppression

In addition to the thermal quenching and oxygen dilution provided by fine water mist droplets [89], the use of fine water droplets to target gas phase combustion also provides water misting systems access to the benefits of chemical inhibition discussed in the previous section. Water droplets can act as carriers of flame inhibiting chemicals, where upon the evaporation of droplets in the high temperature reaction zones, inhibitors that are dissolved in the water crystallise (if in solution) and are released as tiny particles in the flame front, actively suppressing the flame. A viable chemical fire suppressant for use as an additive in water misting suppression systems has to fulfil certain criteria for it to be widely used in practice. As expressed by Robinet et al. [21], the main criteria for a viable water mist chemical fire suppressing additive includes effectiveness, where the inclusion of the suppressant should have noticeable to significant improvements in fire suppression performance, as without significantly enhancing suppression, the addition of the additive is deemed unnecessary. The additive must be safe for both the environment and for humans, as this is central in the push for halogenated alternatives [17]. Additive stability is also crucial, the inhibitor must remain stable (fully dissolved, or in indefinite suspension) to ensure suppression performance is maintained over the lifetime of the system. Other notable mentions include non-corrosive and non-conductive properties which are crucial for the protection of property.

To evaluate the effects of combining water mist and chemical suppressants on suppression efficacy, comparative studies have examined alkali metal salts in various experimental config-

urations. These studies consistently demonstrate enhanced suppression efficiency and provide relative rankings of inhibitor performance. Experimental configurations include explosion rigs [155, 156, 157], pool fires, where the standard configuration of opposed flow is adopted (mist spraying down onto the flame) [24, 158, 159], cup burners in a co-flow that is seeded with water mist droplets [160, 161], counter-flow diffusion flames [162, 163, 103, 100] and variations of a typical laminar diffusion flame [164]. In the majority of cases, enhanced suppression is presented as either an extinction strain rate in counter-flow flames, or extinction delay times for buoyant diffusion flames, where the inclusion of the chemical additive should reduce the time taken to achieve flame extinction/suppression in comparison to pure water mist. However, as mentioned previously in Section 2.2.2, water mist suppression effectiveness is also highly dependent on droplet size distributions and number densities. As a result, comparing the effectiveness of varying concentrations of inhibitors across different studies becomes nearly impossible. While most studies cited here provide global rankings of inhibitor efficacy, they either fail to represent the physics present in large-scale fires or lack the near-field detailed characterisations needed to understand droplet and inhibitor transport in buoyant turbulent diffusion flames. Addressing these limitations requires carefully designed experiments, coupled with advanced measurement techniques capable of quantifying droplet field statistics and observing flame-droplet interactions.

Metal alkali salts (e.g. NaHCO_3 and KHCO_3) are highly suitable for water mist suppression systems as they comply with most of the criteria for a viable chemical suppressant as previously mentioned. However, they have the downside of being both good electric conductors in aqueous solution with corrosive properties [165]. Given that ferrocene $\text{Fe}(\text{C}_5\text{H}_5)_2$ is proven to be an excellent flame inhibitor as a gaseous suppressant, the next step is to identify methods of incorporating ferrocene in water misting systems using fine water mist droplets as carriers of ferrocene into the flame front. However, ferrocene is highly non-polar as the two cyclopentadienyl rings around atomic iron form a symmetric molecule resulting in hydrophobic properties, which makes ferrocene highly insoluble in water [166]. Ferrocene's hydrophobic nature is the primary barrier to its inclusion in water-based suppression applications and has

hindered research development in this field. Few studies on fire suppression have explored various methods of incorporating ferrocene into water. Some approaches, as demonstrated by Koshiha et al., include using oil-in-water micro-emulsions and surfactants as mediums for creating a homogeneous solution of ferrocene in water [167, 168, 169], which have shown small improvements in suppression efficacy. However, these methods focus on the temporary suspension of ferrocene in water, which cannot be applied to real water misting systems as suppression efficacy will vary over time due to the settling of ferrocene particles. These experiments are also poorly characterised, with limited verification from other studies. As a result, the findings remain unconfirmed and require further investigation.

This thesis will present inhibitor rankings of two alkali metal salts as additives in water mist, highlighting their relative suppression performance at varying concentrations. The proposed experiment focuses on a turbulent buoyant diffusion flame, representative of a fire within a water mist-laden co-flow. This approach will enable the unprecedented characterisation of experimental boundary conditions while employing advanced laser diagnostic techniques to observe near-field interactions between droplet evaporation and the catalytic depletion of OH radicals. An exploratory study on the viability of ferrocene as an additive in water mist fire suppression will also be conducted. Utilising multiple methods to implement ferrocene in water, and characterising suppression efficacy.

2.3 NON-INTRUSIVE LASER BASED DIAGNOSTICS

The application of laser diagnostic techniques to combustion research has profoundly advanced the fundamental understanding of various critical aspects of turbulent combustion phenomena. These techniques allow for precise, non-intrusive measurements of key parameters such as temperature, species concentrations, and flow velocities within flames and combustion systems. By providing temporally resolved, high-resolution data, laser diagnostics enables the observation and analysis of combustion processes under realistic conditions, leading to more accurate models and simulations. The fire community has not yet fully exploited the benefit of these methods, hence an objective of this thesis is to employ them to resolve the

structures of buoyant fires and develop a complementary database that can be used for model development.

2.3.1 Planar laser based imaging

Planar imaging techniques, which primarily utilise either fluorescence of excited molecules or Mie scattering from particles, offer significant advantages over traditional line-of-sight imaging methods. Unlike line-of-sight techniques that capture data along a single line through the flame, planar imaging provides a two-dimensional view of the entire field of interest. This allows for comprehensive spatial analysis of a flame or particle/droplet distribution across a plane. Fluorescence-based planar imaging techniques can selectively visualise specific species or radicals within the flame by exploiting their unique emission spectra when excited by a laser at specific wavelengths. This enables the measurement of concentration distributions and/or temperature fields with high spatial resolution [170].

The PLIF (Planar Laser Induced Fluorescence) measurements in this thesis focus on imaging the OH radical, which serves primarily as a marker for the flame front to identify reaction zones within the flame. To achieve optimal wavelengths for OH, a dye laser is tuned and pumped with a Nd-YAG laser. The OH radical is primarily excited at 283 nm [171][172], due to its high fluorescence signal and collection wavelength at around 310 nm [173]. OH quantification is possible at this wavelength and has been performed by Kelman et al. [174]. However, in this thesis, OH is primarily used as a qualitative position marker for the high temperature reaction zones. Planar Mie scattering techniques use laser light scattered by particles to map particle position and size on a 2D plane. This is purely an elastic scattering process that is used in this thesis as a qualitative marker for soot and droplet positions relative to the OH-PLIF. Example experimental setups of simultaneous OH-PLIF and Mie scattering are shown in the methodology section of this thesis.

2.3.2 Droplet sizing techniques

Droplet field statistics of liquid sprays issued from injectors are challenging to measure [80] and require specialised techniques to do so. The most developed technique is Phase Doppler Anemometry (PDA) which was first published by W.D. Bachalo in 1982 [175], which gives real-time data in a small point measurement volume. The technique is widely used in all fields of spray atomisation [176] such as water misting systems to characterise droplet field statistics such as velocity, size distribution, volume flux and more [177, 178]. PDA works on the basis of where two laser beams of the same wavelength are crossed, producing a fringe pattern. Once a droplet passes through the intersection, light is scattered and the phase difference between two Doppler bursts is recorded by two spatially separated detectors, which allows for estimation of the droplet size. For more details on how the technique works, refer to the following references [176, 179, 180]. Example experimental setups of a PDA system are presented in the experimental sections of this thesis. This thesis utilises PDA to characterise experimental boundary conditions for velocity flow fields, droplet distributions and droplet mass flux.

2.4 SUMMARY

This chapter reviews the existing literature on turbulent buoyant fire dynamics and the empirical correlations derived from the multitude of scaling experiments. The empirical correlations are heavily used for CFD model validation, which limits the ability of such models to generalise. As a result, there has recently been an international collective effort to validate modern CFD fire modelling tools by developing sophisticated datasets to resolve complex fire phenomena. However, the literature is generally lacking in observations of near-field flame structures with poorly resolved boundary conditions.

This chapter also explores fire suppression, including physical/thermal suppression through water mist and gaseous chemical suppression, and their respective modelling concepts.

State-of-the-art experiments in the literature are reviewed, highlighting their lack of near-field measurements of droplet/inhibitor transport in the flame front and the lack of well-characterised experimental boundary conditions. Finally, the advanced laser diagnostic techniques employed throughout this thesis (PDA, OH-PLIF and Mie scattering) are briefly described. This thesis utilises these techniques to expand upon the literature, studying the near field flame structures and flame-droplet interactions.

Chapter 3

Sydney Fire Burner and its Characterisation

This chapter presents a new buoyant turbulent fire burner with a key characteristic of being able to control fuel-turbulence. The burner utilises a perforated plate that issues small jets of fuel that generate high shear, hence high levels of turbulence. The plate may be recessed into an outer jacket to control the level of turbulence so that, for the same bulk fuel velocity, different recess distances will result in different levels of turbulence at the burner's exit plane. This is a key feature that enables the generation of high levels of turbulence in a low-mean-velocity buoyant jet, and this is different from the burner of Zhang et al. [181] who used a porous plate at the burner exit plane. This burner introduced here enables a study of turbulence-buoyancy interaction in flames where fuel-turbulence is well controlled and boundary conditions are well-posed and easily modelled. The resulting database complements the existing literature and provides a platform for future quantitative measurements and model development. Fuel injection rates are kept sufficiently low to ensure buoyancy-driven flames. The turbulence generated from the recessed plate at the burner exit plane is characterised using Laser Doppler Velocimetry (LDV) of a non-reacting cold flow.

3.1 METHODOLOGY

3.1.1 Burner design and setup

The burner, shown schematically in Figure 3.1, consists of a tube 35 mm ID (2.5 mm wall thickness) that issues a fuel jet to form simple buoyant flames (label 1 in Figure 3.1a). The burner is made of three components, manufactured from brass and the fuel employed for all experiments herein is compressed natural gas (CNG, which consists of 88.8% CH_4 , 7.8% C_2H_4 , 1.9% CO_2 and 1.2% N_2). The novelty of the burner lies in the inclusion of a perforated plate that can be recessed within the 35 mm outer jacket. The perforated plate, shown in Figure 3.1a (label 2) and Figure 3.1b, has a thickness of 8 mm and 25 through holes each with a diameter of 1 mm. The perforated plate can be mounted on a sliding mechanism (label 3 in Figure 3.1a), which can be recessed into the outer jacket up to a distance $L_r = 100$ mm upstream of the burner exit plane. The perforated plate generates high-velocity jets that issue from the small holes to create high shear and hence large fuel-turbulence levels at the burner exit plane.

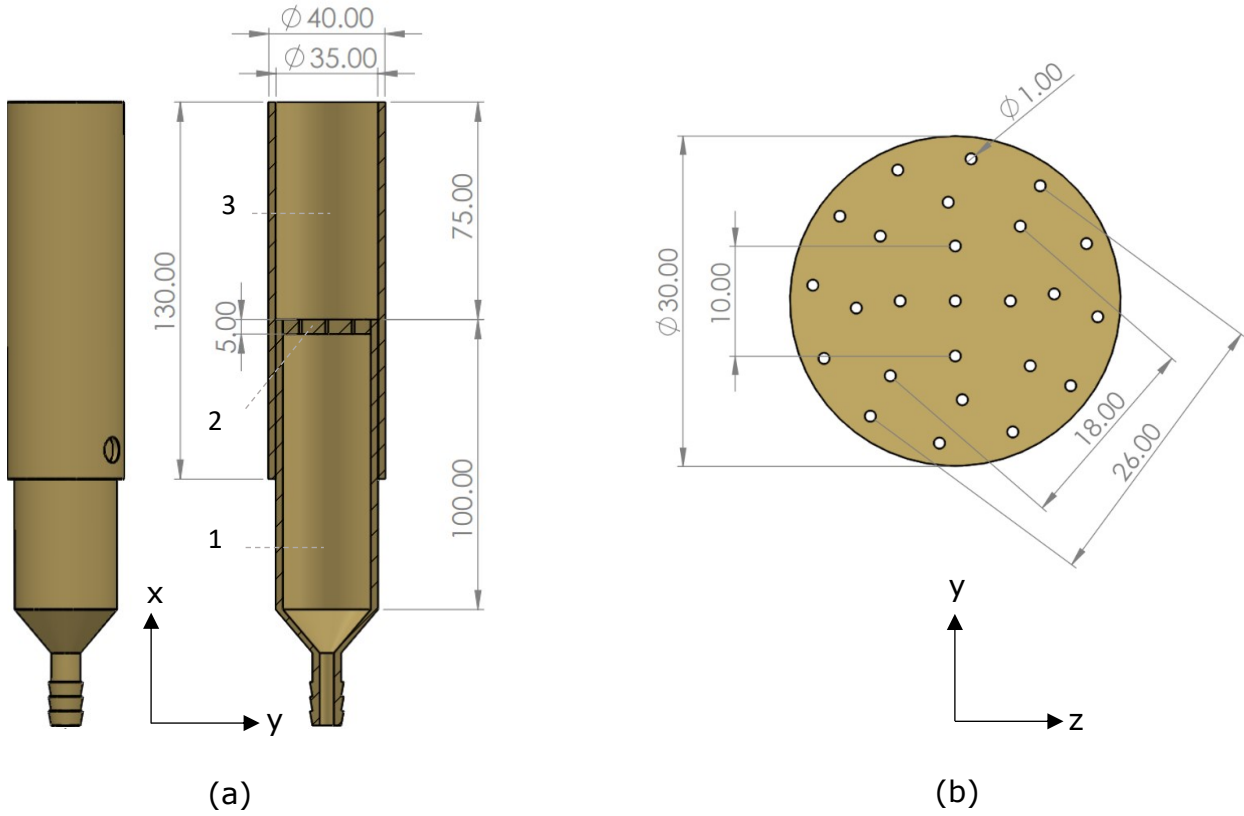


Figure 3.1: Burner design, all dimensions are in mm.

The probe volume (region of interest) is kept 1.5 m below the exhaust duct (1 m below the exhaust hood) in an open atmosphere to ensure that the exhaust does not influence the experiment. Exhaust velocities vary between 0.3 - 0.6 m/s at the exhaust entrance. The co-flow is supplied by a wind tunnel operating under standard atmospheric conditions with filtered lab air. The burner assembly is positioned in the centre of a square wind tunnel with a low-speed co-flow of 0.2 m/s of air to stabilise the flame. A general schematic of the experimental layout used throughout this thesis is shown in Figure 3.2.

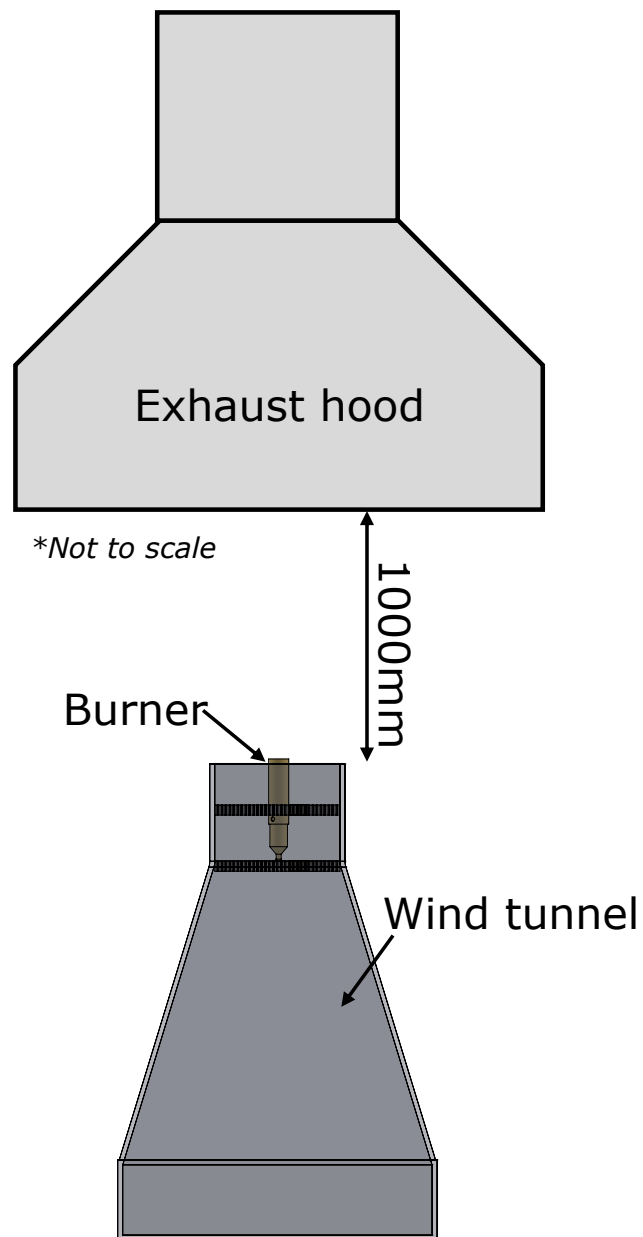


Figure 3.2: Burner placement in the wind-tunnel under an exhaust hood.

Since this burner operates by introducing shear-driven fuel-turbulence, the turbulence level is therefore controlled by increasing the fuel flow rate as it enhances shearing within the fuel flow. Also, for the same fuel flow rate, the turbulence level at the jet exit plane can be controlled by recessing the plate within the annulus. Noting that there are numerous

definitions of the Froude number, the one listed in Equation 3.1 is used here for convenience. Both the Froude number and heat release rate (Equation 3.2) are controlled by the fuel mass flow rate.

$$Fr_f = u_s / \left[(S + 1)^{\frac{3}{2}} \left(\frac{\rho_s}{\rho_o} \right)^{\frac{1}{4}} \left(\frac{\overline{\Delta T_{fa}}}{T_o} g d_s \right)^{\frac{1}{2}} \right] \quad (3.1)$$

$$\dot{Q} = \Delta H_c \dot{m}_f \quad (3.2)$$

The fire Froude number shown in Equation 3.1 characterises the aerodynamic effects with respect to the diameter of the burner exit plane [182]. Where u_s is the nozzle fuel flow velocity, S is the stoichiometric mass air to fuel ratio, ρ_s is the fuel density at the nozzle exit, ρ_o is the ambient air density, ΔT_{fa} is the modified mean flame temperature rise estimated from adiabatic laminar flame temperatures, T_o is the ambient air temperature, g is gravity and d_s is the nozzle diameter. The fuel injection rates are selected to ensure that Froude numbers for the flames studied lie solely within the buoyancy controlled regime defined by Delichatsios [183]. The burner operating conditions are optimised by varying the fuel flow rates, air co-flow rate and plate recess distance to ensure that flame lift-off or blow-off does not occur. The burner operating limits are then selected based on a stability mapping for flame lift-off, with a maximum fuel flow rate of 73.2 SLM, where any further increase in the fuel flow rate causes intermittent flame lift off from the burner exit plane. The heat release rate (HRR) of the fuel is estimated by assuming complete combustion for CNG (50 MJ/kg). To demonstrate the utility of the burner, a single plate recess distance of $L_r = 75$ mm is selected and studied for the five flames of varying turbulence levels (note that F1 does not have the turbulence generating plate). The corresponding fuel flow rate $\dot{v}_f$, Reynolds Re_s (calculated using the 1 mm pinholes as the characteristic length), Reynolds Re_D (burner diameter as the characteristic length), the fire Froude number and dimensionless heat release rates $\dot{Q}^*$ [184] are shown in Table 3.1.

Table 3.1: Burner operating conditions for the different flames sorted by increasing turbulence levels.

Flame	L_r (mm)	$\dot{Q}$ (kW)	$\dot{v}_f$ (L/min)	u_s (m/s)	Re_s	Re_D	Fr_f	$\dot{Q}^*$
F1	N/A	10	18.3	0.317	678	950	0.0064	31.75
F2	75	10	18.3	0.317	678	950	0.0064	31.75
F3	75	20	36.6	0.634	1357	1901	0.0127	63.51
F4	75	30	54.9	0.951	2034	2851	0.0191	95.26
F5	75	40	73.2	1.268	2715	3801	0.0254	127.0

3.1.2 LDV measurements

A commercial LDV (Laser Doppler Velocimetry) system (TSI Model FSA 4000) was used for the single-point measurements of velocity and turbulence level. An Argon-ion laser feeds a two-channel fibre optics assembly to the transmitter while the 300 mm focal length receiver was positioned in a 31° forward scattering configuration with a $3.74 \mu\text{m}$ fringe spacing. Two pairs of beams with wavelengths 514.5 nm and 488.0 nm are used for measuring the axial and radial components of velocity, respectively. Built-in probe volume correction (PVC) in the software (FlowSizer) has been implemented to correct for lower detectability of small particles at the edge of the probe volume. Point measurements of the mean and RMS axial velocity were taken radially along the exit plane of the burner for a non-reacting flow, with similarity in the bulk volumetric flow rates maintained.

The burner was seeded with an ultra-fine mist generated from an ultrasonic nebulizer of water doped with a small concentration of sodium bicarbonate powder (NaHCO_3). Once the droplets form during primary atomisation and undergo thermal expansion and evaporation, the small NaHCO_3 crystals suspended in the flow enable a sufficient number density of droplets/crystals needed to resolve the flow field at the burner exit plane. This doping mechanism was particularly necessary for larger flow rates as droplet evaporation is greatly enhanced due to the larger stream-wise velocity, and therefore no water droplets were

detected at the burner exit plane. The droplet-particle flow exhibited a mono-modal diameter distribution with a geometric mean (d_{10}) at approximately $1\ \mu\text{m}$, meaning that the Stokes number of the droplets/particles is small. Therefore, the droplets/particles can be assumed to follow the flow field generated inside the burner assembly. Careful attention was required to ensure that blockage of the holes in the perforated plate and the flow straightening mesh did not occur, as this was found to influence the results heavily. To account for this, the burner was frequently purged to remove any blockages. Data was sampled for approximately 30 s, with data acquisition rates typically ranging from 5000 Hz in the centre of the burner exit plane and 200 Hz towards the edges of the burner.

3.2 RESULTS AND DISCUSSION

3.2.1 Velocity and turbulence profiles at the exit plane

Radial profiles of the mean axial and RMS velocity fluctuations measured at the burner exit plane for the five cases studied under a cold non-reacting flow are presented in Figure 3.3. The mean burner exit velocity profiles for each flame case are shown in Figure 3.3a, while the profiles for the RMS velocity are shown in Figure 3.3b. The presented RMS values, u'_i , are computed as per Equation 3.3. The addition of the perforated plate changes the mean and RMS axial velocity profiles considerably. The RMS fluctuations range from 0.12 m/s for F1 to 2 m/s for F5. Upon increasing the turbulence levels, Figure 3.3a shows an increasingly distinct “M” shaped mean velocity profile with peak velocities occurring near the wall for the higher turbulence F3 - F5 cases. In each flame presented, shear-driven turbulence is raised by increasing the bulk fuel flow rate, with the exception of flames F1 and F2, which possess the same bulk mass flow rates to highlight the effect of the turbulence-generating plate on the velocity profile. The resultant velocity distributions shown are a combination of both an increase in overall bulk flow velocity and the subsequent enhancement of shear turbulence due to the addition of the plate (F2 – F5). Previous studies have also shown similar “M” shaped velocity profiles for high blockage ratio perforated plate turbulence

generation [185][186]. The increase in the fuel-turbulence level is associated with the design of the perforated plate, which demonstrates that the burner is performing as intended. For mean and RMS velocity profiles of flames without the turbulence generating plate at higher HRRs, please see Appendix A.

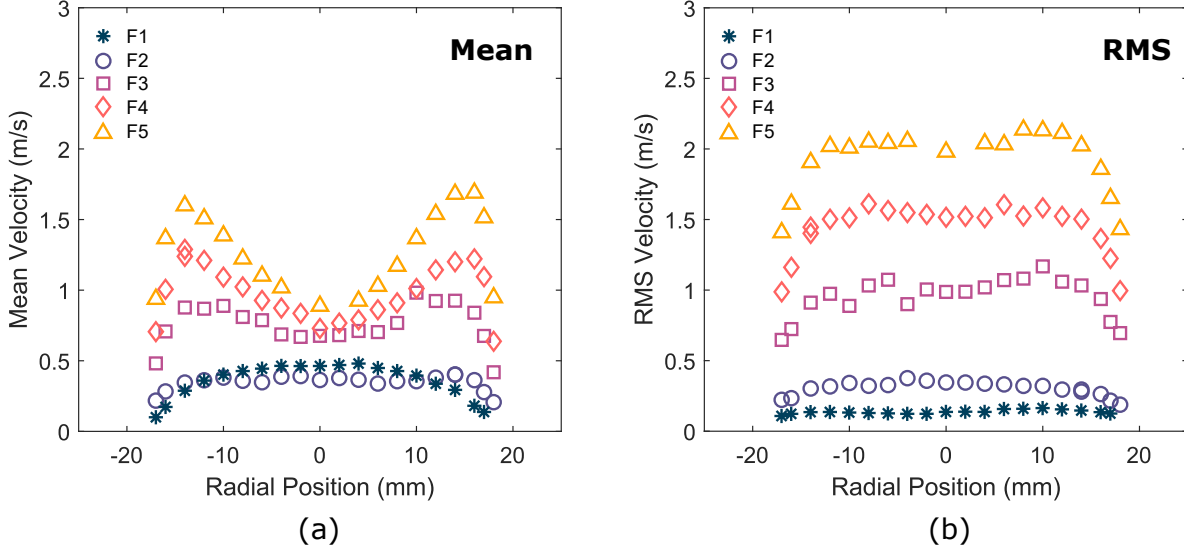


Figure 3.3: Exit plane mean and RMS velocity profiles for all the flames studied herein.

The flames have been sorted by increasing levels of fuel-turbulence (F1 – F5). A single metric for the inlet turbulence level to categorise each flame has been developed, termed the fuel-turbulence, ϵ (m/s), which is defined per Equation 3.4 and shown for each flame in Table 3.2. The flow RMS u'_i is the summation of the radial component (u_{x_i}) orthogonal to the burner exit plane and the azimuthal component (u_{y_i}), assuming symmetric flow as shown in Equation 3.3. The fuel-turbulence, ϵ , is defined by a discretised radial integral of the measured velocity RMS u'_i summed over the incremental annular area from the centreline to the outer surface of the burner and then normalised by the total cross-sectional area of the burner. Fuel-turbulence varies from 0.135 - 1.873 m/s for flames F1 to F5 respectively.

$$u'_i = \sqrt{u_{x_i}^2 + 2u_{y_i}^2} \quad (3.3)$$

$$\epsilon = \sum_{i=0}^n u'_i (r_{i+1}^2 - r_i^2) / r_n^2 \quad (3.4)$$

Table 3.2: Bulk fuel velocity u_s , bulk fuel-turbulence levels ϵ and centerline Integral length l_0 and time scales τ_f .

Flame	u_s (m/s)	τ_f (s)	l_0 (m)	ϵ (m/s)
F1	0.317	1.17E-02	5.14E-03	0.135
F2	0.317	1.48E-02	5.12E-03	0.283
F3	0.634	8.15E-03	6.49E-03	0.918
F4	0.951	4.59E-03	4.94E-03	1.383
F5	1.268	4.18E-03	4.91E0-03	1.873

The LDV measurements are exploited to calculate the integral length scale (l_0) at the exit plane from the single-point Eulerian auto-correlation function $\rho(t)$. This assumes Taylor's frozen turbulence hypothesis and the integration of $\rho(t)$ to obtain an integral time scale (τ_f) using Equation 3.5, which is multiplied by the local mean velocity to obtain an approximate integral length scale. Due to the random sampling nature of the LDV data, the slotting technique by Nobach [187] is used to calculate the single-point Eulerian auto-correlation function.

$$\tau_f = \int_0^\infty \rho(t) dt \quad (3.5)$$

The integral time scales τ_f and integral length scales l_0 of the axial velocity component of all flames are presented in Table 3.2. The time scales decrease with increasing levels of fuel-turbulence, suggesting an increase in the turnover rate of turbulent structures. The length scales, however, seem to be very similar for all cases, this indicates that the size of the largest turbulent structures are purely governed by burner geometry, resulting in similar

integral length scales in all the flames.

3.2.2 Validation of the turbulence-generating mechanism

This section reviews the association between fuel-turbulence and HRR (fuel flow rate) both with and without the turbulence-generating plate to ensure increased fuel-turbulence levels are not solely a function of increasing fuel flow rate but a function of the burner design. Figure 3.4 shows the burner exit plane fuel-turbulence levels for all HRRs studied herein using Equation 3.4. It is clearly shown that without the perforated plate, increases in fuel-turbulence levels are minor as the fuel flow rate increases, scaling linearly from 0.135 – 0.483 m/s. Whereas, with the addition of the plate, fuel-turbulence levels increase substantially from 100% to 300% for the 10 kW to 40 kW flames respectively.

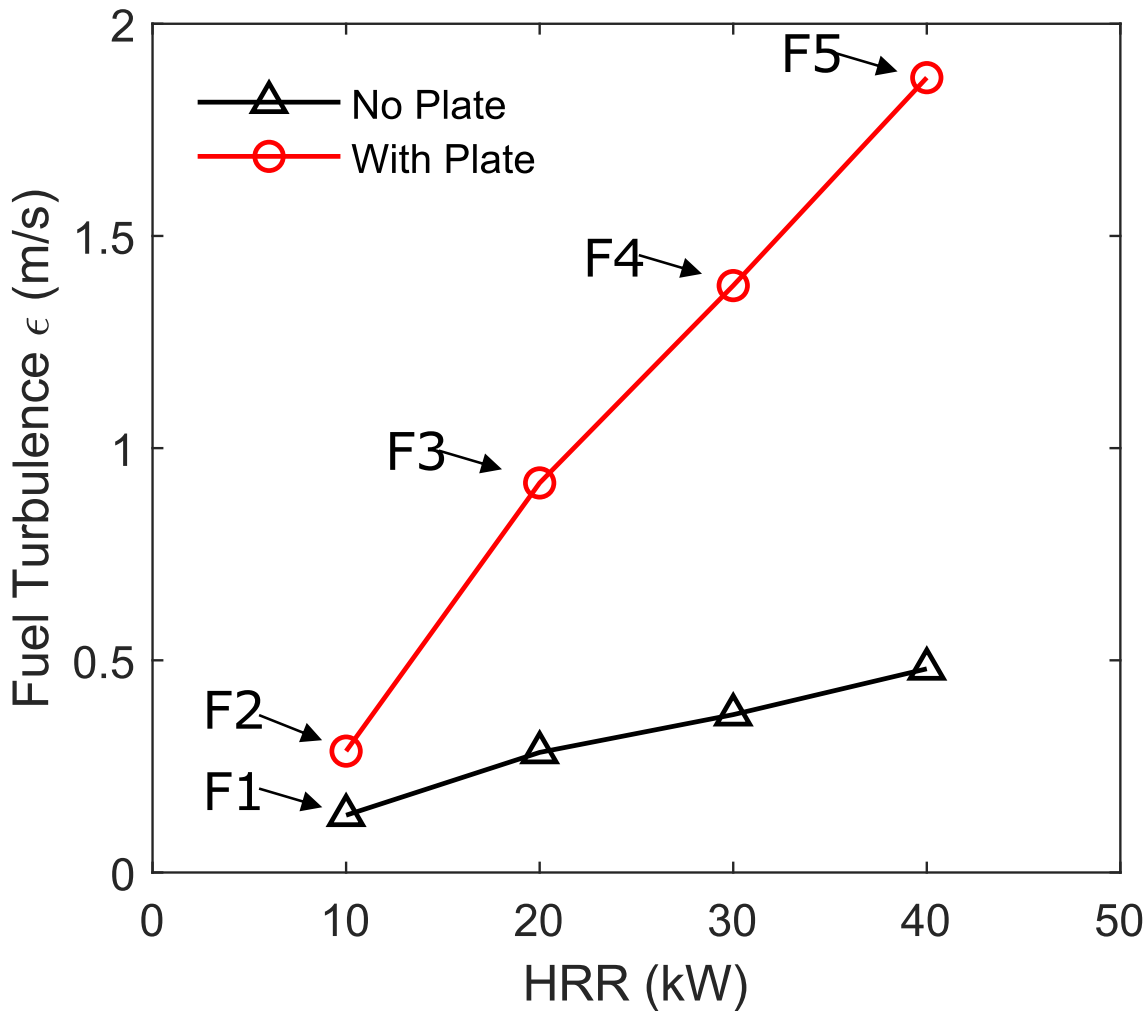


Figure 3.4: Exit plane fuel-turbulence for all HRRs with and without the turbulence generation plate.

3.2.3 Flame heights and exit plane flame structure

Visible heights for all the flames studied are quantified and shown in Table 3. Mean flame heights are defined following the methodology of Zukoski [184], with a 50% flame intermittence criterion employed. Videos of the flames were taken at 50 Hz for 120 s resulting in 6000 images used to approximate the mean flame height. The individual video frames are binarized and then averaged temporally to produce a probability distribution of the flame intermittence.

Table 3.3: 50% intermittent mean flame heights.

Flame	L_f (m)
F1	0.52
F2	0.55
F3	0.67
F4	0.76
F5	0.82

To understand the role of diffusion and entrainment forces on the overall flame structure, DSLR images are taken of the flame neck region for each flame studied from Table 1, with an example of instantaneous images presented in Figure 3.5. The transition point from a blue flame to a yellow flame nominally corresponds to the onset of soot particle formation. It is observed that with increasing levels of fuel-turbulence, the flame luminosity and structure change at the flame neck. The changes observed are solely a property of the turbulence level independent of HRR ($\dot{Q}$) and not due to the increase in Reynolds numbers. For images of the flames without enhanced fuel-turbulence, please see Appendix A Figure A.1.

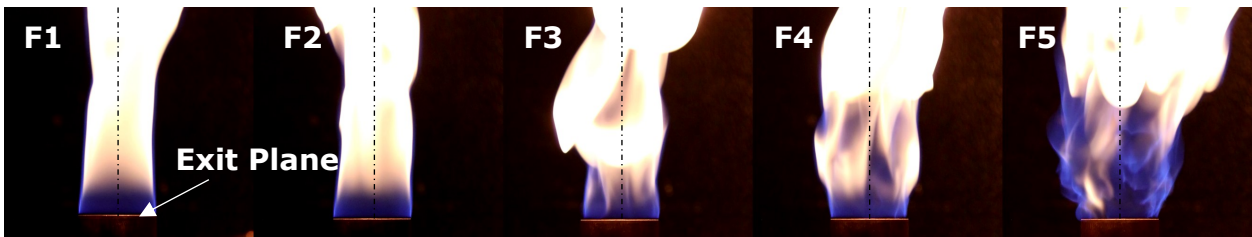


Figure 3.5: Instantaneous DSLR images showing the onset of soot formation and oxidation near the burner exit plane for all flames with increasing fuel-turbulence.

Under increased fuel-turbulence levels, the axial location for the onset of soot formation changes where the blue region extends further downstream, however, some sooting also occurs in this region as observed by streaks of yellow noted in flames F4 and F5. The delayed onset of sooting suggests that increased fuel-turbulence levels reduce soot residence times,

therefore reducing soot formation close to the burner exit plane. It is also important to highlight that F1 shares similar qualitative characteristics to F2, even though the relative fuel-turbulence is double from F1 to F2. This is due to both flames having low absolute levels of fuel-turbulence, whereas F3 to F5 have much larger absolute levels of fuel-turbulence (see Table 3.2). This suggests that the turbulence intensity at the burner exit plane has a strong effect on soot formation, given the visual differences between all the flames. Another important observation is that flame F5 lies at the lift-off limit, with partial lifting occurring occasionally. These observations serve as a prelude for the quantitative analysis obtained from the high-speed imaging. They also reinforce the capacity of the burner to control the mechanism of oxidiser transport into the pre-neck region of flame, which influences soot formation and oxidation. Reconstruction of the flame's radiative power using a multi-point source method [52] was conducted on increasing fuel-turbulence levels at a constant HRR by recessing the turbulence generating plate further. This showed a reduction in the flame radiative fraction with increasing fuel-turbulence levels, perhaps suggesting that increased turbulent mixing between fuel and oxidiser in the flame leads to cleaner combustion and less soot. For details and results on this analysis, please see Appendix A.5.

3.3 CONCLUSIONS

This chapter presents the characterisation of a novel canonical burner that enables the study of buoyant flames with controlled levels of fuel-turbulence. This is achieved by using a recessed perforated plate that raises the turbulent velocity fluctuations at the burner exit plane as defined by a velocity RMS. LDV measurements across the burner exit plane provide point measurements of velocity which are also used to compute the integral time and length scales. The main findings are listed below:

- LDV measurements at the exit plane show that the lowest turbulence flames have a parabolic velocity profile akin to that of laminar pipe flow with low levels of velocity RMS (0.135 m/s). Increasing the fuel flow rate to a maximum of 73.2 SLM, the velocity

profile adopts an “M” shaped structure with a velocity RMS of 1.873 m/s.

- The LDV measurements were exploited to obtain integral time (s) and length scales (m). Both of which are in the order of 4×10^{-3} .
- The turbulence generating plate was validated to show that not only does it significantly increase the fuel turbulence levels, but that it is primarily driven by the change in burner geometry rather than the increase in fuel flow rate.
- Flame heights are determined using the 50% flame intermittency as the criterion for flame height, resulting in 0.52 - 0.82 m from flames 1 to 5.

Chapter 4

High-Speed Imaging of Buoyant Fire Dynamics

This chapter presents the effect of induced fuel-side turbulence on the temporal and spatial structure of fires. The flame structure is studied through the high-speed imaging of planar laser-induced fluorescence (PLIF) of the OH radical and Mie scattering of soot (OH-PLIF-Scattering) of flames with varying levels of fuel-turbulence. Various instability modes are observed along side a flame pinch-off phenomenon. Statistics are obtained from the images showing various quantities under the influence of increased fuel-side turbulence.

4.1 METHODOLOGY

4.1.1 Joint high-speed imaging of OH-PLIF and Mie scattering of soot

The optical setup employed for the joint high-speed imaging of OH radicals and soot Mie scattering is shown in Figure 4.1. OH-PLIF approximates the high temperature reaction zone (flame sheet) while the Mie scattering is an approximate measure of soot intensity

in the flame. Soot Mie scattering at 532 nm is generated by a frequency doubled 120 W Nd:YAG laser (Edgewave HD30II-E) operating at a repetition rate of 10 kHz and a 9 ns pulse duration. The vertically polarised 532 nm Mie scattering beam is attenuated to 1 mJ/pulse to avoid excessive scattering signal levels and laser-induced incandescence by a combination of a half-wave plate and a thin film polarizer. For OH fluorescence excitation, a frequency doubled 30 W Nd:YAG laser (Edgewave InnoSlab IS8II-E) operating at a frequency of 10 kHz and a wavelength of 532 nm, is used to pump a dye laser (Sirah Allegro) using Rhodamine 6G dissolved in ethanol. The dye laser beam is tuned such that after the frequency doubling the UV wavelength corresponds to the Q1(6) OH A-X (1,0) transition at 283.01 nm with 100 μ J/pulse energy and 10 ns pulse duration. After correction for the different focal lengths of the UV and the 532 nm beams, the two beams are overlapped, expanded in the vertical direction and passed through a 300 mm focal length cylindrical lens to form the laser imaging sheet. The combined laser sheets at the measurement zone are approximately 50 mm in height with a nominal thickness of 200 μ m.

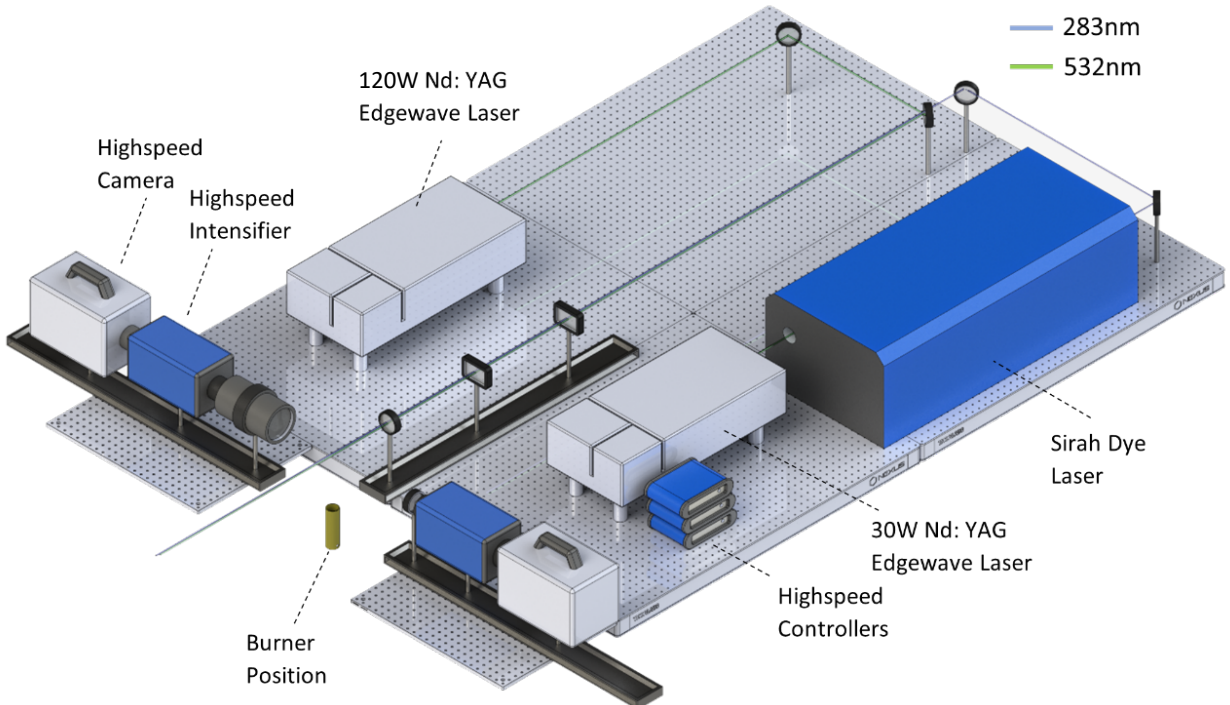


Figure 4.1: Experimental and laser setup for the simultaneous high-speed imaging of OH-PLIF and Mie scattering of soot.

The soot Mie scattering signal is collected orthogonally to the laser sheet with a 50 mm $f\# = 1.8$ Nikkor lens connected to a two-stage high-speed intensifier (LaVision HighSpeed IRO) and the subsequent image is recorded by a high-speed CMOS camera (LaVision High-Speed Star 6). Interferences from flame luminosity are removed using a 10 nm FWHM, 532 nm bandpass filter, combined with a 200 ns intensifier gate. The OH-PLIF signal is collected orthogonally to the laser sheet on the opposite side to the Mie scattering collection system, with a 96 mm $f\# = 1.65$ UV lens (2xLAPQ/APMQ-300.0–60.0-PM CVI Laser Optics) [173], coupled to an identical high-speed intensifier and high-speed CMOS camera as the Mie scattering collection system. The fluorescence from the OH A-X (1,1) and (0,0) bands are collected, while simultaneously blocking laser scattering and flame luminosity using a 200 ns intensifier gate and a combination of filters that includes a 300 nm long-pass filter, a 15 nm FWHM 315 nm bandpass filter and a 1 mm thick UG11 coloured glass filter. The UV OH PLIF beam is delayed by 200 ns from the 532 nm Mie scattering beam to avoid any cross-talk between the two processes. Both cameras are set to acquire images at 250 Hz, a much lower rate than the laser frequency of 10 kHz to ensure a greater sampling time of the relatively low-speed buoyant flames examined in this study, yet still sufficient to temporally resolve the flame structures between successive images.

4.1.2 Image pre-processing

The raw camera images must be pre-processed before performing any qualitative or quantitative analysis. Multiple calibration images are taken throughout the experiment to correct for variations in camera background (darkfield) and intensifier flatfield, optical throughput uniformity and laser sheet profiles, with the appropriate corrections applied in pre-processing. A 3×3 median filter followed by a 5×5 Gaussian filter is applied to images after background subtraction to minimise the effects of noise. Both cameras have been de-warped using a grid calibration plate applying a 3rd order polynomial geometric transformation [188] resulting in an RMS mapping error of less than 1 pixel over the region of interest. The spatially mapped cameras have a projected image pixel size of 0.5 mm/pixel for the OH camera and

0.4 mm/pixel for the soot scattering camera. The de-warped images have a maximum window size of 65 mm (height) by 130 mm (width). Both the OH-PLIF and Mie scattering of soot images have a threshold applied zeroing all pixels below that of 10 counts and 5% of the maximum counts. Figure 4.2 shows an example flowchart showing how the pre-processing is performed, with example images at each stage. The first row of images shows the OH-PLIF, the second row presents filtering techniques to clean the OH-PLIF image, and the last row shows image processing techniques for the Mie scattering of soot.

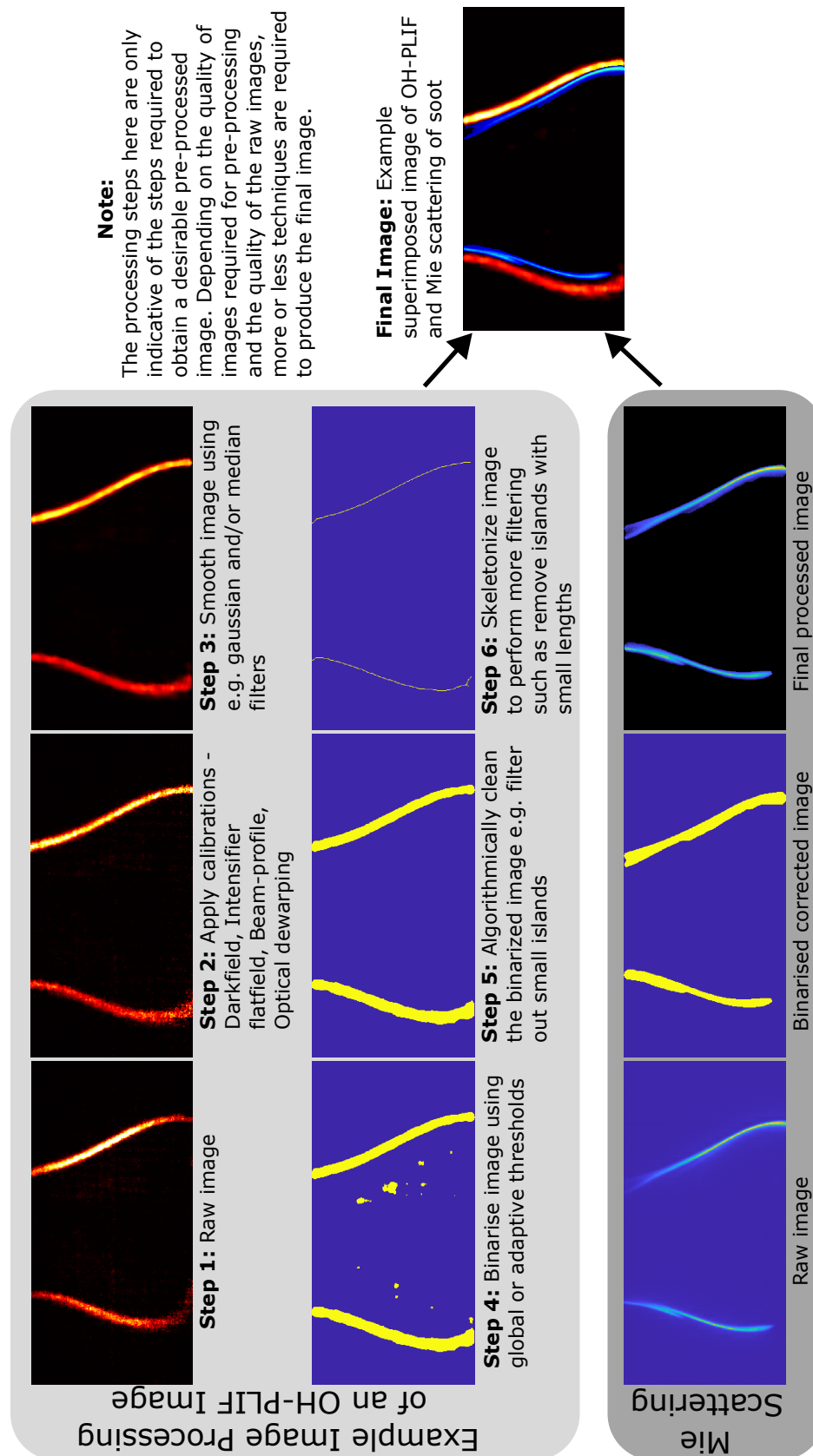


Figure 4.2: Example list of steps taken to pre-process images from the raw camera image to a final, superimposed image of OH-PLIF (Hot red colormap) and Mie scattering of soot (Parula colormap).

4.2 RESULTS AND DISCUSSION

4.2.1 Flame structure

Instantaneous DSLR images of all the flames F1 - F5 are shown in Figure 4.3 with the burner position marked in red. These images illustrate the flame structure of the different flames due to increasing levels of fuel-turbulence. What is generally observed is an increase in a side to side sinuous motion in the flames with increased levels of fuel turbulence, which is not seen in flames with lower fuel turbulence. These images are indicative of the effect/presence of the turbulence generating plate on the overall flame structure, which will be revealed through the high-speed laser images presented in this section.

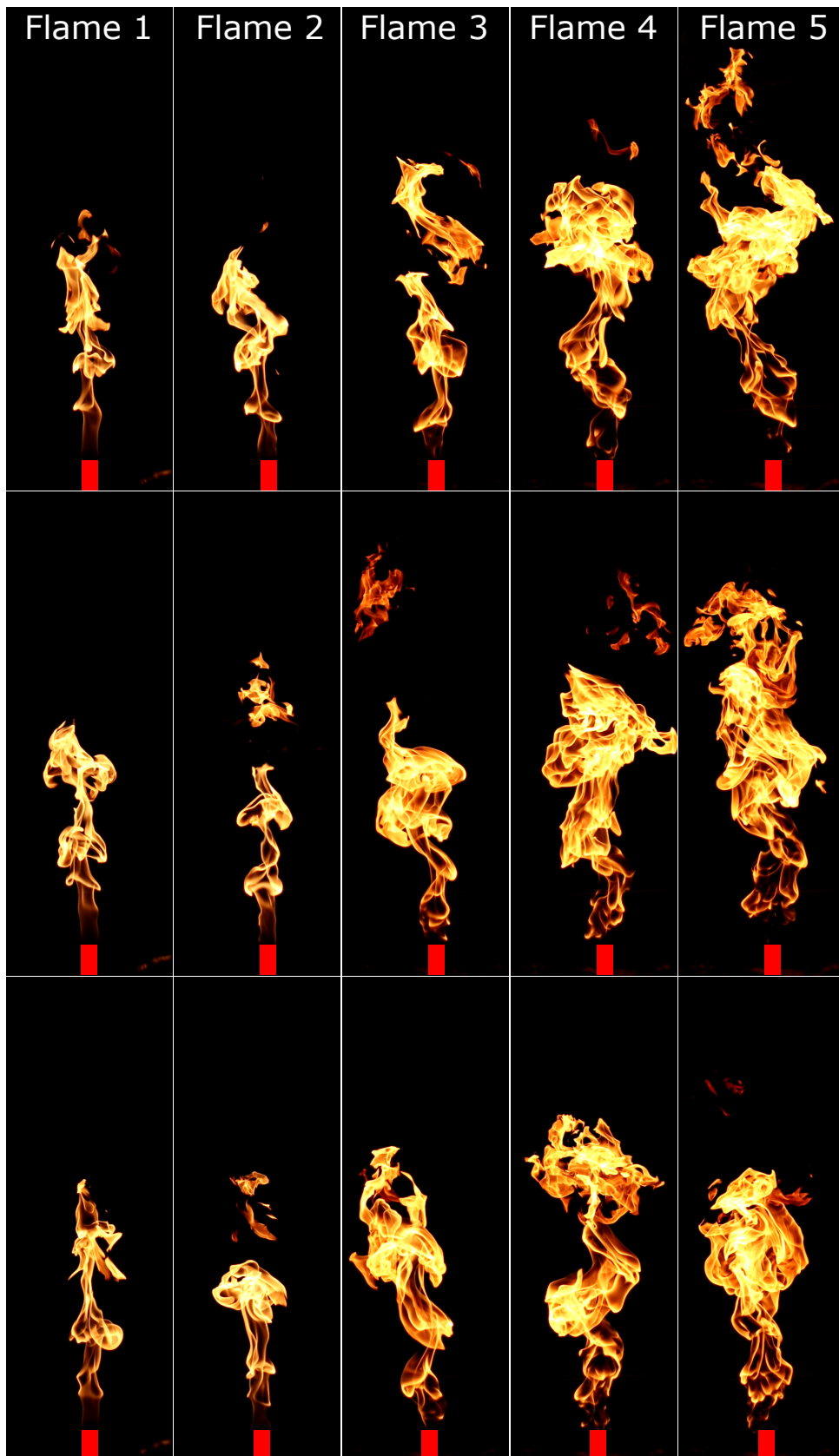


Figure 4.3: Example DSLR images for Flames 1 to 5 with the burner position marked in red.

Simultaneous measurements of OH fluorescence and Mie scattering of soot are taken for a portion of the flame length between 0–250 mm ($x/D = 0$ –7.14) above the burner exit plane. This region is preferable for analysis, as the boundary condition at the burner exit plane defines the global flame structure [189]. A comparison of the characteristic flame structure from $x/D = 0$ –7.14 for increasing fuel-turbulence is shown on the instantaneous exemplar images in Figure 4.4. Each window shown spans an axial distance of $x/D = 1.43$ (50 mm). Corresponding DSLR images of the flame are shown next to the high-speed OH-PLIF and scattering images. Measurements of OH and soot for each axial window are recorded simultaneously. The soot and OH-PLIF signal intensities vary along the flame axis, however, for clarity in visualising the overall flame structure, the colour scales have been normalised to the maximum intensity in each axial measurement window. Images are obtained at a rate of 250 Hz for 20 s duration, with a total quantity of 5000 images taken of OH-PLIF and soot scattering respectively for each flame. Superimposing the high-speed images of soot and OH in a time series reveals the temporal joint evolution of soot and OH layers marking the reaction zones.

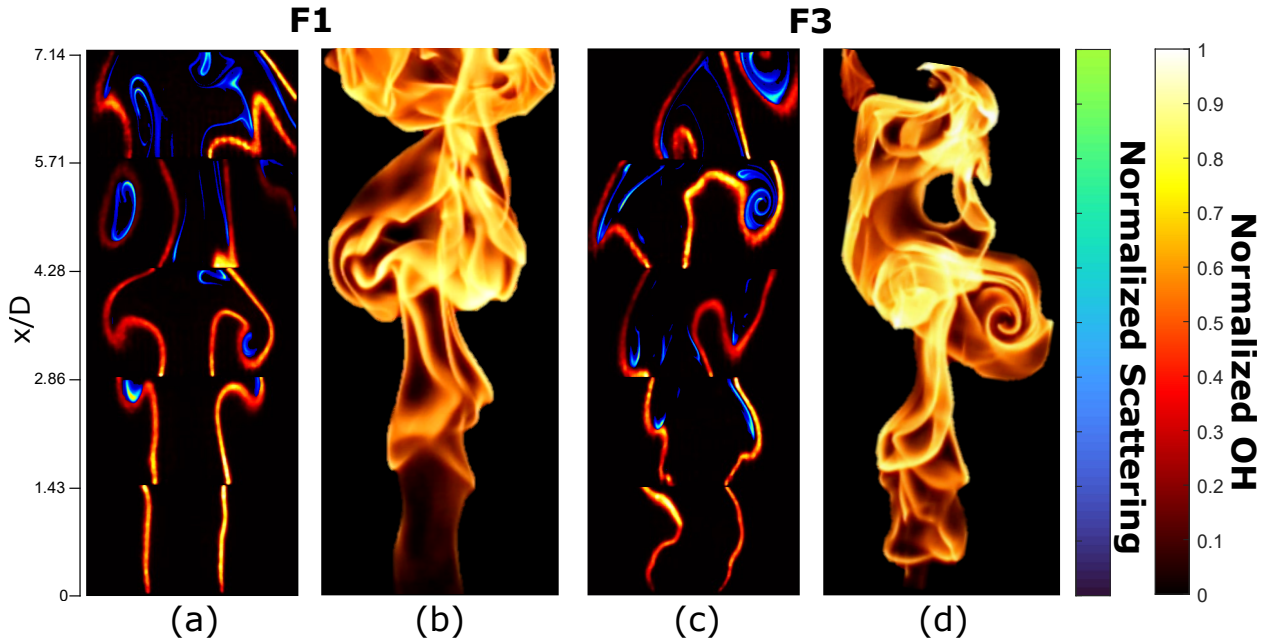


Figure 4.4: Superimposed instantaneous images of OH-PLIF (hot red colourmap) and Mie scattering of soot (cold blue colourmap) for flame 1 (F1) and flame 3 (F3). (b,c) Corresponding time-independent instantaneous DSLR images of the flames at the same scale as the high-speed images.

Flame F1 shown in Figure 4.4a and b (lowest turbulence) will be used to describe the overall flame structure, which will be compared to Figure 4.4c and d (higher turbulence) to highlight the effect of the fuel-turbulence level on the overall flame structure. For flame F1, immediately above the burner rim where the flame is stabilised, there is a region ($x/D = 0 - 1.43$) that is defined by a near-laminar flame sheet. The flame front in this region is almost completely vertical, and no soot scattering is measured. There is little perturbation or curvature associated with the OH layers, indicating that the transport mechanisms of fuel and oxidiser into the reaction zone are diffusion-controlled. Further downstream of the flame stabilisation zone, the onset of the classic flame puffing phenomena occurs at the flame neck ($x/D \approx 1.43 - 2.86$) [190]. Here, the periodic puffing motion of the flame generates toroidal vortices in a large, symmetric plume that facilitates air entrainment into the flame as the vortices dissipate during the rollover of the plume. These periodic motions occur along the flame axis, with the size of the toroidal vortices increasing as they are advected downstream.

The high-speed imaging of OH and soot scattering reveals the occurrence of a highly periodic flame pinch-off instability, which hitherto has not been characterised in buoyant turbulent fires before and will be discussed in the proceeding section.

The series of stacked images on the right (Figure 4.4c and d) shows flame F3, with increased fuel-turbulence generated by the perforated plate. The fuel-turbulence is approximately 0.918 m/s (Table 3.2). It is apparent from both the laser and DSLR imaging that the addition of fuel-side turbulence strongly affects the flame structure. At the flame stabilisation zone ($x/D = 0 - 1.43$), the flame, which is stabilised on the burner rim, is wrinkled considerably due to the sheared flow at the exit plane. This creates asymmetric buoyancy effects along the flame length, which is observed by a large curvature of the OH sheets. It is also interesting to note that soot formation occurs further upstream compared to the less turbulent case. The influence of raising the fuel-turbulence level on entrainment forces is pronounced in the third axial measurement window ($x/D = 2.86 - 4.28$). Here, the symmetrical plume and distinct puffing motion have been replaced by an asymmetric vortex structure in a plume. It appears that entrainment forces are stronger, and act primarily on a single side of the flame sheet. The plume structure experiences an asymmetric rollover motion that breaks the base flame structure into an assortment of flamelets. For more example images/videos of OH and Mie scattering of soot, please see the supplementary material presented by Xiao et al. [1]. For example, OH-PLIF and Mie scattering images of the flames without the turbulence generating plate, please see Appendix A Figures A.2 to A.5.

4.2.2 Flame pinch-off instability at the flame neck

High-speed imaging of OH-PLIF and soot scattering imaging reveals the periodic occurrence of a flame pinch-off instability occurring at the flame neck for all flames. Examples are shown in Figure 4.5. Flame pinch-off refers to the separation of the main flame body at the flame neck, resulting in the formation of a detached pocket flame that is advected downstream [191]. This detachment is associated with a periodic break or partial extinction/quenching occurring at the flame neck; buoyancy forces are responsible for flame oscillations that ultimately

separate the flame [192]. Pinch-off instabilities are typically studied using laminar flickering jet diffusion flames by imposing acoustic forcing on the inlet jet boundary condition to phase-lock the periodic flame oscillations. This creates a resonant effect, where significant vorticity enhances the entrainment of cold air [192]. As the modulated frequency approaches the resonant frequency, the flame neck elongates and there is a marked increase in the pinch-off occurrence frequency [193][194]. Pinch-off instabilities formed under these conditions are symmetric and possess a varicose structure.

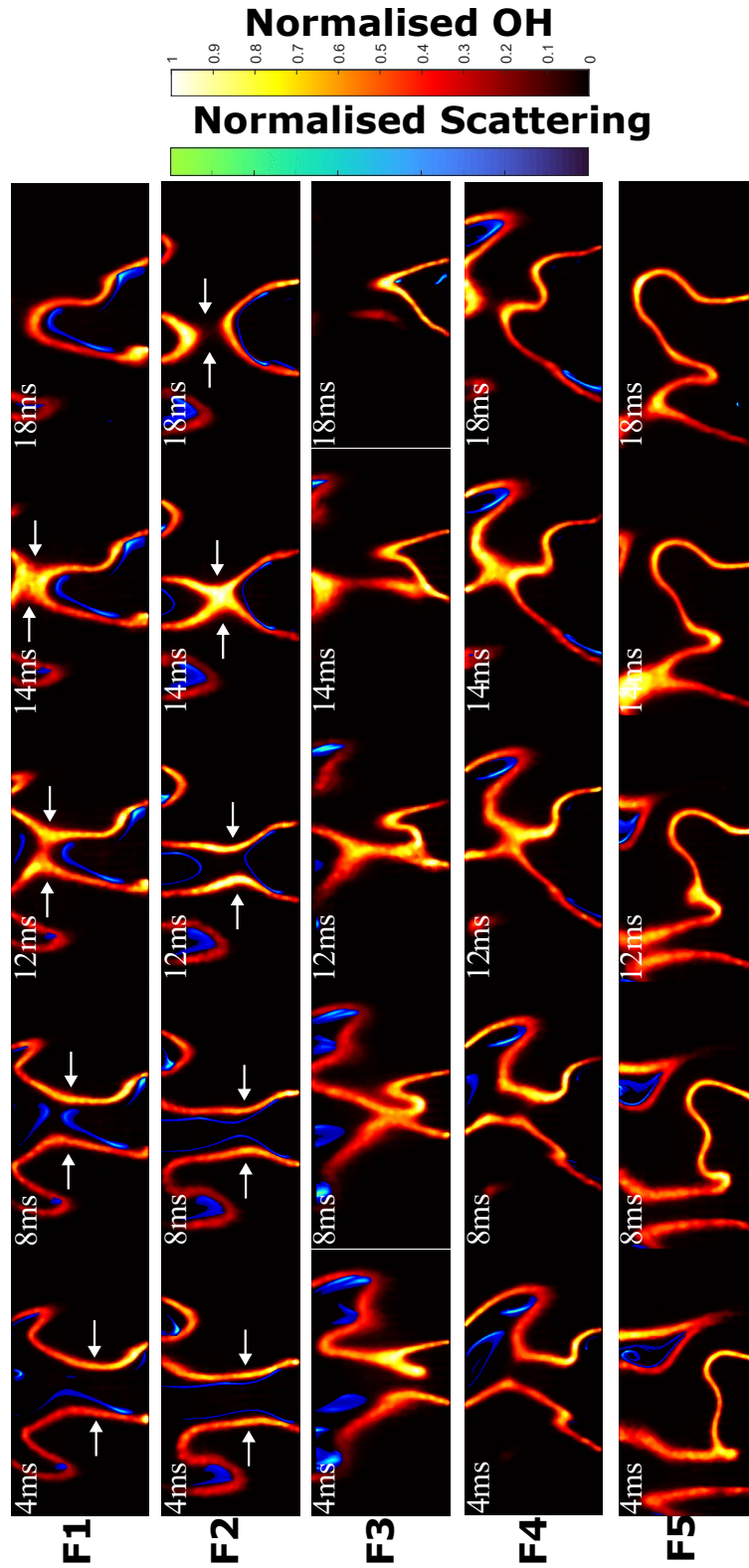


Figure 4.5: Superimposed OH and Scattering time evolution of flame pinch off events from F1 (top) – F5 (bottom). Images are taken at the third axial window ($x/D = 2.85-4.28$).

Intermittent pinch-off of the buoyant flames studied are observed to occur within a spectrum between two distinct modes based on the fuel-turbulence level, which consist of, (i) a varicose mode (Figure 4.5 F1) characterised by a symmetric flame neck and plume structure, (ii) a sinuous mode characterised by an asymmetric flame neck and plume structure (Figure 4.5 F5). Descriptions of these instabilities have been provided by Cetegen and Dong [195] for classical buoyant diffusion flames. The low turbulence flame (F1) demonstrates the same type of varicose structures at the flame neck driven by the Rayleigh Taylor instabilities (also see Appendix A Figures A.2 to A.5). However, it is observed that by raising the fuel-turbulence level (F1 to F5), flame pinch-off is instead increasingly characterised by a sinuous motion. This occurs due to the perturbations along the flame neck that arise from the introduction of lateral angular entrainment forces.

The effect of fuel-turbulence on the pinch-off instability mode and formation time sequence for each flame at increasing levels of fuel-turbulence can be observed from the example images in Figure 4.5. Each example image corresponds to approximately 4 ms time increments (left to right) for flames F1 to F5. F1 and F2 (low absolute turbulence levels) show the same varicose pinch-off instability mode, characterised by a symmetric flame neck and twin vortices developing between $x/D = 2.85 - 4.28$ that is responsible for the excessive straining and quenching of the flame neck at the instant of pinch-off (as marked by arrows). The measurements show that pinch-off occurs within a very narrow temporal window. Both flames F1 and F2 are qualitatively indistinguishable from one another due to having low absolute turbulence levels ($0.135 - 0.283$ m/s respectively). After pinch-off, the pocket flame is advected downstream out of plane within this time frame. With increasing fuel-turbulence, there is an increasingly warped flame neck region as opposed to the classical symmetric plume structure found in the low turbulence case (F1 and F2). This is the flame shifting towards the sinuous pinch-off instability mode which causes flame oscillations that can shift both in and out of the laser sheet. The warped flame results in asymmetric “flame pocket” structures that significantly increase the entrainment rate into the pocket which further stretches the flame neck. At sufficiently large stretch rates, localised quenching occurs in the form of a

sinuous pinch-off mode at the flame neck.

Example schematics of the two instability modes are provided respectively in Figure 4.6 which corresponds to flame F1 - a varicose-like instability, and Figure 4.7 which corresponds to flame F4 - a more sinuous-like instability. Both modes are shown to be defined by the angle of the entrained flow relative to the gravity vector. This angle is known to control the acceleration of entrained air into the flame, which therefore regulates the entrainment strength required to overcome the thermal expansive and diffusive forces at the flame neck. If the entrained flow velocity is large, the flame neck experiences local strain. In the purely buoyant case, the entrainment vector is almost orthogonal to gravity and the flame neck axis, which squeezes the flame neck symmetrically from both sides resulting in local quenching. This is driven by the entrainment vector overcoming the vertical buoyancy component that leads to flame stretching. For F1 (Figure 4.4) this process occurs periodically as the entrainment vector is primarily controlled by the symmetric eddies in the downstream plume that results in the classical puffing motion. This phenomenon has been thoroughly characterised through joint high-speed OH-PLIF/PIV measurements by Ahn et al. [194]. They also suggest that separation at the flame neck occurs due to excessive straining that results in the formation of a stagnation point between the flame base and the advected flame pocket. These results appear to show that the symmetric nature of flame pinch-off is linked to the classical buoyant puffing instability.

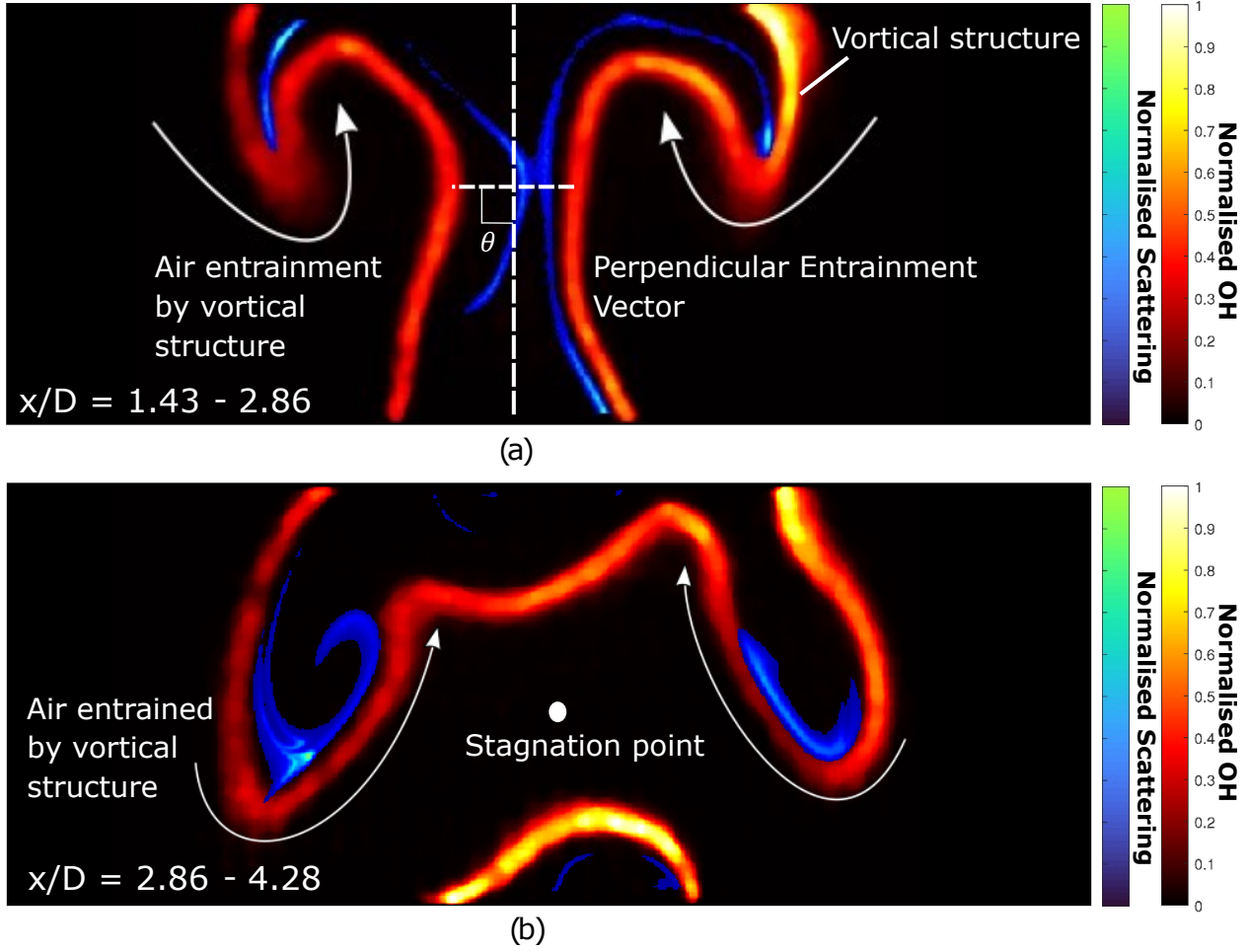


Figure 4.6: Illustrations of air entrainment flow patterns under the instability mode of low fuel-turbulence (F1), whereby local quenching by air entrainment of a symmetrical flame neck leads to a pinch-off. OH-PLIF (Hot red) and Mie scattering of soot (Jet blue) intensities have been normalised for visual clarity. The annotated arrows showing the entrainment directions are intended to be solely illustrative. The images are taken at the third axial window ($x/D = 2.85-4.28$).

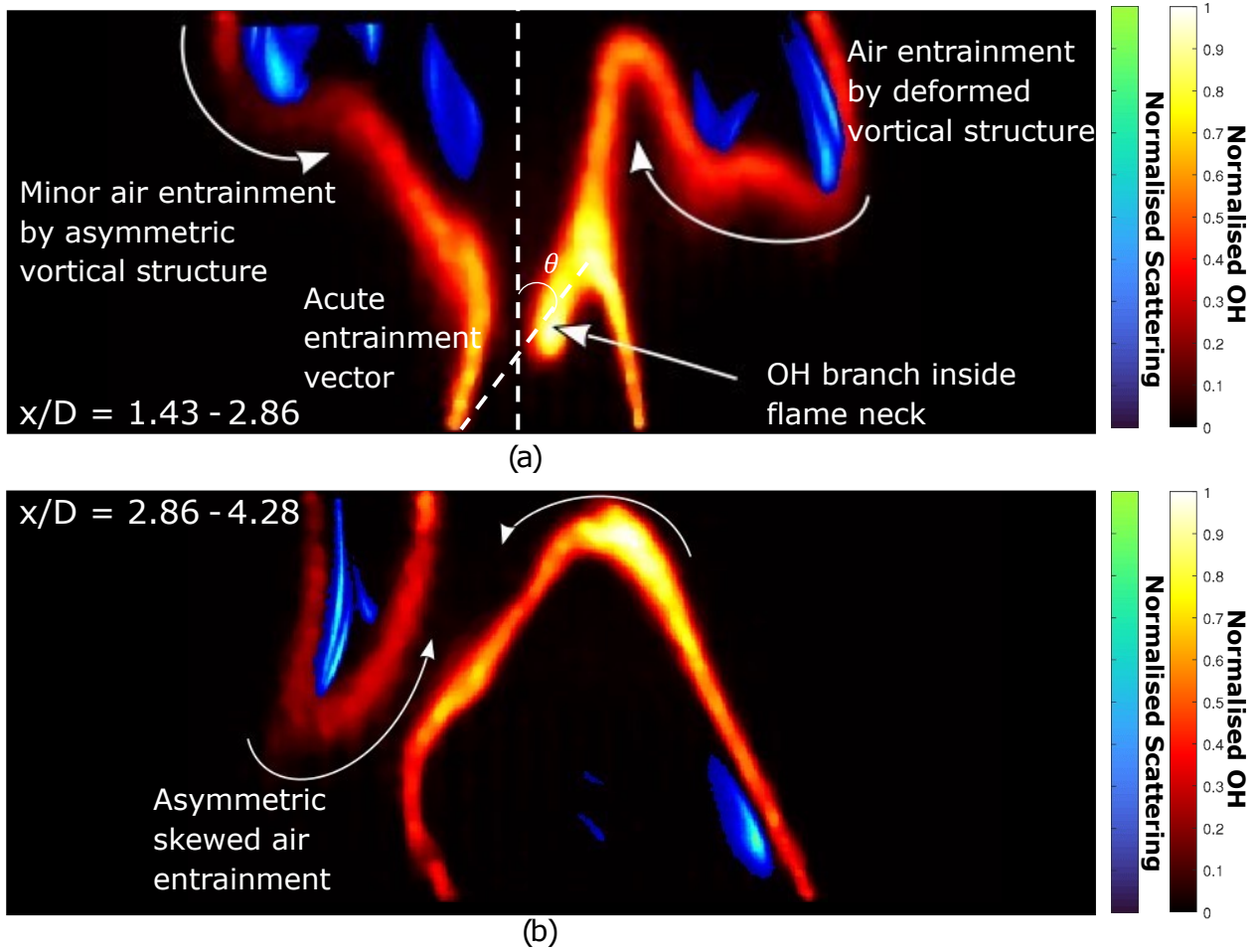


Figure 4.7: Illustrations of air entrainment flow patterns under the instability mode of increased fuel side turbulence (F_4). OH-PLIF (Hot red) and Mie scattering of soot (Jet blue) intensities have been normalised for visual clarity. The annotated arrows showing the entrainment directions are intended to be solely illustrative. The images are taken at the third axial window ($x/D = 2.85-4.28$).

Upon increasing fuel-turbulence, significant asymmetries are introduced into the flame neck region. The illustrative OH-PLIF images for F_4 (Figure 4.7) show that air is entrained into the flame neck at an acute angle relative to the gravity vector leading to the asymmetric neck structure. The observed shift from the varicose to sinuous instability mode at the flame neck region is unique for buoyant flames as this transition is typically observed significantly downstream once the flame is fully turbulent [195][196]. However, in this case, the modification of the fuel-turbulence level enables this transition to occur very close to the burner exit

plane, with no symmetric flame neck forming. The sinuous pinch-off structure is driven by asymmetric flame deformation and large orientation angles, which enables a greater air entrainment vector that is imposed on one side of the flame wall than the other. This is visualised in Figure 4.7, which shows the OH branch established well inside the flame neck due to strong angular entrainment forces quenching the flame. This creates a new pathway for air entrainment into the separated flame at the same acute angle, which enables downstream advection of the flame pocket. This pinch-off mode inhibits the capacity for the flame downstream to undergo periodic buoyant motions as a distinct puffing instability cannot form. The images show that the oxidiser transport mechanism into the overall flame structure is mostly driven by angular entrainment at the local flamelet level and is dramatically different to the low turbulence buoyant flame (F1), which is controlled by periodic motions.

4.2.3 Temporal evolution

The temporal evolution of the flame structure and fluctuating quantities are analysed using high-speed (250 Hz) signals of OH-PLIF and Mie scattering of soot. Characteristic samples of the temporally resolved signals of the binarized Mie scattering and the corresponding flame width at the flame neck region are shown in Figure 4.8. These signals are extracted from the flame neck region ($x/D = 1.43 - 2.86$), where flame puffing and pinch-off instabilities occur. Soot scattering is analysed by integrating rows of the binarized image centred at $x/D \approx 2$, with a window height of 10 pixels. The flame width is quantified by approximating the distance between the skeletonised flame sheets extracted from the OH-PLIF images at the single pixel row near $x/D \approx 2$. The signals for each quantity are measured over a 20 second period at 250 Hz (5000 images). The frequency spectra for each flame case are obtained by employing a Fast-Fourier Transform (FFT) algorithm on the time series data for both signals. The region of interest selected for the spectral analysis is deliberate as the flame neck region defines the onset of turbulence-driven perturbations in the flame. Therefore, strong spectral responses that characterise the turbulent fluctuations of the flame are expected. This is confirmed by the spectral response of the flames, as shown in Figure 4.8b. In the absence

of induced turbulence (F1), a distinct spectral line is identified at approximately 6.4 Hz for both the soot scattering and flame width spectra. This is the fundamental frequency of the flame, that matches the classical puffing phenomena expected for buoyant oscillatory flames. This result aligns remarkably well with the well-established $D^{-1/2}$ scaling relationship by Cetegen and Ahmed [197] and Hamins [198] in Equation 4.1.

$$f = 1.5D^{-1/2} \quad (4.1)$$

where D is the characteristic burner diameter (35 mm). The puffing frequency f carries little dependency to $\dot{Q}$ for the flames as shown in Table 4.1. Both the flame width and scattering signals are closely correlated, suggesting that soot formation on the high-temperature rich side of the flame occurs as the flame widens and undergoes a “puffing” instability sequence observed by the periodic toroidal vortex structure shown in Figure 4.4.

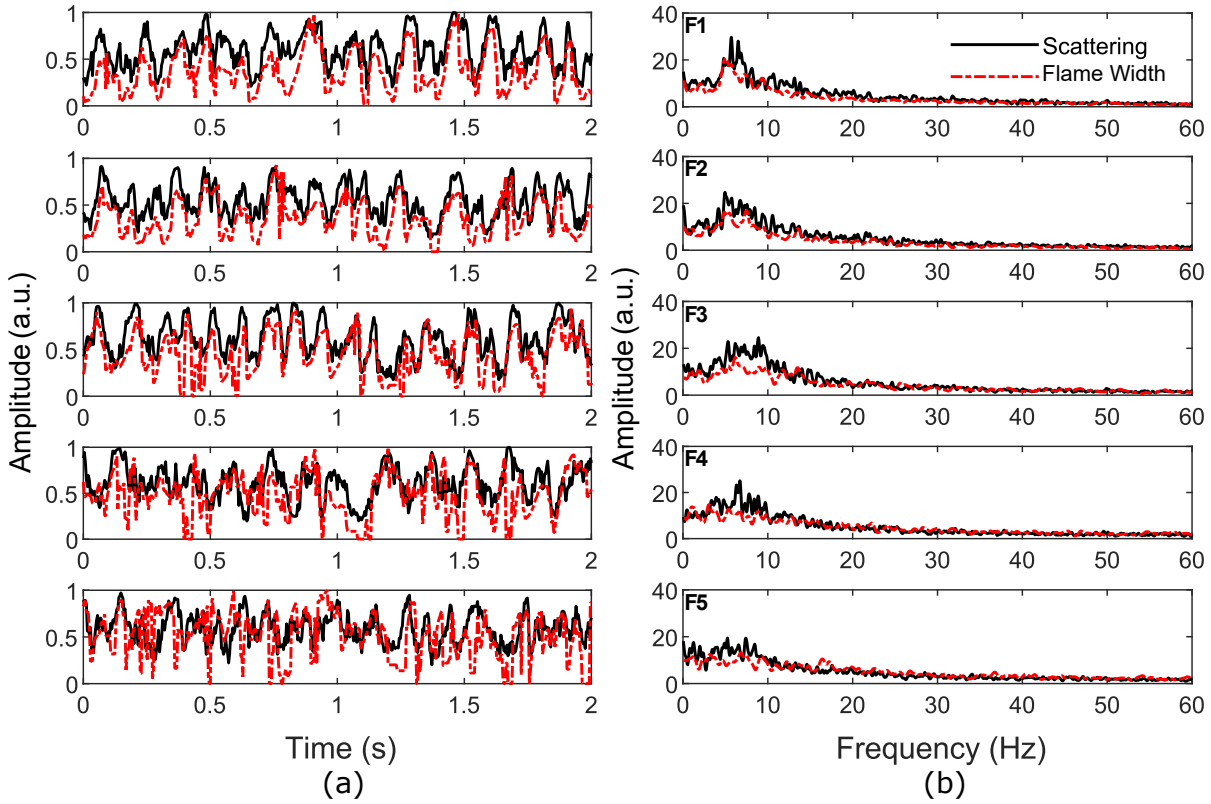


Figure 4.8: 2 second time history of (a) flame width and scattering area for all the flames (F1 - F5). (b) frequency response of flame width and the integrated scattering signal.

Table 4.1: Puffing frequencies and cross-correlations of the flames.

Flame	Peak Frequency f (Hz)	Cross-Correlation Coefficient σ
F1	6.40	0.648
F2	6.10	0.664
F3	7.10	0.604
F4	6.60	0.552
F5	6.10	0.371

Increasing the fuel-turbulence level elicits a disparate spectrum, with a considerably flatter spectral response. A fundamental frequency becomes more difficult to extract with increasing

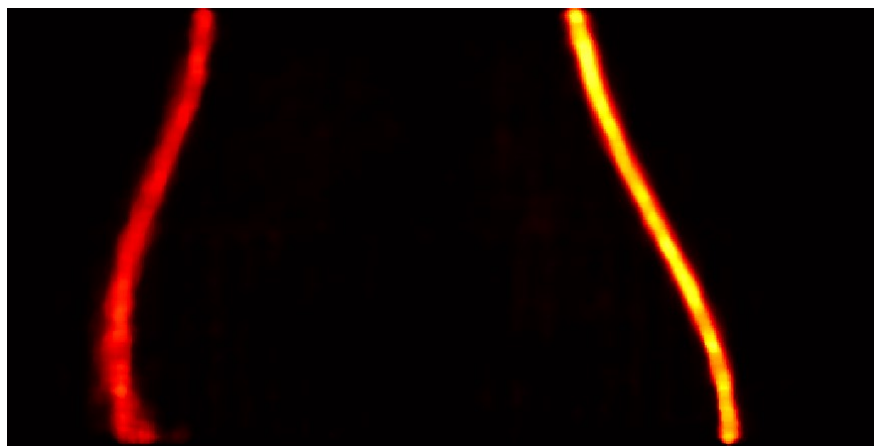
levels of fuel-turbulence (F1 to F5). The peak (albeit convoluted) signal is interpreted to vary between 6.1 – 7.1 Hz depending on the flame; however, no identifiable correlation is found between the different flames. The increasingly flat spectra demonstrates the role of air entrainment and local flame stretching and quenching on the temporal flame structure. The disappearance of a fundamental puffing frequency from the spectra from flames F2 – F5 highlights how large periodic eddy structures typical for small buoyant flames are eliminated resulting in a highly deformed flame structure.

The cross-correlation of soot scattering and flame width is shown in Table 4. The large cross-correlation coefficient of these quantities shows that temporal variations in the physical structure of the flame are closely related to the presence of soot. This is particularly relevant at low fuel-turbulence levels, where buoyant puffing instabilities are dominant and the images from F1 (Figure 4.6b) reveal that soot generally coalesces in regions of high vorticity. F1 and F2 have low absolute turbulence intensities (0.135 m/s and 0.283 m/s respectively), which correspond to similar correlation coefficients. Higher turbulence levels increasingly disrupt this process by breaking the formation of symmetrical ‘puffing’ through highly angled entrainment vectors, which in turn reduces the correlation between flame width and soot scattering. This suggests that either, there is an increase in soot oxidation or that soot formation is reduced due to smaller residence times within the flame neck region by increasing fuel-turbulence.

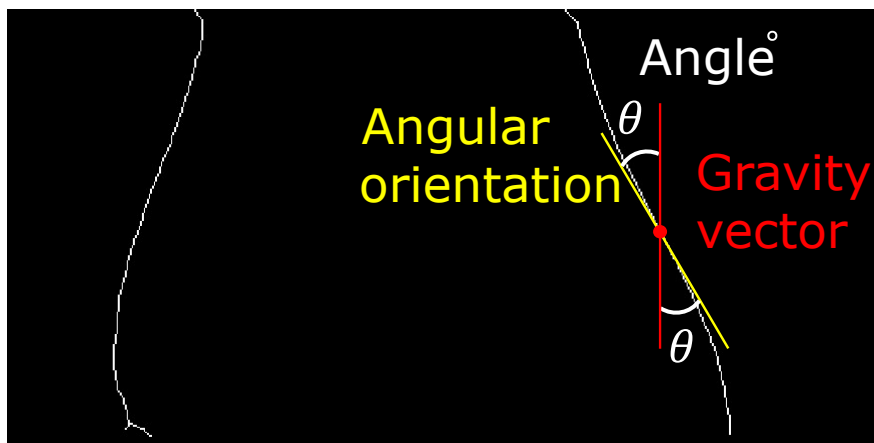
4.2.4 Flame orientation

The spatial structure of the flame is characterised and used to identify the onset of turbulence and the wrinkling break-up of the flame. This is quantified by extracting the mean and RMS angular orientations of the OH layer relative to the vertical gravity vector shown in Figure 4.10. This is done by first pre-processing the OH images as shown previously in Figure 4.2. The images are then skeletonised such that at each point on the skeleton, a centred window of 5 pixels (2 points before and 2 points after the pixel of interest) is used to approximate the angular orientation of the skeleton with respect to the gravity vector (vertical axis). The

orientation angle is not sensitive to the size of the interrogation windows used. This is done along the entire length of the skeleton to obtain a distribution of angular orientations along the OH layer. The OH orientations are established with respect to the vertical axis and temporally averaged. The angular orientation of the OH layer is intended to provide insight into the role of entrainment forces acting on the flame from the air side. Figure 4.9 shows graphically how the flame orientation angles are obtained from the skeletonised OH-PLIF image.



Pre-processed OH-PLIF



Post-processed OH skeleton

Figure 4.9: Example image processing for a single point of the flame orientation angle.

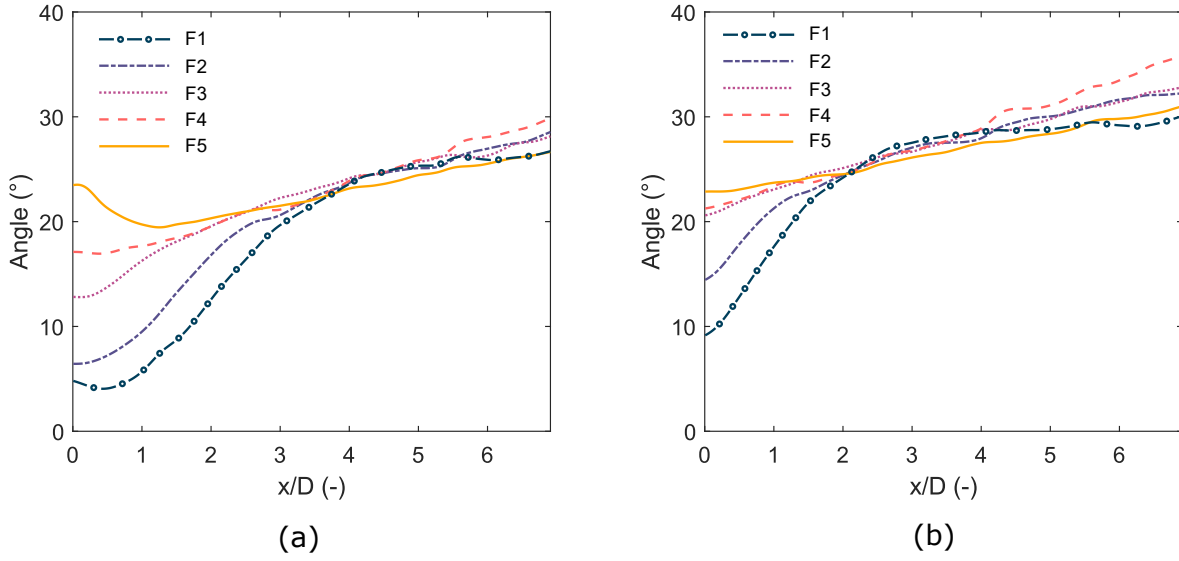


Figure 4.10: Mean (a) and RMS (b) of angular deviations of skeletonised OH layers with respect to the gravity vector for all the flames.

For all the flames (F1 – F5), at the exit plane of the burner ($x/D \leq 0.5$), both the mean and RMS orientation angles increase monotonically with fuel-turbulence. This trend is expected as the Reynolds number is greatest at the burner exit plane. Due to the strong inertial forces, angular perturbations are the smallest near the burner exit plane and oxidiser transport into the flame is diffusive. Between $x/D = 0.5 - 3.5$, the mean angle of the OH layer for the varying flames increases dramatically but eventually converges to approximately 22° between $x/D \approx 3 - 3.5$. Correspondingly, the RMS angles also converge between $x/D \approx 2 - 2.5$. The large angular perturbations in this region suggest that lateral entrainment forces are increasingly promoted below the flame neck from F1 to F5. The convergence of the flame orientation angles between $x/D \approx 3 - 3.5$ marks the transition to a buoyancy-driven flow. The angular orientations remain converged for all flames but increase linearly downstream at each axial position of x/D . The convergent nature of all the flames suggests a loss of turbulence memory as the flame develops downstream. Despite the dominance of buoyancy, the asymmetric perturbations and sinuous pinch-off instabilities in the flame neck region increasingly inhibit the formation of periodic puffing instabilities, as discussed earlier. Instead,

the flame is deformed at the flame neck which leads to a complete breakup into flamelets further downstream.

The magnitude and perturbations of the flame neck control whether varicose or sinuous pinch-off instabilities form. Once fuel-turbulence is introduced and increased, the shearing of the fuel stream facilitates lateral angular entrainment below the flame neck, leading to large flame perturbations, which force the sinuous pinch-off instability that drives the flame breakup process.

4.2.5 Flame front curvature

The preceding analysis has shown that increased fuel-turbulence in the near field has the effect of promoting lateral entrainment, thereby initiating pinch-off events resulting in flame break-up that marks the transition to turbulence. The onset of flame puffing and wrinkling are analysed by calculating the local flame front curvature from the binarised and skeletonised OH-PLIF images. This approach is normally undertaken for premixed turbulent flames [199], however, it is expected that as the turbulent structures such as vortices and asymmetric wrapping become more prominent, the local flame curvature increases. From the skeletonised data for each of the 5000 images (as shown in Figure 4.9), a cubic spline is fit to each $x(s)$ and $y(s)$ coordinate along the skeleton path s . The local curvature κ along the skeleton path is computed using Equation 4.2 [200].

$$\kappa = \frac{\dot{x}\ddot{y} - \dot{y}\ddot{x}}{(\dot{x}^2 + \dot{y}^2)^{3/2}} \quad (4.2)$$

The temporal and spatial evolution of the local curvature is presented in the form of probability density functions (PDF) in Figure 4.11, which shows the curvature PDF compiled from 5000 images for each interrogation window (representing the spatial coordinate x/D). The results show that both F1 and F2 exhibit narrowband distributions of curvature close to the exit plane. This is consistent with the near-vertical laminar flame sheets observed in Figure 4.4a. This distribution broadens for F2 at both 0 mm and 50 mm above the

burner exit plane, which results from the 100% increase in fuel-turbulence levels and starts to wrinkle the laminar flame front. As the fuel-turbulence level is increased from F1 to F5, the PDFs near the exit plane (0–50 mm) broaden considerably, clearly showing that increased fuel-turbulence promotes flame front wrinkling. Interestingly, curvature continually increases even to a point where curvature at the exit plane seems to be greater than that downstream of the flame (F5). Beyond 100 mm ($x/D = 2.86$), all the PDFs regardless of fuel-turbulence levels collapse towards a single distribution, suggesting that this region from 100–150 mm marks the transition towards buoyancy-driven turbulence defined by large vortical structures that possess large curvature. It should be noted that this transition region effectively corresponds to where pinch-off and puffing instabilities first occur (Figure 4.4 at $x/D = 2.86$). This shows a clear demarcation of axial boundaries whereby the flame transitions from a buoyant laminar diffusion regime to a buoyant flame driven by turbulence.

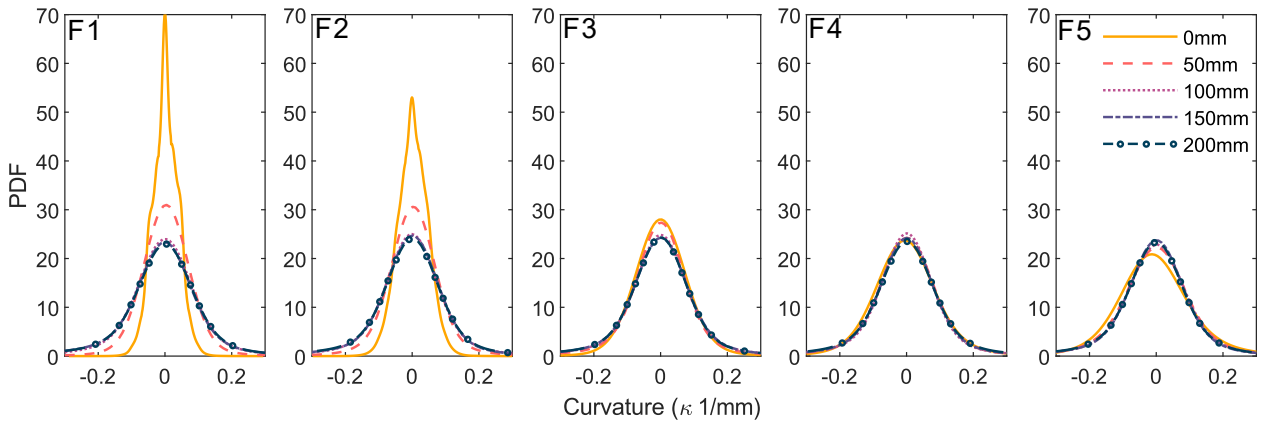


Figure 4.11: Curvature PDFs of skeletonised OH layers for F1 - F5 at each axial window (50 mm traverse distance).

4.2.6 OH distribution

Both the spatial distribution and intensity of the OH signal are primarily defined by the local strain rate and fuel-turbulence. To understand how these quantities vary spatially and temporally, they are coupled to create a normalised OH intensity parameter, F_{OH}^- , which

effectively marks the flame surface area normalised by the OH intensity in each image. PDFs of this parameter are presented at each axial window for flames F1 – F5. The PDFs are calculated following Equation 4.3 using the same processing techniques as shown in Figure 4.2. In other words, the OH signal included in the calculation of F_{OH}^- is conditioned by the presence of the flame sheet. Images are then normalised and integrated spatially. This method is similar to a spatially averaged presence index proposed by Franzelli et al [201].

$$F_{OH}^- = \sum_{i=1}^{n_x} \sum_{j=1}^{n_x} F_{OH} / F_{OH_{max}} \quad (4.3)$$

For F1 – F5, PDFs of F_{OH}^- at each axial window is presented in Figure 4.12. The parameter F_{OH}^- effectively marks the spatial presence and intensity of the OH signal at a given measurement location. As observed from instantaneous images (Figure 4.4), the OH signal possesses a greater spatial occupation area in the image as the axial length increases due to the formation of buoyant instabilities followed by the break-up of the flame. The PDFs confirm this trend, with more narrow distributions observed across F1 – F5 from 0–100 mm. It is interesting to note that the PDFs at 0 mm, 50 mm, and 100 mm (except for F1 at 0 mm) continuously broaden with increasing fuel-turbulence. This shows that the flame surface area monotonically increases due to the introduction of flame wrinkling promoted by lateral entrainment earlier in the diffusion-dominated “jet” component of the flame. Further downstream from 150–200 mm, the PDFs asymptotically collapse to a singular PDF with increasing axial distance, marking the location where buoyancy-driven turbulence completely dominates the flame structure.

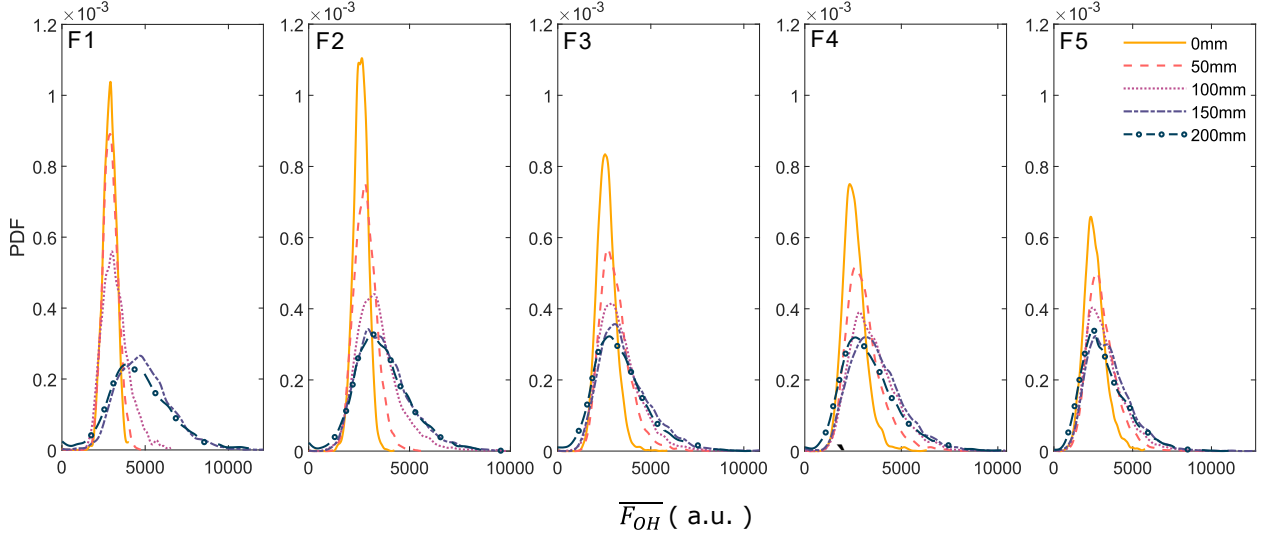


Figure 4.12: Normalised OH spatial presence distribution probability density functions for F1 - F5 at each axial window for the 5000 acquired images.

4.3 CONCLUSIONS

This chapter presents the evolution of flame structure with increasing levels of fuel turbulence. The flames are spatially and temporally resolved by simultaneous high-speed imaging measurements of OH-PLIF and Mie scattering of soot at several locations downstream of the burner exit plane. It was shown that by raising fuel-turbulence levels:

- The angular orientation of the flame sheet in the near-field along the vertical axis increases with increasing fuel-turbulence. Fluctuations in the flow at the burner exit plane promote lateral angular entrainment into the flame neck region, leading to large flame perturbations and flame breakup.
- Probability density functions of the flame front curvature and OH intensity (marking flame surface area) increasingly broaden in the near-field region of the flame (before the puffing location) as flame wrinkling occurs resulting from lateral entrainment. The onset of the transition to buoyancy-driven turbulence also shifts more upstream.

- Puffing instabilities extracted from the high-speed measurements in the buoyant flames free from fuel-turbulence generation align closely with empirical models. Puffing instabilities are observed in all flames, with an increasingly flat spectral response with increasing fuel-turbulence. Cross correlations of the flame width and soot scattering at the flame neck decrease with increasing fuel-turbulence.
- A pinch-off instability commonly associated with buoyant pool fires has been observed to initially take place at the flame neck. This occurs due to the lateral entrainment vector, where air-side entrainment forces overcome the diffusive and thermal expansive forces in the flame sheet that quench the flame until separation into a flame base and pocket.
- Increasing fuel-turbulence transitions the flame from a varicose to a sinuous instability. This inhibits the capacity for the flame to generate a classical puffing instability, thereby shifting the mechanism of oxidiser transport into the flame.

These results demonstrate that the burner can modify entrainment into the near-field region of the fire. This enables the burner to control key processes defining turbulent fires such as the dominant buoyant flame instabilities, turbulence-radiation interaction, and soot formation. Therefore, this chapter provides valuable measurements of flame structure and develops a platform for future quantitative measurements to characterise buoyancy-turbulence interactions and help further develop and validate numerical models.

Chapter 5

Chemically Enhanced Water Mist Fire Suppression

This chapter presents near-field measurements of water mist droplets suppressing a buoyant turbulent diffusion flame. Compressed natural gas (CNG) buoyant diffusion flames are stabilised on the Sydney Turbulent Buoyant Fire Burner, which is surrounded by a low-velocity air co-flow that is seeded with fine water mist droplets ($d_{32} = 50 \mu\text{m}$). The water mist is doped with varying concentrations of metal alkali salts (NaHCO_3 , KHCO_3) that release radical scavenging molecules, providing enhanced suppression capabilities through chemical inhibition in addition to the quenching effect from the water droplets. Joint Mie scattering and OH-PLIF are employed at a high repetition rate of 400 Hz to image the droplet field and OH structure, which are deemed here to approximate the high-temperature reaction zone. The simultaneous imaging technique allows for the observation of interactions between the flames reaction layers and the water mist droplets. The spray boundary condition across the wind tunnel exit plane is quantified using PDA. Flame extinction limits are measured by defining the critical condition at which the flame destabilises and lifts off the burner exit plane. A stability map is developed to quantify suppression efficacy in terms of the water mist flow rate and inhibitor concentration. Joint OH-PLIF images of selected cases at varying

extinction levels show that the addition of inhibitor introduces frequent breakages in the OH layers, marking regions of local extinction and re-ignition. Large mass fractions of inhibitor in the water, which, once evaporated, produce excess salt crystals in the local extinction zones that cause streaks of salt clouds that line both the lean and rich sides of the flame. The chemical scavenging effects of the OH radical by NaHCO_3 and KHCO_3 are quantified by evaluating the reduction of the mean OH fluorescence signal in the flame at varying locations. Probability density functions for the OH area characterise local extinction in the flame due to the radical scavengers. The order of OH radical depletion and localised extinction in the flame due to the water mist follows: $\text{KHCO}_3 > \text{NaHCO}_3 > \text{H}_2\text{O}$.

5.1 METHODOLOGY

5.1.1 Misting system setup

The Sydney buoyant turbulent fire burner is seated inside a square (250 x 250 mm) wind-tunnel supplying an air co-flow of 0.2 m/s. Details on the burner design [1] can be found in Chapter 3. The suppression studies in this chapter use a turbulent buoyant diffusion flame with a fixed heat release rate of 20 kW, which is generated using compressed natural gas (CNG) supplied through a mass flow controller at 36.6 SLM. Figure 5.1 shows a schematic of the water mist-laden co-flow, with the burner housed in the centre of the wind-tunnel protruding 10 mm above the wind-tunnel exit plane. The air co-flow is seeded with a fine water mist, generated by six hollow cone atomising nozzles (red type KBN) evenly distributed radially around the burner. A characterisation of a single nozzle is performed in the following Section 5.1.4 of this chapter. The nozzles are recessed 350 mm below the burner exit plane to slow down droplet velocities, allowing for homogeneous mixing of the water mist and air co-flow. Each nozzle produces a hollow cone of fine water spray with a cone angle of 80° . Two layers of honeycomb (19 mm cell) screens are placed 100 mm upstream of the burner lip to straighten the mist co-flow. The 100 mm recess is crucial for droplet field homogeneity, as any recess distance less than 100 mm, results in the mesh significantly impacting the

exit plane flow field structure (refer to Appendix B.1 for a convergence study). To ensure steady-state flow, measurements are taken at least five minutes after the water mist system is turned on, as the build-up process of water films or deposits on the internal surfaces of the wind-tunnel produces transient results.

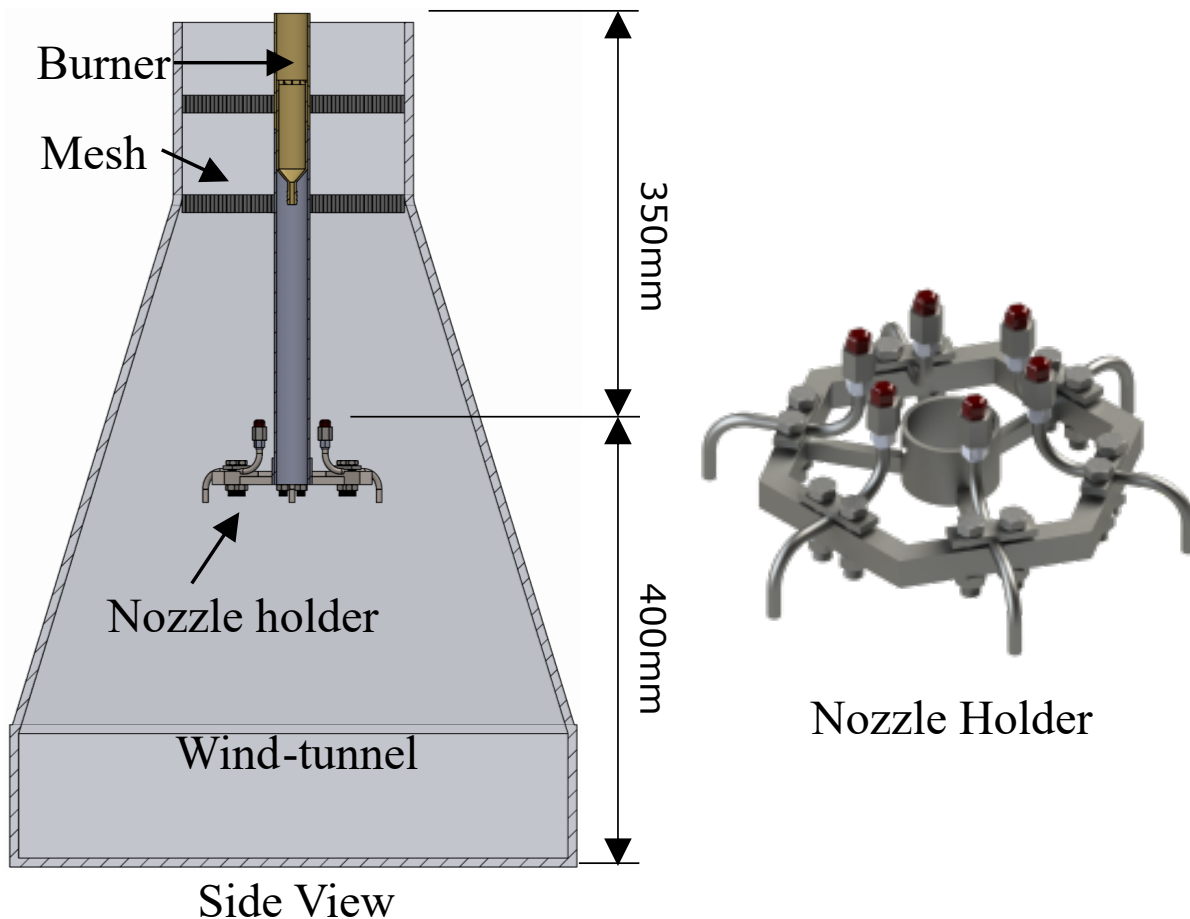


Figure 5.1: Schematic of water mist system and nozzle holder.

A collection tank placed in the wind-tunnel is used to measure the total amount of water loss due to obstacles downstream of the mist pathway. Exit plane PDA measurements and measurements of the total amount of water collected in the wind tunnel determine the exit plane water mist flow rate. The misting nozzles are pressurised by a gear pump that draws water from an upstream reservoir. A water pressure regulator installed before the nozzles with a 5-micron particulate filter controls the nozzle inlet pressures, which therefore, control

the volumetric flow rate of water mist. The wind-tunnel sits approximately 1.5 m below an exhaust hood, ensuring minimal effects of exhaust velocity on the flame and mist dynamics. The experimental setup is in an open atmosphere, although shielded from atmospheric draft without disturbing/inhibiting air entrainment from the flame.

5.1.2 Flame cases for high-speed imaging

Two alkali metal salts, potassium bicarbonate (KHCO_3) and sodium bicarbonate (NaHCO_3), are chosen as inhibiting agents as they are well-known powerful inhibitors with relatively low thermal decomposition temperatures into their respective radical scavenging molecules: KOH and NaOH [132]. Both KHCO_3 and NaHCO_3 are highly soluble in water with solubility limits of 33 g/100 mL and 8.7 g/100 mL at 20 °C, respectively. The salts are dissolved in water and stored in containers that feed the gear pump. Flame stability limits are generated that map flame suppression efficacy over the water mist flow rate and inhibitor concentration range, the volume flow rate of water mist and inhibitor concentrations proposed for further analysis are shown in Table 5.1, with a discussion of the selection process of these cases detailed in Section 3.2. The $\sigma(\%)$ parameter represents the percentage of the solubility limit in water (at standard atmosphere) for the given salt, “w/v” is the mass concentration of salt dissolved in water, “ $\dot{v}$ ” is the total volumetric flow rate of water mist exiting the wind tunnel, and “% B_f ” is the flow rate percentage of the blow-off/extinction limit (Figure 5.7 dashed line) using 52.3 mL/min (pure water) to adjust the flow rate at the respective concentrations tested (i.e. +10 % = +5.23 mL/min).

Table 5.1: Flame cases for high-speed imaging.

Case	Inhibitor	σ (%)	%w/v (g/100mL)	$\dot{v}$ mL/min	% B_f
1	—	—	—	34.0	92.0
2	—	—	—	52.3	100
3	—	—	—	56.9	109
4	NaHCO ₃	40	3.48	27.3	87.0
5	NaHCO ₃	40	3.48	42.5	101
6	NaHCO ₃	40	3.48	47.4	114
7	KHCO ₃	40	13.2	14.0	92.3
8	KHCO ₃	40	13.2	21.2	100
9	KHCO ₃	40	13.2	26.4	110

5.1.3 PDA setup for spray characterisation

A commercial three-axis component Phase Doppler Anemometry (PDA) system (Artium Technologies Model PDI-300) was used for single-point measurements of droplet velocity, diameter distributions and volume flux at the wind-tunnel exit plane. Two PDI-300 transmitters with a focal length of 500 mm are focused simultaneously on the probe volume, while the 500 mm focal length receiver was positioned in a 40° forward scattering configuration with respect to transmitter one and a 60° forward scattering configuration with transmitter two, all beams have a 3.74 μm interference fringe spacing. Three pairs of beams with wavelengths 532.0 nm, 561.0 nm and 660.0 nm are used for measuring the droplet diameters, and the axial and radial components of velocity. Built-in probe volume correction (PVC) in the software (AIMS) has been implemented to correct for lower detectability of small particles at the edge of the probe volume. Point measurements of droplet diameters, volume flux and the mean axial and radial velocities were taken 5 mm above the exit plane of the burner for a stable reacting flame (if allowed) with a constant supply of water mist. Data was sampled for 60 s (or 20,000 droplet scattering realisations), with data acquisition rates of approximately 500

Hz in regions of high flux near the burner and 50 Hz in regions of low flux near the edges of the wind tunnel.

5.1.4 Single nozzle characterisation

A characterisation of droplet spray statistics for a single KBN red type nozzle is performed at 10 and 20 mm downstream of the nozzle orifice with the nozzle pointing downwards. Figure 5.2 shows radial profiles of droplet distributions of d_{10} , d_{32} and both axial and radial velocities. These measurements are taken at a constant nozzle pressure of approximately 0.7 MPa, which is equivalent to 150 mL/min in Figure 5.4. Each measurement location has a droplet size distribution that follows an approximate Rosin-Rammler profile, where the d_{10} ranges between 8 - 41 μm at an axial location of $z = 10$ mm and maintains a very similar profile at $z = 20$ mm. The d_{32} ranges from 18 - 62 μm at $z = 10$ mm and broadens at $z = 20$ mm with a range of 22 - 60 μm . The axial velocity profiles show peak velocities of 6 m/s at the wings of the hollow cone at $z = 10$ mm, dropping to 4 m/s at $z = 20$ mm. The radial velocities show peak velocities of 4 m/s at $z = 10$ mm dropping to 2.5 m/s at $z = 20$ mm. The overall peak radial velocities are slightly lower than the axial velocities, which shows that the angle of the hollow cone is less than 90° . At an operating pressure of 0.7 MPa, the hollow cone angle is measured to be approximately 70° .

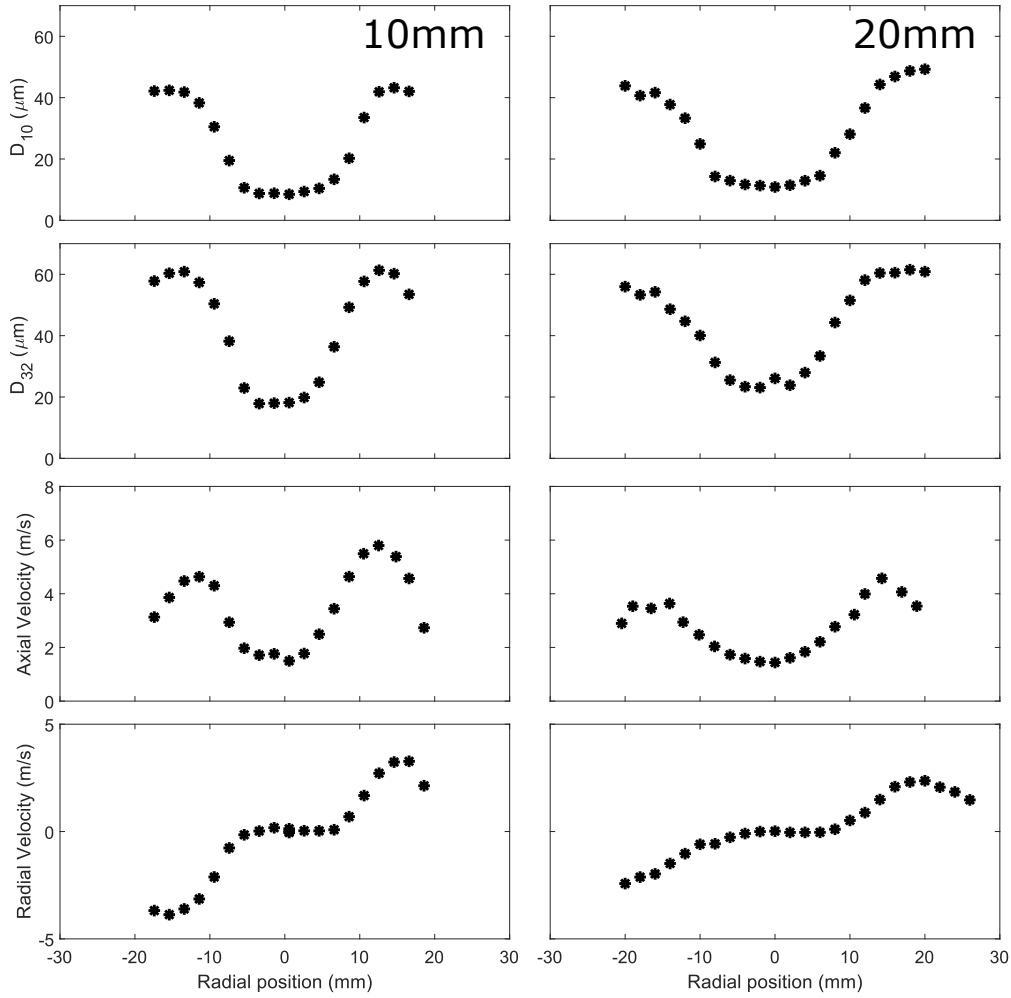


Figure 5.2: Centreline radial profiles of droplet distributions, axial and radial velocities for a single nozzle at 10 mm and 20 mm downstream of the nozzle orifice.

5.1.5 Exit plane boundary condition characterisation

Cross-sectional centreline profiles for the wind tunnel exit plane of velocity, diameter, and flux distributions measured with PDA are shown in Figure 5.3 for three water mist flow rates. All measurements are conducted with a 20 kW flame stabilised at the burner exit plane (where applicable). The mean absolute droplet velocity at the wind-tunnel exit plane varies from 0 m/s at the edges of the wind-tunnel to 1 m/s, increasing towards the burner rim. Droplet velocities are predominantly in the axial direction, with near zero radial components.

d_{10} (geometric mean) and d_{32} (Sauter Mean Diameter) droplet profiles across the exit plane are relatively uniform at $20\text{ }\mu\text{m}$ and $50\text{ }\mu\text{m}$, respectively. The droplet size distributions at all measured locations closely follow a Rosin-Rammler profile. The d_{10} increases above the burner rim to $25 - 30\text{ }\mu\text{m}$ at $\pm 20\text{ mm}$ as the small droplets either evaporate or are advected downstream by the flame sheet/fuel-flow, with only larger droplets remaining towards the fuel side. The volume flux of water mist at the wind-tunnel exit plane varies between 0 cm/s near the edges to 0.01 cm/s near the burner rim, dropping to near zero above the burner where the flame sheet is located. Unfortunately, full droplet size distributions are not readily available, though these distributions can generally be approximated by a Rosin-Rammler distribution given a d_{50} (Further clarification can be provided upon request).

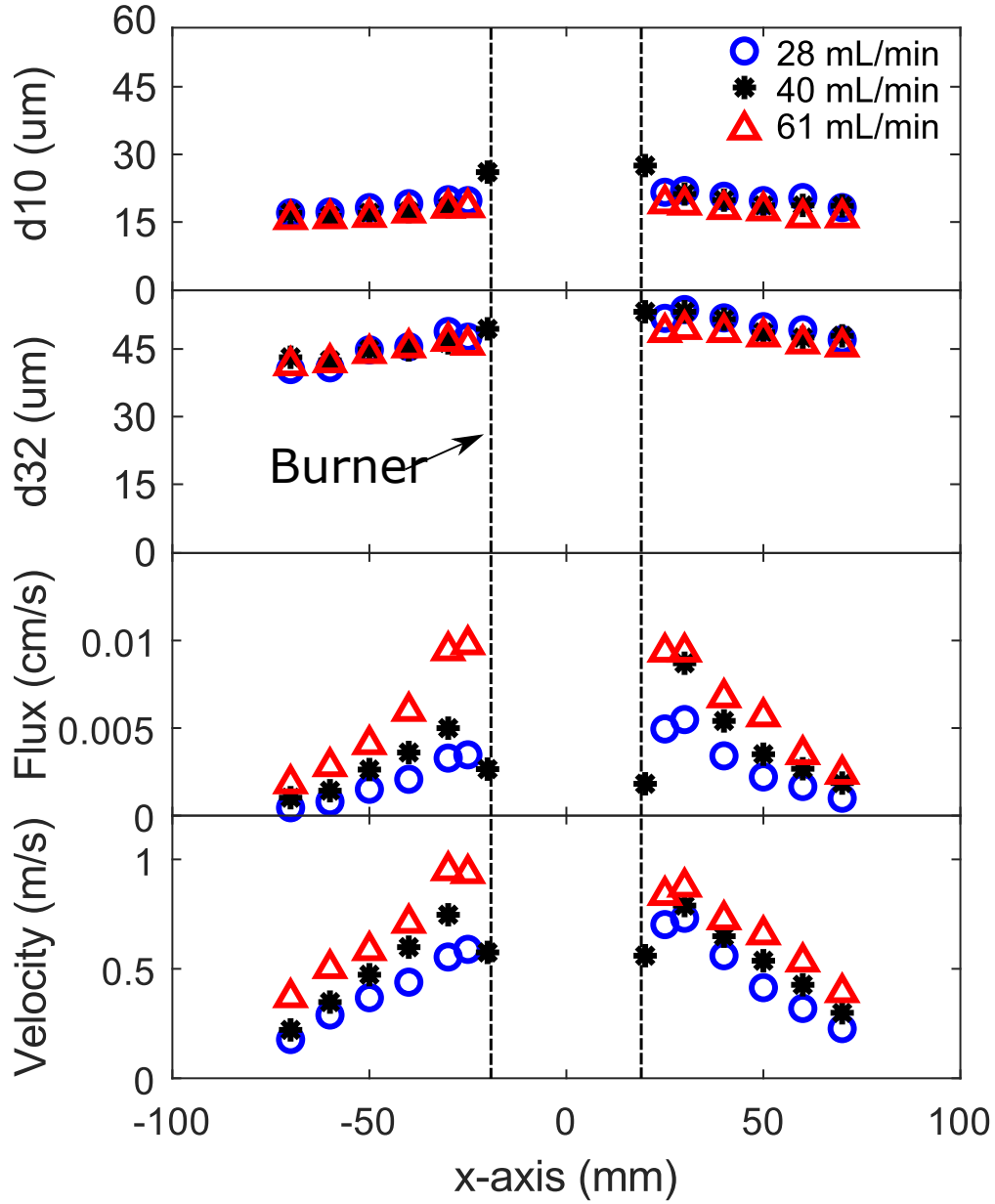


Figure 5.3: Exit plane centreline droplet diameters (d_{10} and d_{32}), volume flux and mean droplet velocities.

Integrating the volume flux profile (measured with a grid resolution of 10×10 mm) across the entire wind tunnel exit plane enables the computation of the total volumetric flow rate of water exiting the wind tunnel. Measurements of exit plane volume flow rate with PDA are then validated by measuring the total volume of water collected in the collection tank after a

set period, where the difference between the input flow rate and the water collected inside the wind-tunnel is the approximate total flow rate of water mist exiting the wind-tunnel. The volume flux is calculated using a transit time method developed by Artium Technologies that measures the probe volume droplet number density [179]. Figure 5.4 shows integrated volume flux PDA measurements of three exit plane flow rates for each of their total input nozzle flow rates. The flow rates selected cover most of the flow rate range used in this chapter. A linear fit provides a calibration factor for all measurements herein to convert the known input nozzle flow rates to the final water flow rate that exits the wind tunnel. Full PDA maps of exit plane boundary conditions for the three different flow rates are shown in Appendix B.3. PDA measurements with the addition of high concentrations of an alkali salt (60 % KHCO_3) possess negligible effects on the droplet properties as shown in Appendix B.2 Figure B.6. The total measured flow rates from the collection tank, and PDA integrated volume flux are within 5 % of each other. A comprehensive set of PDA measurements are also performed at select axial distances along the flame. These results were used to estimate droplet evaporation rates and show the reduction in droplet flux at downstream locations for a single flame. These results can be found in Appendix B.2.

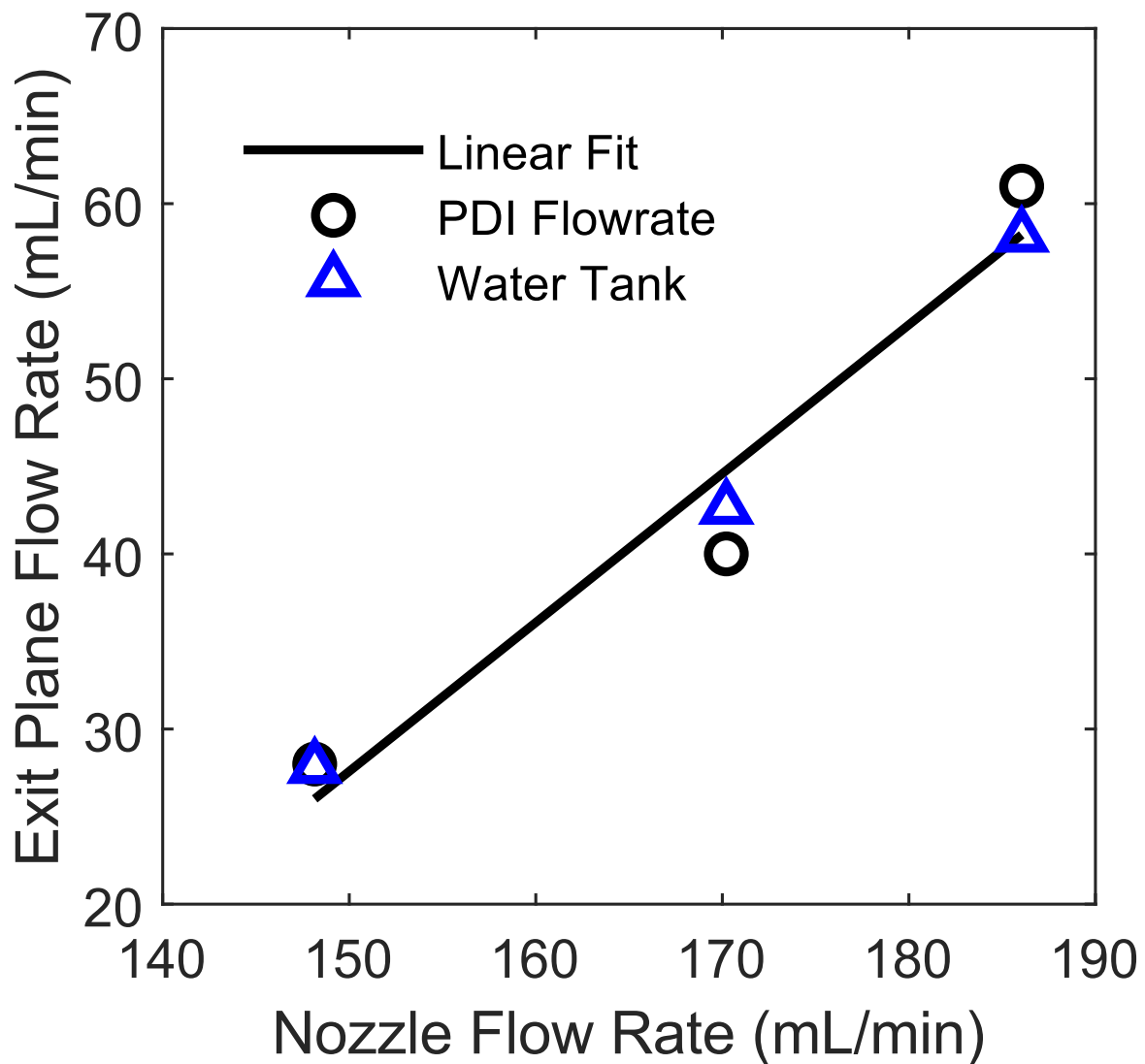


Figure 5.4: Measured exit plane water mist flow rate vs nozzle input flow rate, validating the PDA volume flux by measuring the collected water in the wind tunnel.

5.2 RESULTS AND DISCUSSION

Once the boundary conditions have been characterised, further experiments can be performed to identify how the flame behaves with varying flow rates of water mist and varying concentrations of sodium and potassium bicarbonate. A flame stability map will be created showing

regimes of flame extinction, which is then used to guide the case selection process for the high-speed imaging of OH-PLIF and Mie scattering of droplets.

5.2.1 Flame stability limits

The flame extinction limits are heavily influenced by both the flow rate of water mist and inhibitor concentration. Stability maps are created to identify extinction regimes and to contrast inhibitor efficacy at various concentrations. The extinction delay time measured in a steady-state water mist flow is the time elapsed after flame ignition until blow-off occurs. The experimental process is as follows: (i) turn on both the water mist co-flow and flow of fuel. (ii), ignite the fuel at the burner exit plane, producing a stable flame. (iii), measure the time taken from ignition to flame blow-off (extinction delay time). Figure 5.5a shows an example set of extinction times for pure water and a 20 kW flame. Each data point on the extinction delay time (lift-off time) curve is created from an ensemble average of 20 time recordings for the same water mist boundary conditions and flame. The 20 time recordings create a single average data point with the standard deviation plotted as error bars. The error bars show that with increasing extinction delay times, the standard deviation of extinction times increases dramatically, and vice versa. This alludes to the stochastic nature of the inhibition process and how sensitive the extinction limit is to the boundary conditions. At a high flow rate of water mist, in this case, 70 mL/min, it becomes very difficult to experimentally resolve the extinction times as blow-off occurs extremely fast. Also, the act of non-uniform flame ignition (blow torch) may influence the time it takes for the flame to blow-off in cases close to zero seconds. Flame extinction is defined by destabilisation of the flame base where the flame lifts off (blow-off) the burner rim, transitioning the flame from an anchored flame (Figure 5.6b, left) to a lifted flame (Figure 5.6b, right).

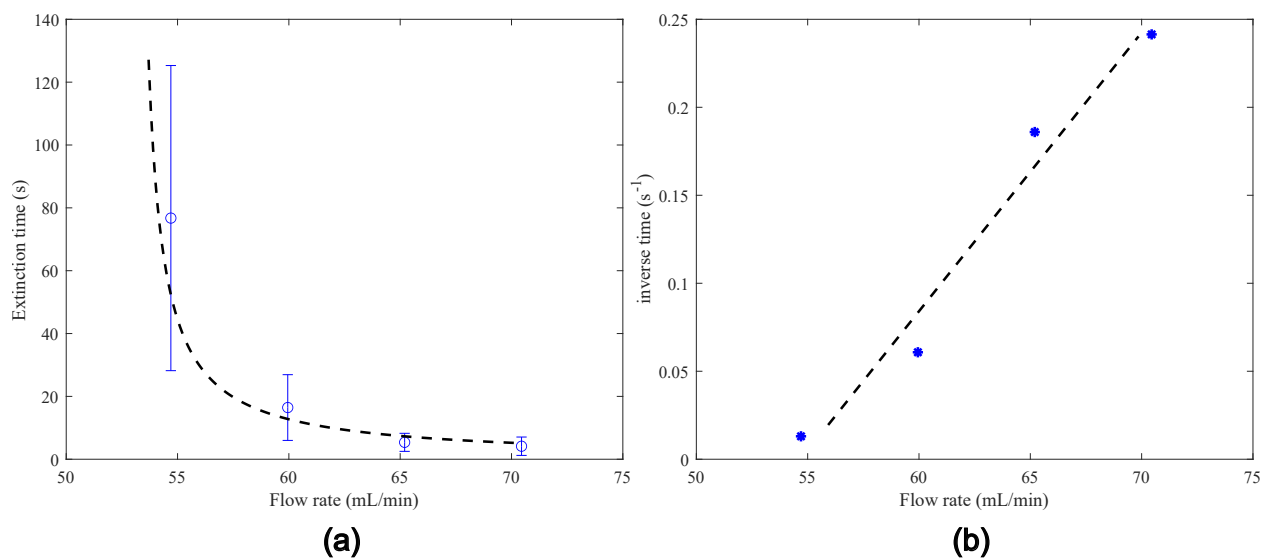


Figure 5.5: Average extinction delay times for pure water at varying flow rates of water mist. Error bars correspond to the standard deviation of each ensemble point which is an average of 20 time recordings.

Figure 5.6a shows examples of the average extinction delay times with respect to the flow rate of water mist issuing from the wind tunnel at varying inhibitor concentrations. Interestingly, all flames, regardless of inhibitor and/or salt concentration, show the same inversely proportional decay profile in average flame extinction delay times, only translated in the x-axis (flow rate mL/min) depending on the inhibitor and concentration. The extinction time exhibits similar trends as previously studied in literature [89], where extinction times are inversely proportional to the application rate of water. This proportionality is also shown in Figure 5.5b, where a linear trend is observed between the inverse of time vs flow rate.

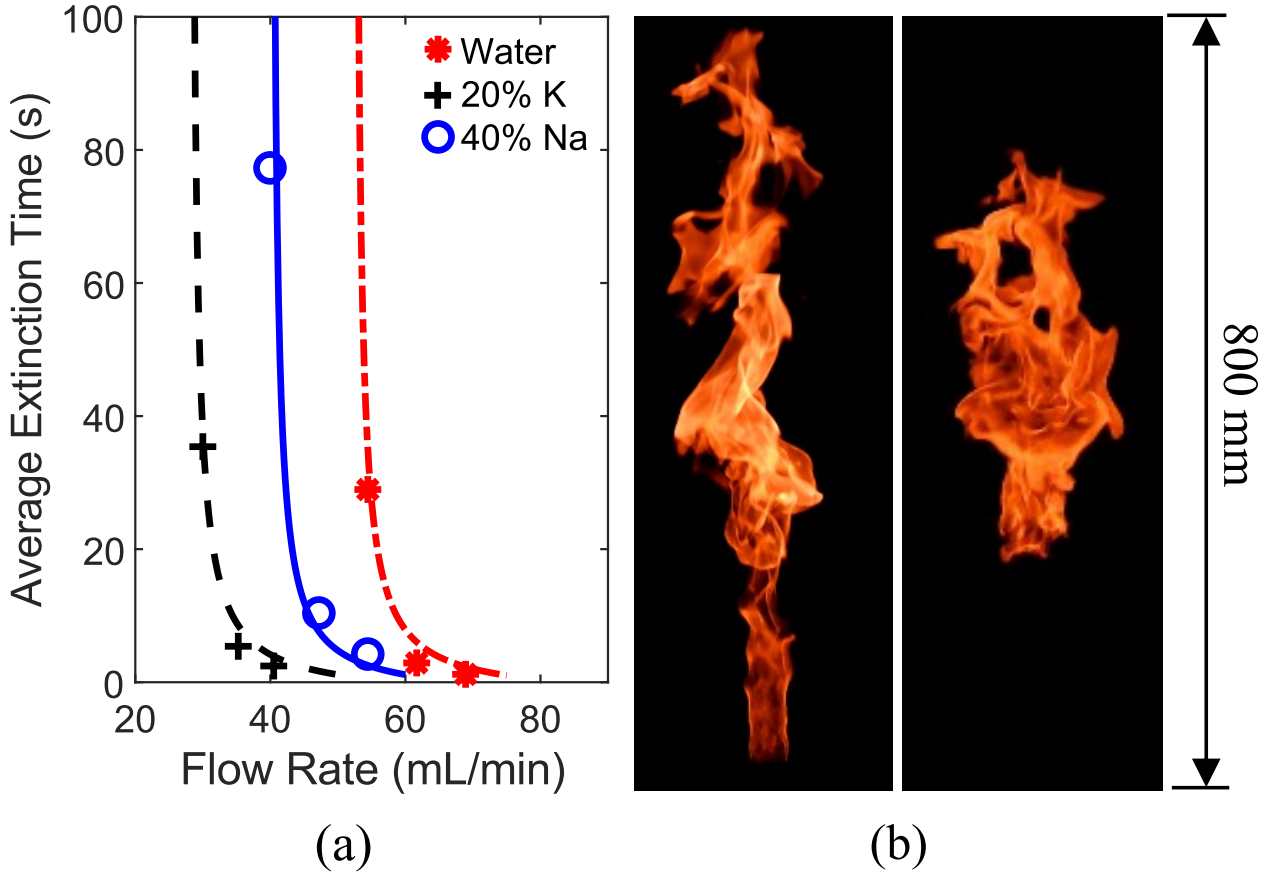


Figure 5.6: (a) Average flame extinction delay times at select flow rates and concentrations, with (b) DLSR images of a stable flame and a flame undergoing extinction/blow-off.

Therefore, the extinction process can be defined by Equation 5.1, where “ t ” is the average time to extinction (s), “ $\dot{v}$ ” is the flow rate of water mist that exits the wind tunnel in mL/min and “ c_1 ” is the maximum achievable flow rate of mist where the flame is unconditionally stable.

$$t \propto (\dot{v} - c_1)^{-1} \quad (5.1)$$

Equation 5.1 enables the transformation of Figure 5.6a from extinction time vs mist flow rate space into mist flow rate vs inhibitor concentration space. The extinction delay time parameter is analogous to an extinction probability, due to the process’s inherently stochastic

nature [202]. Figure 5.7 shows the stability limits for a 20 kW flame with varying water mist flow rates and inhibitor concentrations. Five concentrations for each alkali salt up to $\sigma = 60\%$ are used to construct the stability map, which is shown in Figure 5.7 for KHCO_3 (Figure 5.7a) and NaHCO_3 (Figure 5.7b), respectively. The dashed line in the boundary plot represents the “ c_1 ” term of Equation 5.1. This delineates the requirements for flame extinction given a water mist flow rate and concentration of inhibitor.

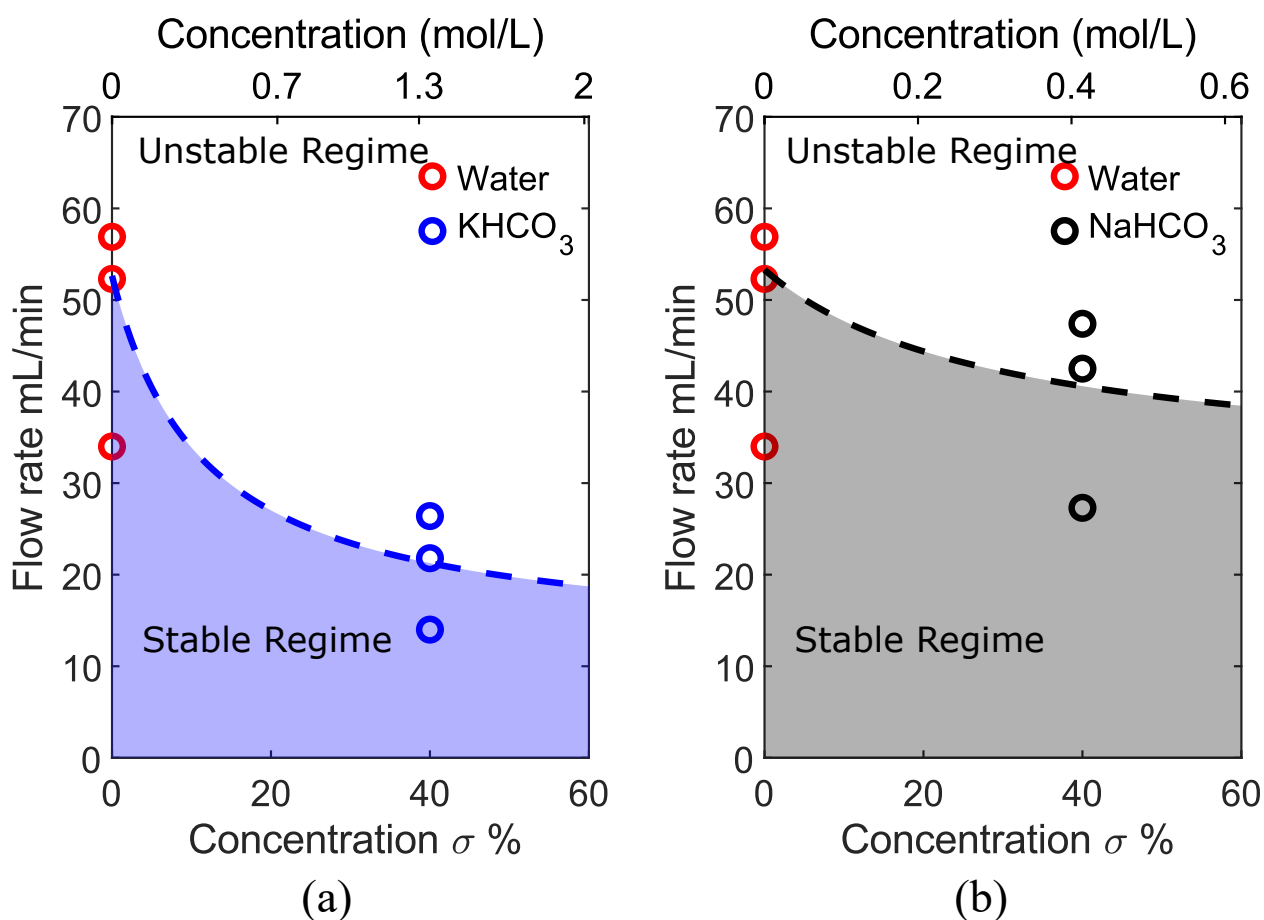


Figure 5.7: Flame extinction stability map of varying water mist flow rates with increasing concentrations of (a) KHCO_3 and (b) NaHCO_3 , with selected cases for high-speed imaging.

The addition of salt at increasing concentrations for both metal alkali compounds shows decreases in the water flow rate requirements for blow-off. However, it is apparent that there are diminishing returns for suppression efficacy, where the improvements in chemical

inhibition at larger concentrations start to plateau. At $\sigma = 60\%$ NaHCO_3 , there is a 29 % improvement in suppression compared to pure water, reducing the flow rate requirements from 54 mL/min to 38.5 mL/min. The addition of KHCO_3 to water shows a dramatic improvement in flame suppression compared to NaHCO_3 and pure water. For example, at $\sigma = 60\%$ KHCO_3 , the flow rate of water mist required for flame suppression is reduced by 64 % compared to pure water. The effectiveness of KHCO_3 also follows a similar inversely proportional decay profile with each incremental increase in salt concentrations, albeit the gradient is considerably sharper than NaHCO_3 . The improvement in suppression efficacy is measured at the same molar concentration for both salts at 0.62 M, which lies at $\sigma = 60\%$ NaHCO_3 and $\sigma = 18.91\%$ KHCO_3 . At this concentration, KHCO_3 shows a 47 % reduction in the flow rate of water mist required for flame suppression, almost double the effectiveness of NaHCO_3 (29 %). The difference between the salts in terms of suppression efficacy is consistent throughout the molar concentration range.

The superior flame inhibition mechanism of KHCO_3 results from a more efficient chemical catalytic process, which trends in the direction of increasing atomic weights for alkali metals. One contributing factor is perhaps because larger elements such as K have an increased capacity for third body collisions compared to that of Na [203], which increases catalytic reaction rates. Further investigations are conducted using high-speed laser imaging, where a selection of water mist flow rates and inhibitor concentrations are chosen for analysis, and these are located on the stability map of Figure 5.7. Three concentrations, 0 % inhibitor (H_2O), 40 % NaHCO_3 and 40 % KHCO_3 at three flow rates relative to their blow-off limits (dashed line) at approximately $B_f = 108, 100$ and 92% , are selected as they maintain similarity in stability regimes.

Figure 5.8 shows instantaneous DSLR images for qualitative comparisons between the flame inhibition characteristics of the alkali salts relative to pure water. Example images are shown from cases 1, 4 and 9 with similar flow rates of water mist at approximately 30 mL/min. The flames with water mist (and inhibitor) have increased camera exposure times for viewing clarity. The baseline image is a 20 kW flame without water mist in the air co-flow.

The flame structure exhibits previously shown classical buoyancy-driven instabilities [1]. The second image shows the addition of pure water mist in the co-flow, where a substantial reduction in visible flame luminosity is observed, suggesting a reduction in soot formation due to the lower gas temperatures. The introduction of NaHCO_3 dramatically increases the visible flame luminosity, with a characteristic bright orange colour resulting from the strong atomic sodium $3p \leftarrow 3s$ lines at 588.9 nm and 589.59 nm. Small local extinction zones are observed as holes in the flame brush. The addition of KHCO_3 increases the flame luminosity through the potassium emission at the $5s \leftarrow 5p$ lines at 404 nm and the $4p \leftarrow 4s$ lines 766.5 nm and 769.9 nm. Compared to NaHCO_3 and pure water, KHCO_3 is observed to produce considerably larger localised extinction zones in the flame sheet. In some cases, clear passage through the entire flame is observed.

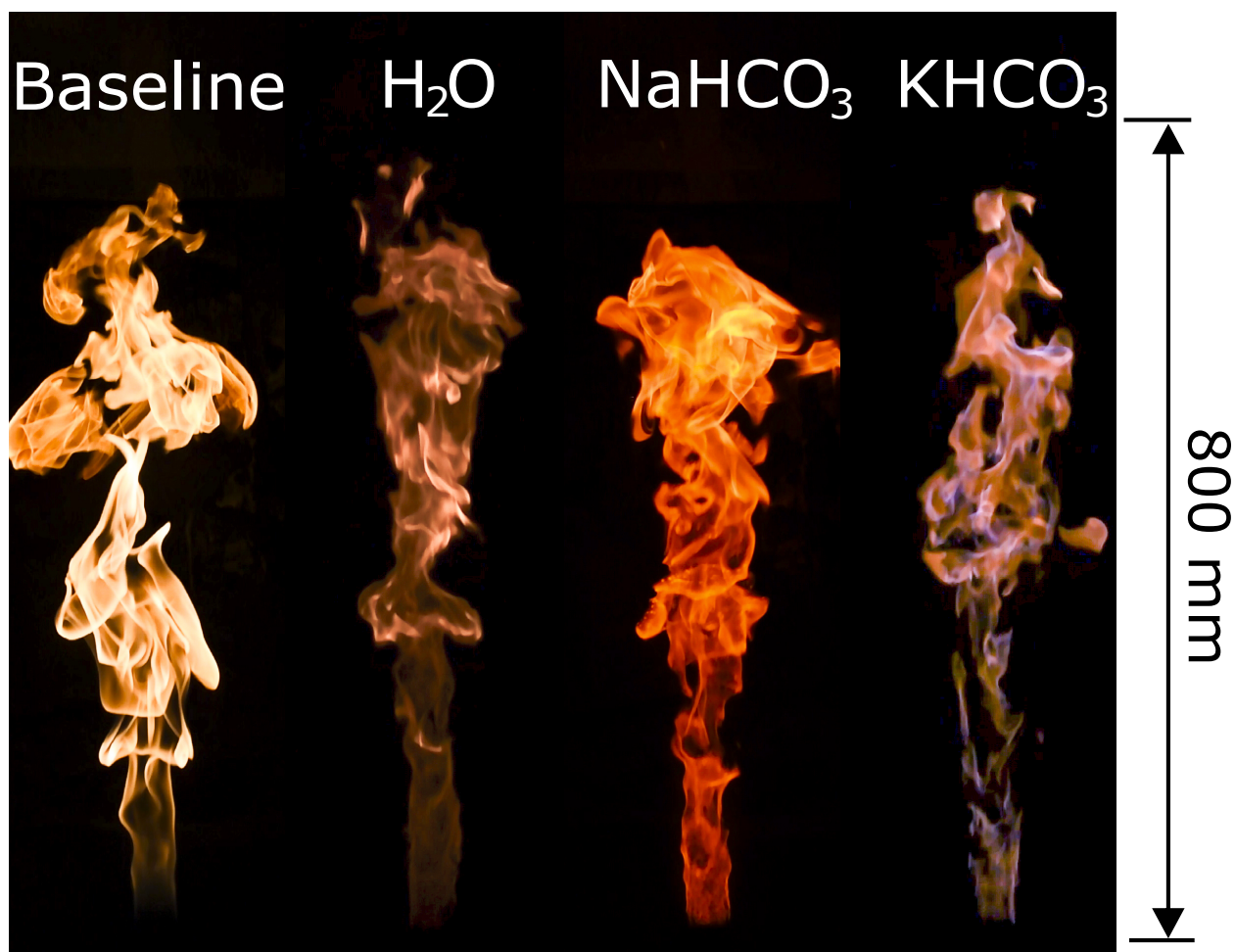


Figure 5.8: Example DSLR images of a 20 kW flame with and without water mist and with different inhibiting salts.

Both NaHCO_3 and KHCO_3 salts, when released from the water mist droplets, undergo a thermal decomposition process, eventually releasing the key radical scavengers NaOH and KOH , respectively [130]. The kinetic mechanisms behind the catalytic cycle of inhibition for NaOH and KOH , Equations 5.2 and 5.3, are similar and have been previously studied in great detail [129, 130], with the inhibition cycle ultimately having the net effect of reacting the intermediary hydrogen and hydroxyl radicals to form water (Equation 5.4).





Extinction pockets observed in the flame sheet are caused by the chemical scavenging of the OH and H radicals. It is postulated that the water droplets act as a carrier of the chemical inhibitor, whereby upon droplet evaporation, salt crystals form and are transported into the flame reaction zones. This extinction mechanism will now be evaluated through joint high-speed scalar imaging of the key intermediate radical OH and the droplet field.

5.2.2 Spray flame interaction

Simultaneous measurements of OH-PLIF and Mie scattering of droplets are taken for a portion of the flame length between 0 – 240 mm above the burner exit plane. The cropped measurement window spans 30 mm in height and 90 mm in width. A total of 2000 joint images are taken at a frequency of 400 Hz, spanning a temporal window of 5 seconds. High-speed images of the droplet and OH fields are superimposed, showing the joint evolution of water mist relative to the flame front. A comparison of flame structure with a mist flow rate of approximately 30 mL/min with different salts is shown in the instantaneous example images (Figure 5.9).

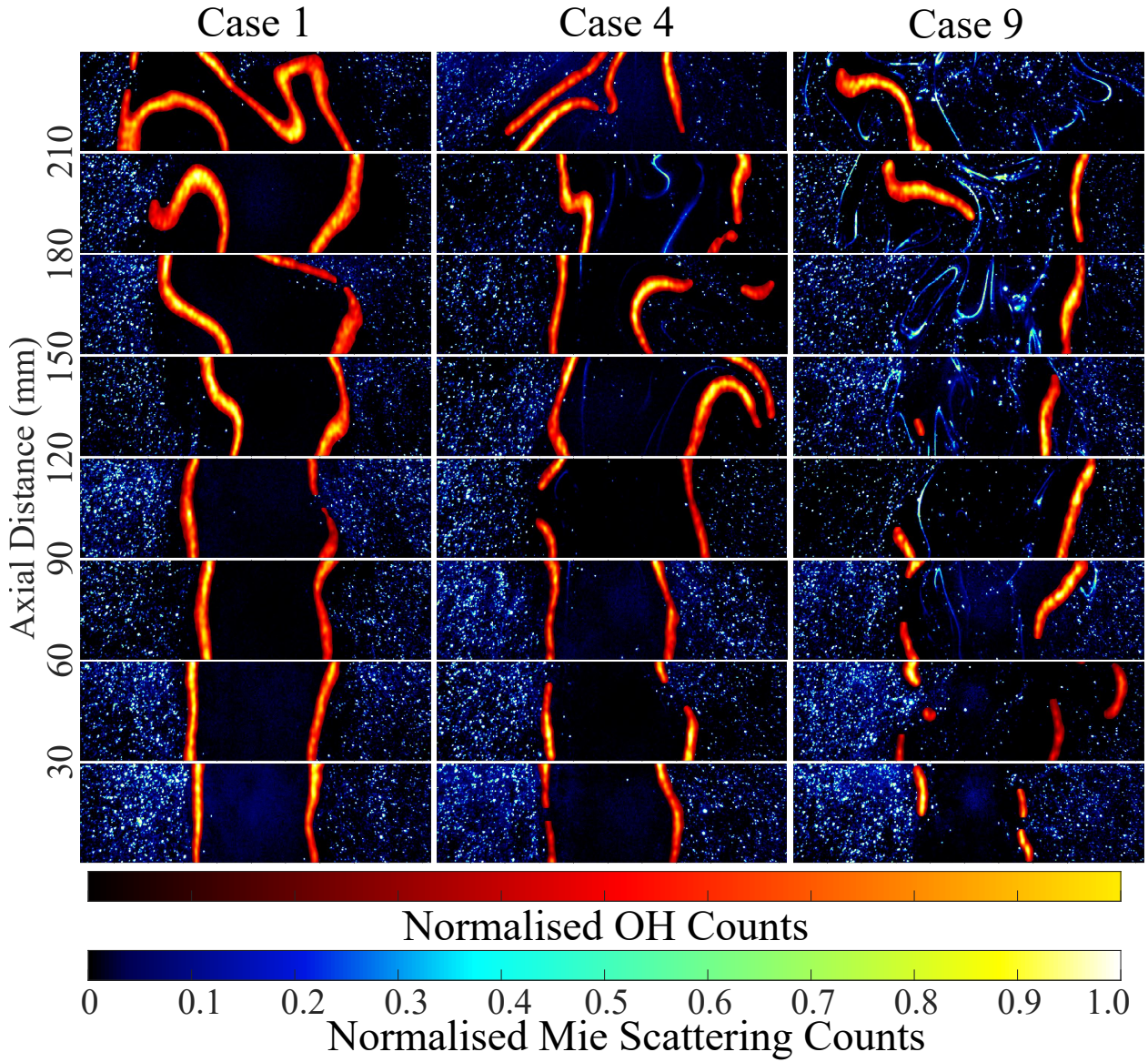


Figure 5.9: Simultaneous superimposed high-speed images of OH-PLIF and Mie scattering of droplets for cases 1, 4 and 9 with normalised OH and Mie scattering for viewing clarity.

The series of images for pure H_2O (left) shows an almost continuous flame sheet. Droplets from the co-flow populate the lean side of the flame and advect in tandem with the OH layers. Droplets rarely penetrate the OH layer, suggesting that complete droplet evaporation primarily occurs prior to or within the flame sheet. The primary mechanism for flame suppression for the pure water case is, therefore, gas-phase cooling. The addition of $\sigma = 40$

% NaHCO_3 (Case 4, middle) shows discontinuities in the OH sheet structure from the burner exit plane onwards, indicating the effect of NaOH on the radical scavenging of OH. Further downstream (180 – 210 mm), rope-like Mie scattering structures are observed periodically on the rich side of the flame. KHCO_3 (Case 9, right) shows a dramatic depletion of OH radicals in the flame structure. The flame front is highly discontinuous, with multiple breaks in the OH layers, some spanning the entire measurement window of 30 mm. Similar to prior cases, droplets seldom advect into the fuel stream, despite the breakages in the OH layer, indicating that most of the droplets are consumed and have released the alkali salt crystal upon reaching the OH front. The breakages in the OH layers for both Case 4 and 9 are due to the increase in the local chemical time scales by the radical scavengers NaOH and KOH, decreasing the local Damköhler number, and causing excessive flame strain resulting in local extinction.

Figures 5.10, 5.11 and 5.12 each show a series of stacked images for cases 2, 5 and 8 respectively. Each single image is time-independent of the other images, presented here only to show characteristic flame structures. Cases 2, 5 and 8 all lie in the same stability regime at $B_f \approx 100\%$. Interestingly, the flames all lie on the same stability limit, yet drastically different flame structures are observed between each of the cases. Figure 5.10 shows case 2 (pure H_2O), where similar to as described before, droplets populate the air side with minimal penetration into the fuel side of the flame. The OH layers are still quite continuous throughout the length of the flame even though it's on the edge of the stability limit. Figure 5.11 shows the inclusion of NaHCO_3 where discontinuities show up as breakages in the flame front. At $B_f = 100\%$, the flow rate of water mist is lower than that of the pure water case (52.3 mL/min to 42.5 mL/min), however, the radical scavenging of NaHCO_3 makes up for the reduced flow rate in water mist, providing enhanced suppression. More droplets are seen on the fuel side as holes in the flame front allow for a low temperature pathway for droplets to traverse from the air to the fuel side. Figure 5.12 shows the inclusion of KHCO_3 at $B_f = 100\%$. The flow rate of water is reduced drastically down to 21.2 mL/min, however, large breakages in the flame front are seen in all the images increasing in size with axial distance. KHCO_3 provides significantly enhanced suppression even with massively reduced flow rates of water mist.

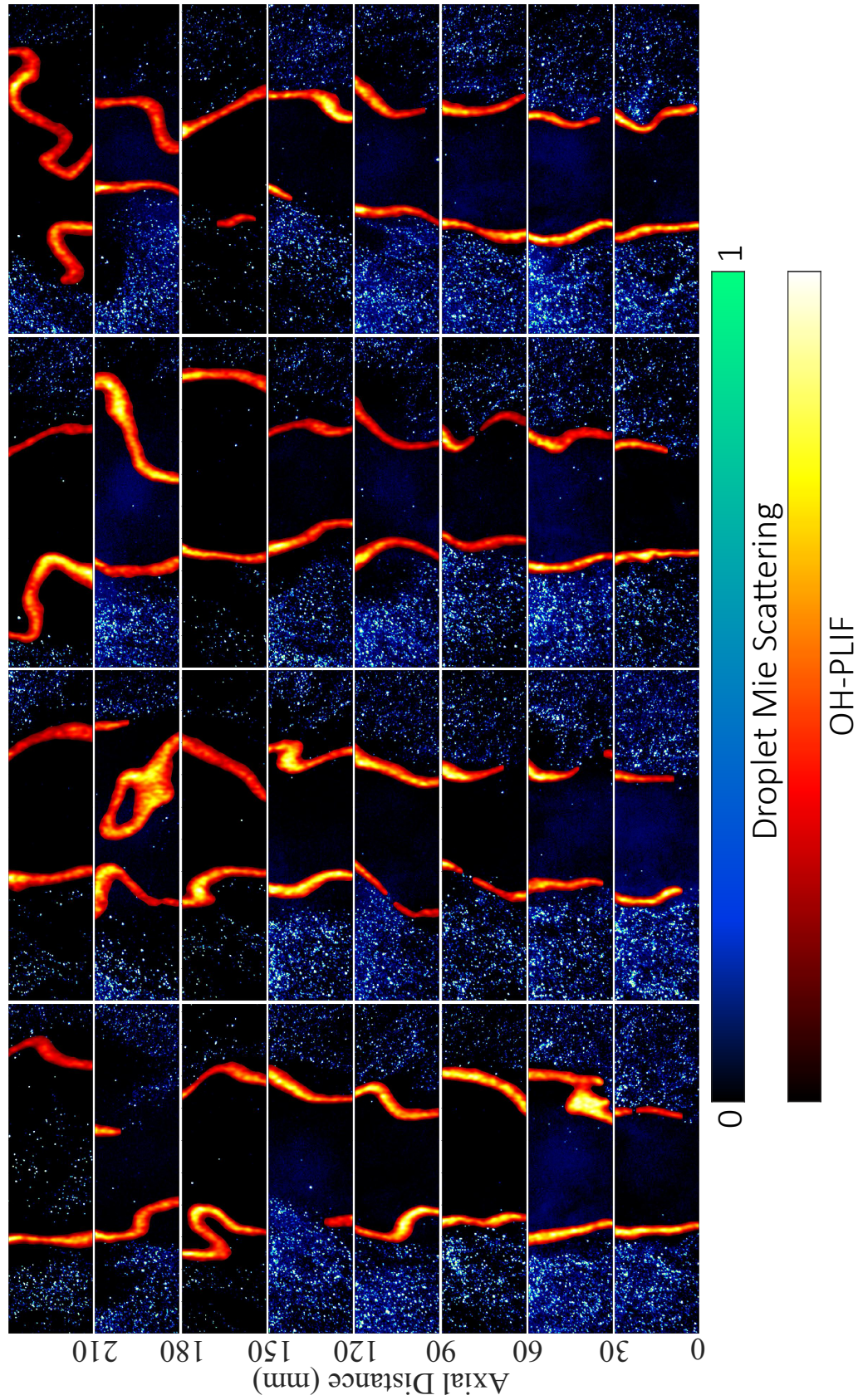


Figure 5.10: H_2O , simultaneous superimposed high-speed images of OH-PLIF and Mie scattering of droplets for case 2, water only on the stability limit.

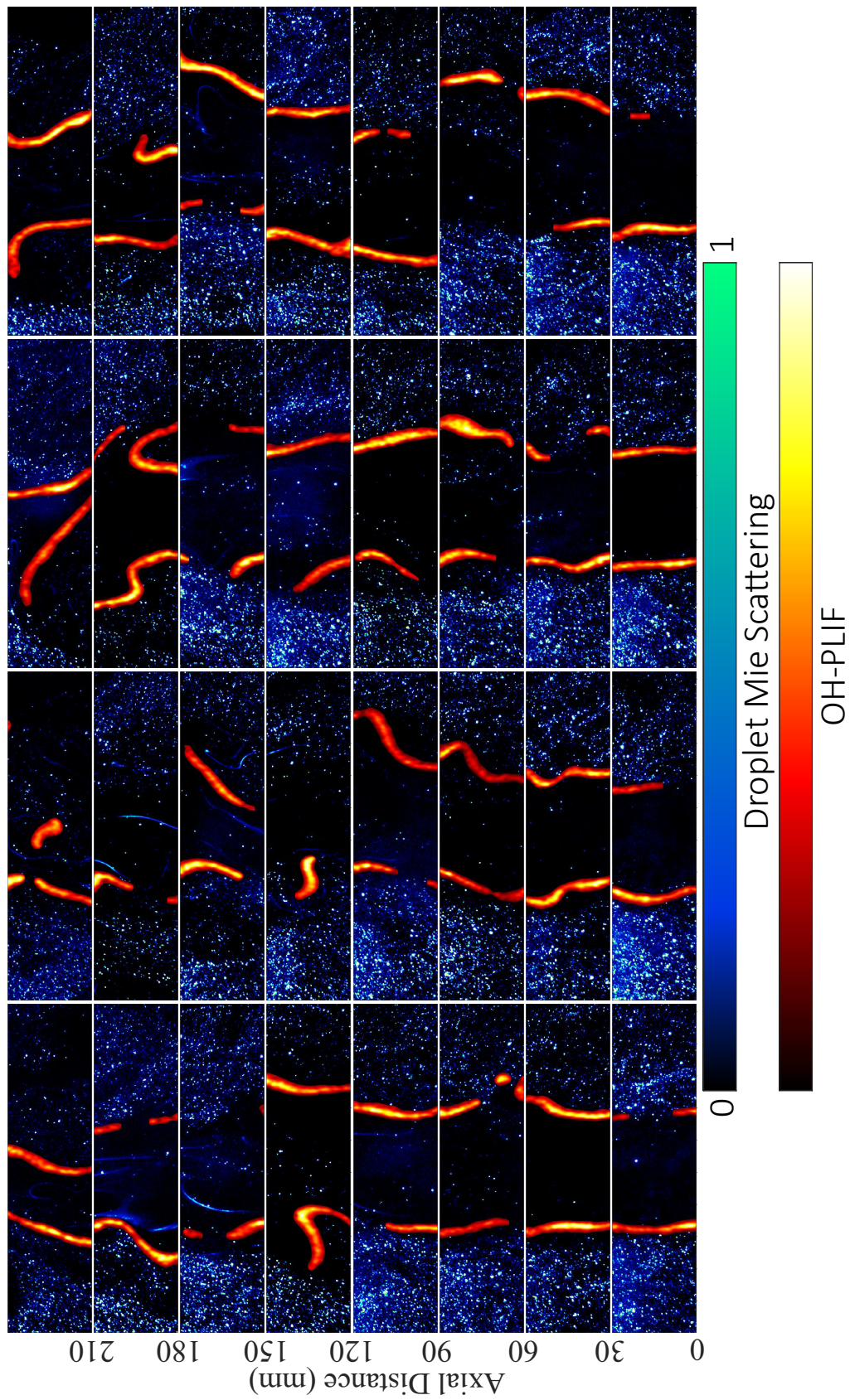


Figure 5.11: NaHCO_3 , simultaneous superimposed high-speed images of OH-PLIF and Mie scattering of droplets for case 5, on the stability limit.

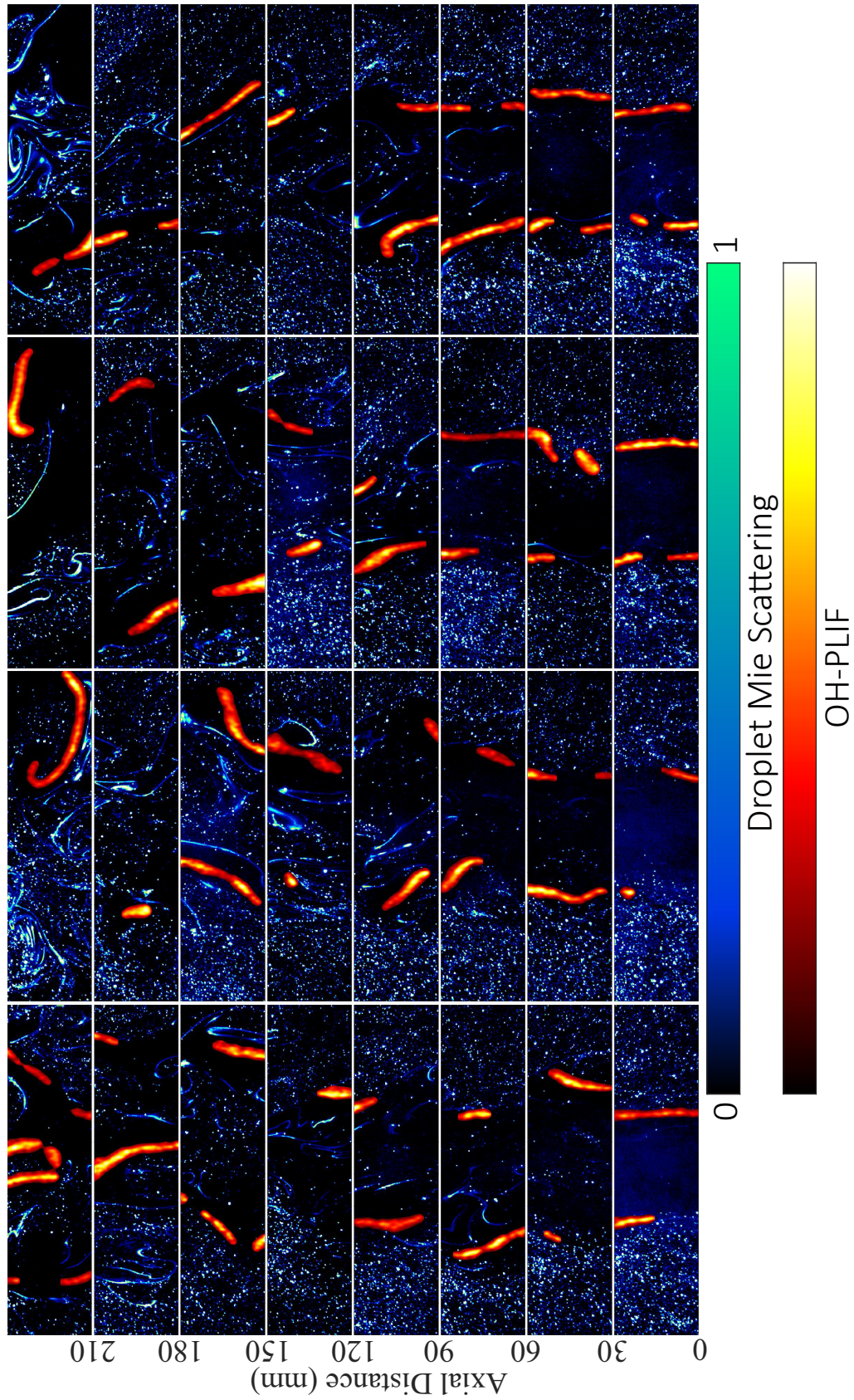


Figure 5.12: $KHCO_3$, simultaneous superimposed high-speed images of OH-PLIF and Mie scattering of droplets for case 8, on the stability limit.

Figure 5.12 shows excessive amounts of this rope-like Mie scattering on both the air and fuel sides of the flame. It is believed that the rope-like scattering signal is un-decomposed agglomerated salt crystals released from the droplets. Since Figures 5.10, 5.11 and 5.12 all lie within the same extinction stability regime, and no rope-like scattering occurs for pure H_2O flame, but with the addition of NaHCO_3 and subsequently KHCO_3 , the scattering increases, suggesting that the inclusion of salt is the main driver for this excess Mie scattering. Previous studies have shown that alkali metal salts (NaCl , KCl) have no impact on soot formation, if any, a reduction in soot volume fraction was observed [204]. Therefore, it can be assumed that the rope-like scattering is not attributed to the Mie scattering of soot from an increase in soot production but rather the Mie scattering off unconsumed clouds of salt crystals formed from the evaporation of droplets. The presence of large amounts of unconsumed salt crystals hints to the diminishing improvement in suppression efficacy with increased salt concentration (Figure 5.7a). This suggests that excess salt has not gone through the thermal decomposition process to form NaOH or KOH , therefore not contributing to flame inhibition.

A time series displaying example local flame extinction and re-ignition sequences are shown in Figure 5.13. Each image corresponds to 5 ms time steps for cases 2, 5 and 8 ($B_f = 100\%$) between 30 - 60 mm above the burner exit plane. The high temporal resolution of the measurements enables insight into the characteristic timescales dominating the process of local extinction and re-ignition. The pure water case shows an occasional example of breakage on the left side of the flame, which is advected downstream with the flame front, followed by eventual rejoining the OH layer at 15 ms, marking re-ignition. Due to the high temporal resolution and low velocity, it is highly unlikely that these events result from out-of-plane motion [1]. NaHCO_3 follows a similar process to H_2O , the extinction pocket on the left side of the flame advects downstream, however, it does not reconnect within the time frame observed. KHCO_3 shows increased OH depletion with multiple breakages observed in both the left and right OH layers. More droplets are now present in the fuel stream, as breaks in the flame front allow droplets to advect from the air side to the fuel side in the absence of a flame sheet. These sets of high-speed images presented in this section may prove to be

extremely useful for future attempts at model validation.

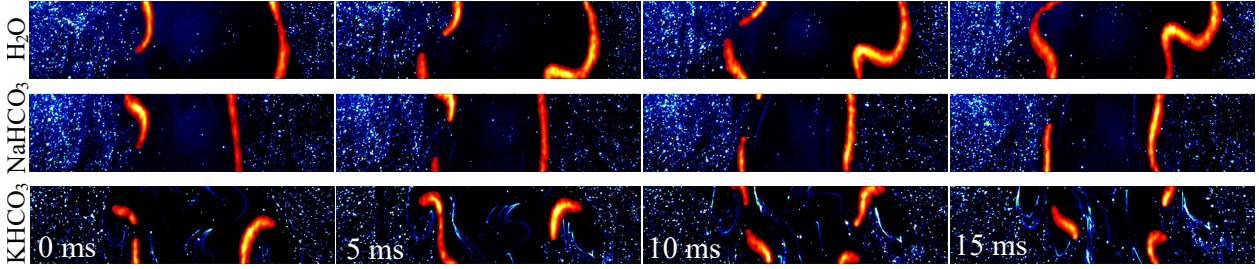


Figure 5.13: Superimposed OH-PLIF and Mie Scattering time evolution of different salt inhibitors in their respective stability regimes at approximately $B_f = 100\%$. Case 2 H_2O at 52.3 mL/min, Case 5 $NaHCO_3$ at 42.5 mL/min and Case 8 $KHCO_3$ at 21.2 mL/min.

5.2.3 Chemical scavenging of OH radicals

The effect of flame suppression by varying the flow rate of water mist and inhibitor is now compared quantitatively by examining the OH fluorescence signal intensity from the high-speed images. The OH fluorescence signal is obtained in the linear regime and is therefore controlled by both the local gas temperature and OH concentration, assuming that the local quenching environment is similar between the cases [205]. Figure 5.14 shows the maximum OH counts for an average ensemble of images taken along the flame for all the cases studied, three salt concentrations with their respective percentages of blow-off ($\% B_f$).

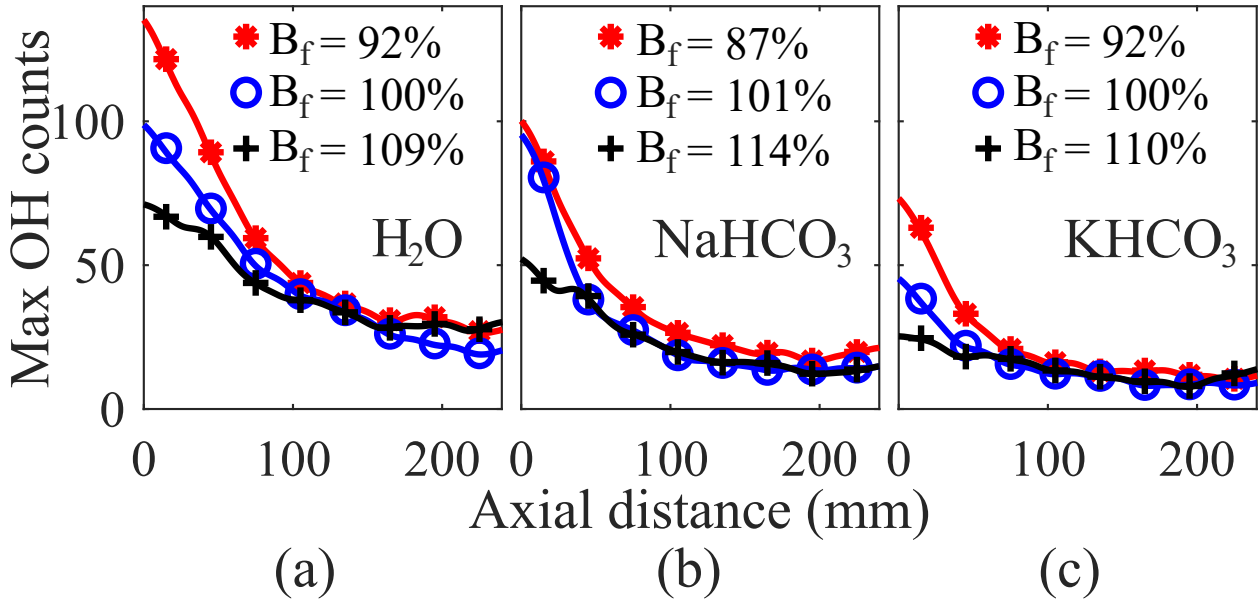


Figure 5.14: Maximum of the mean OH signal at each measurement window axially along the flame for all cases.

Figure 5.14 a shows cases 1, 2 and 3 with the peak OH signal obtained at the exit plane, ranging from 138 counts for $B_f = 92\%$ to 70 counts for $B_f = 109\%$. The OH signal plateaus at approximately 30 counts at 170 mm, with no further reduction in OH fluorescence. OH counts decrease non-linearly with respect to the increase in the percentage of the blow-off limit, correlating with the inversely proportional decay in extinction times previously shown in Figure 5.6a. Cases 4, 5 and 6 (Figure 5.14 b) shows the OH signal ranging from 100 to 50 counts at the exit plane, respectively. OH in the presence of NaHCO₃ is further reduced when compared to pure water mist, with OH counts plateauing to 20 at 125 mm. Local extinction zones seen as breakages in the flame front (Figure 5.9 Case 4) are responsible for the reduction in the maximum mean OH counts. Cases 7, 8 and 9, with the inclusion of KHCO₃ in Figure 5.14c exhibit a dramatic reduction in OH fluorescence with an observed 70 to 25 counts at the exit plane, plateauing at an axial distance of 100 mm to approximately 10 counts. The overall reduction in the signal highlights distinctly the effect of radical scavenging, and this is reflected by increases in the number of breakages in the flame front (e.g. Figure 5.9 Case 9), where the large local extinction zones are present along the entire length of the flame.

5.2.4 Local extinction and re-ignition statistics

Local extinction and re-ignition events are statistically analysed by integrating the total physical area corresponding to the OH signal. This is viewed as a surrogate for flame surface area, and hence a decreasing surface area is indicative of pockets of local extinction (by decreases in the surface area). Probability Density Functions (PDFs) of the OH area are shown at each axial location for all the cases studied herein Figure 5.13. The OH area is computed by binarising the background and laser intensity profile corrected OH images using a fixed threshold, which is integrated to obtain the total OH area. Figure 5.15 shows PDFs of OH area for cases 1 - 9 at select axial locations. Cases 1, 2 and 3 (H_2O) show that the mean OH area increases with axial distance, suggesting that as the flame broadens, the water mist has minimal effect on the OH area, as shown with the continuous growth of the flame front (Figure 5.9). Increasing the % B_f of pure water mist results in OH layers at the exit plane that are increasingly distributed with a minor reduction in the mean OH area. Introducing the water mist slightly decreases the average size of the flame front at the exit plane due to local extinction and re-ignition events. The flame base becomes increasingly unstable near the burner rim, causing intermittent flame blow-off. NaHCO_3 shows similar trends to that of pure water mist, with slightly broader PDFs of OH area with increasing axial distance, with average OH area reduced relative to H_2O . This indicates that a smaller average length/size of the OH layers is due to an apparent increase in the local extinction rate. The bimodal PDF shown in case 6 at 0 mm is due to intermittent lift-off on one side of the flame front, intermittently halving the OH area. KHCO_3 shows a dramatic broadening of the PDFs near the exit plane, with a decrease in peak OH areas with increasing axial distance. Extreme localised extinction events increase in frequency up to 240 mm downstream of the burner exit plane as observed by the widened PDFs. This is evident in both the DSLR (Figure 5.8) and high-speed (Figure 5.9) images, where the breaks in the flame front increase in size along the flame. The statistical results show that flame extinction is promoted in the order of $\text{KHCO}_3 > \text{NaHCO}_3 > \text{H}_2\text{O}$.

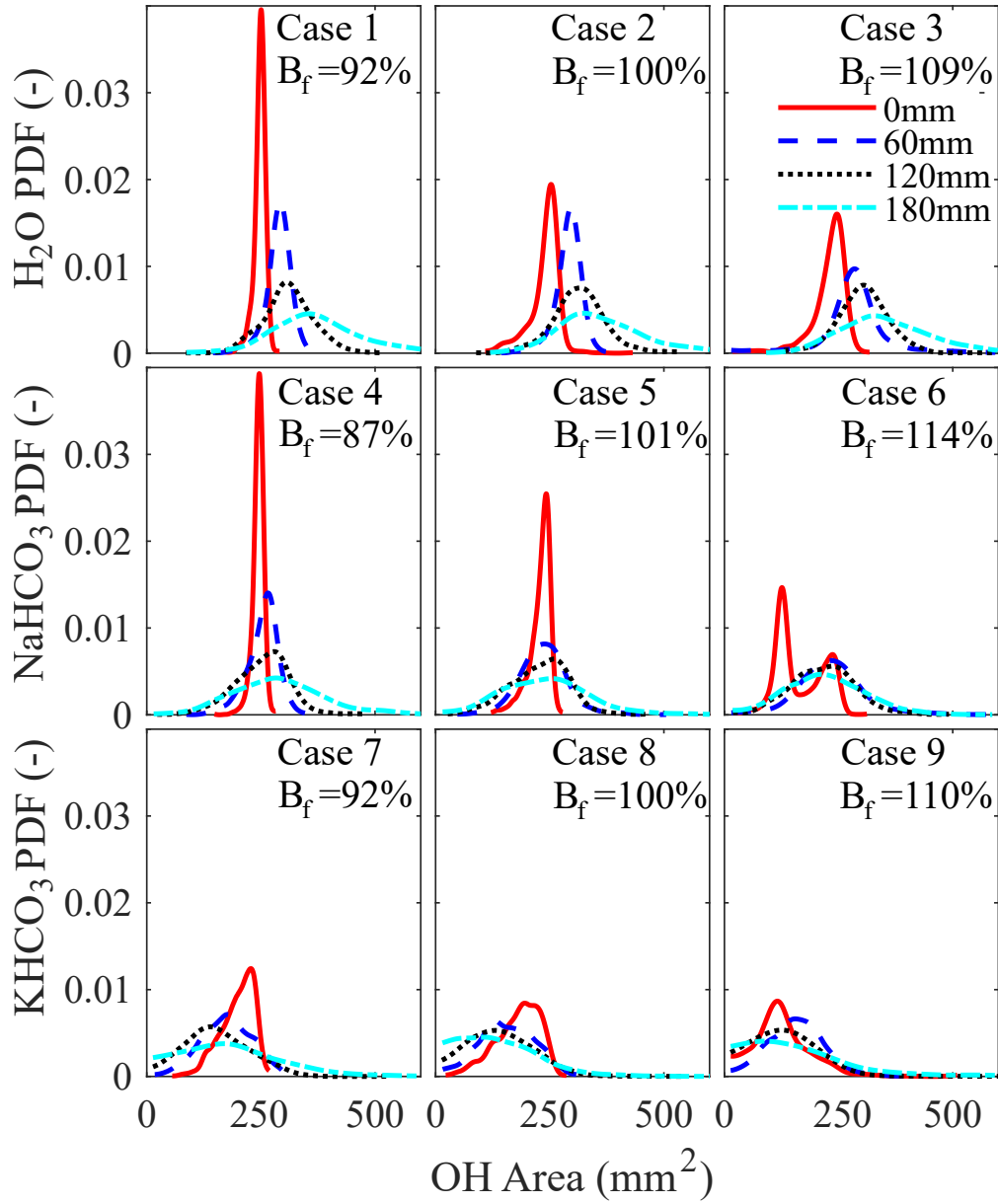


Figure 5.15: PDFs of OH area for all cases studied at select axial locations along the flame.

5.3 CONCLUSIONS

This chapter presents the first near-field measurements of chemically enhanced water mist suppression of a buoyant turbulent diffusion flame, showing water mist droplets acting as carriers of salt inhibitors. A canonical laboratory scale water mist fire suppression experiment

is characterised using various methods to assess both the boundary conditions and flame suppression efficacy of different inhibitors at different concentrations. High-speed simultaneous imaging of OH and Mie scattering of droplets qualitatively shows how the flame structure changes with the addition of an inhibitor. The key findings of this chapter are as follows:

- PDA measurements of the exit plane present provide a detailed characterisation of the boundary conditions, including full maps of droplet distributions, droplet velocities and water mist volume flux, along with a reconstruction of total water mist exit plane flow rates using PDA measured flux.
- Average flame extinction delay times regardless of inhibitor or concentration are shown to be inversely proportional to the flow rate of water mist. A flame stability map presents suppression efficacy by varying both the flow rate of water mist and the concentration of alkali metal salt. KHCO_3 has demonstrated far superior suppression capabilities when compared to NaHCO_3 on both a concentration and molar basis, reducing the flow rate required for extinction by upwards of 64 % at a 60 % inhibitor concentration.
- OH depletion and local extinction zones caused by the chemical scavenging of the OH and H radicals are observed through high-speed images, forming breaks in the flame sheet. Mean OH counts decrease with increasing flow rate of water mist and continue to decrease with the addition of an inhibitor, with KHCO_3 showing more OH depletion than NaHCO_3 .
- PDFs of OH area indicate that with enhanced mist suppression, the average OH area starts decreasing due to extinction pockets forming in the flame sheet, with instances of competing phenomena of extinction and re-ignition.

This chapter provides valuable insights into chemically enhanced water mist fire suppression by observing the chemical scavenging of the OH radical by inhibitor-delivering droplets. The flame stability maps provide an unprecedented characterisation of inhibitor efficacy, showing

relative suppression performance between different concentrations of inhibitor ($\text{KHCO}_3 > \text{NaHCO}_3$). The high-speed simultaneous imaging of OH and Mie scattering of droplets provides the first insights into near-field flame droplet interactions, which will be crucial for future attempts at model validation.

Chapter 6

High Fidelity Flame Droplet Interactions

This chapter presents an extension to the simultaneous high-speed OH-PLIF and Mie scattering of droplets presented in the previous chapter. It is known that the efficacy of water mist fire suppression systems is highly sensitive to boundary condition parameters such as droplet size and distributions, velocity and mass flux. This is because all these parameters heavily influence droplet evaporation and penetration depth within a flame, which defines the local loss of sensible enthalpy. With the inclusion of a chemical inhibitor (KHCO_3), another layer of complexity is added, which is inhibitor transport in the flame front, resulting in a highly complex and coupled environment of flame extinction. By increasing both the temporal and spatial resolution of the images, individual droplets can be tracked into the flame front, observing local flame extinction. This provides a deeper phenomenological understanding of flame front quenching and droplet evaporation.

6.1 METHODOLOGY

The experimental setup of the water mist fire suppression system is identical to that of the previous chapter, a co-flow seeded with water mist. From the flame stability maps obtained in the previous chapter (Figure 5.7), four flame conditions are selected in the stable regime. The water mist flow rates and salt concentrations selected for further analysis are shown on the left of Figure 6.1. These cases have been chosen such that Flames 1, 2 and 3 are at a constant flow rate of water mist at $\dot{v} \approx 21$ mL/min (droplet boundary conditions unchanged), with increasing concentrations of KHCO_3 (0, 20 and 40 %) dissolved in water. Flame 4 is chosen to illustrate the differences between increasing the mass flow rate of water (from 21 to 52 mL/min) vs increasing the concentration of inhibitor, maintaining the same blow-off regime between Flames 3 and 4. Further details of the flame cases are shown in Table 6.1. The image on the right of Figure 6.1 shows the imaging region of interest, illustrating the enhanced spatial resolution compared to the previous chapter. The DSLR image shows an example flame with a red box highlighting the approximate size of the imaging window relative to the entirety of the flame. The boundary conditions and flame are assumed to be axisymmetric about the centre of the burner, therefore only the left side of the flame is imaged (direction of incident laser beams). The imaging technique and processing are discussed in the following sections.

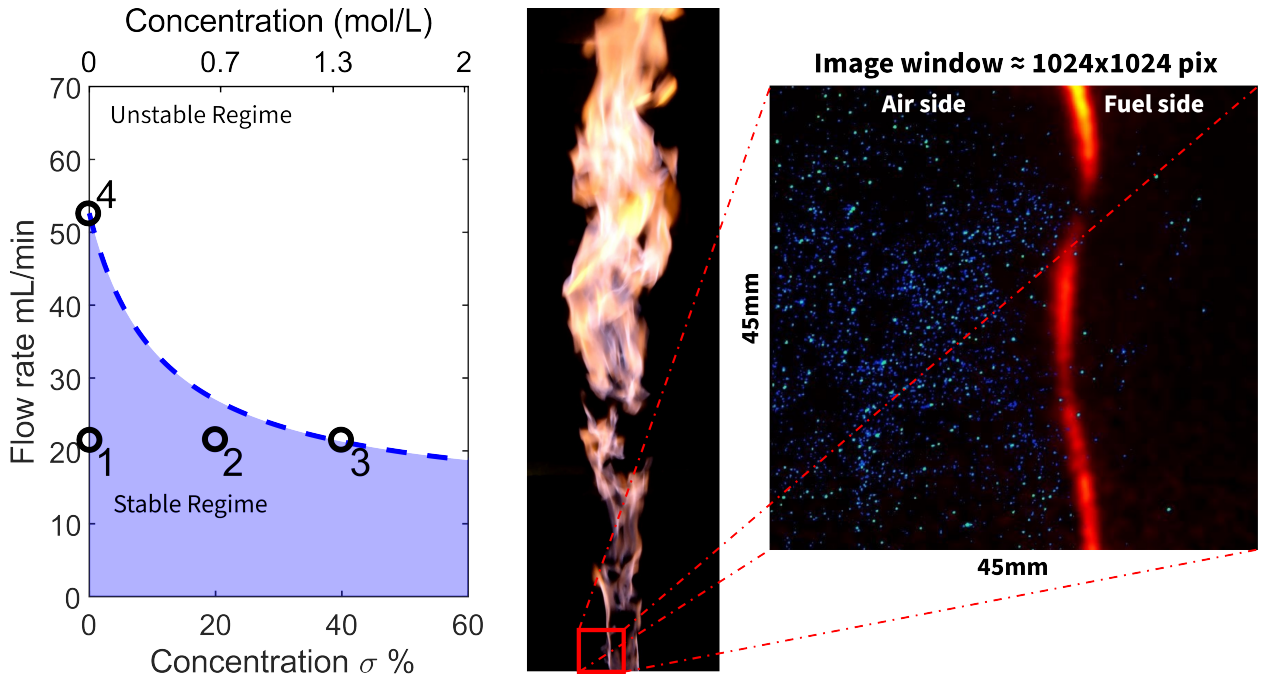


Figure 6.1: Flame stability limits for KHCO_3 for Flames 1-4 (left) and an example superimposed OH and Mie scattering image with a corresponding DSLR image of the imaging window of interest (right).

Table 6.1: Flame cases for high-speed imaging

Flame	Concentration σ (%)	% w/v (g/100mL)	$\dot{v}$ (mL/min)	% B_f
F1	0	0	21.2	40
F2	20	6.6	21.2	91
F3	40	13.2	21.2	100
F4	0	0	52.3	100

6.1.1 Joint high-speed imaging of OH-PLIF and Mie scattering of droplets

The optical setup employed for the joint high-speed imaging of OH radicals and droplet PTV (Particle Tracking Velocimetry is attempted, but the results are not presented in this thesis)

is shown in Figure 6.2. The OH-PLIF and Mie scattering is similar to the previous chapter (Chapter 4). The main difference here is that the 532 nm Mie scattering beam is collimated to a nominal thickness of 1.5 mm, and the UV beam is positioned at $z = 0$ mm in the centre of the 532 nm beam. The droplet Mie scattering signal is collected with three high-speed CMOS cameras (Lavision HSS6). One camera was placed orthogonal (90 deg) to the x-y plane (laser sheet) with a 100 mm $f\# = 16$ Canon lens. One camera at 130 deg with a 105 mm $f\# = 22$ Nikkor lens and another camera at 230 deg with a 105 mm $f\# = 22$ Nikkor lens. Flame luminosity interference is eliminated with a 532 nm bandpass filter (10 nm FWHM), combined with a $5 \mu\text{s}$ camera gate on each of the Mie scattering cameras.

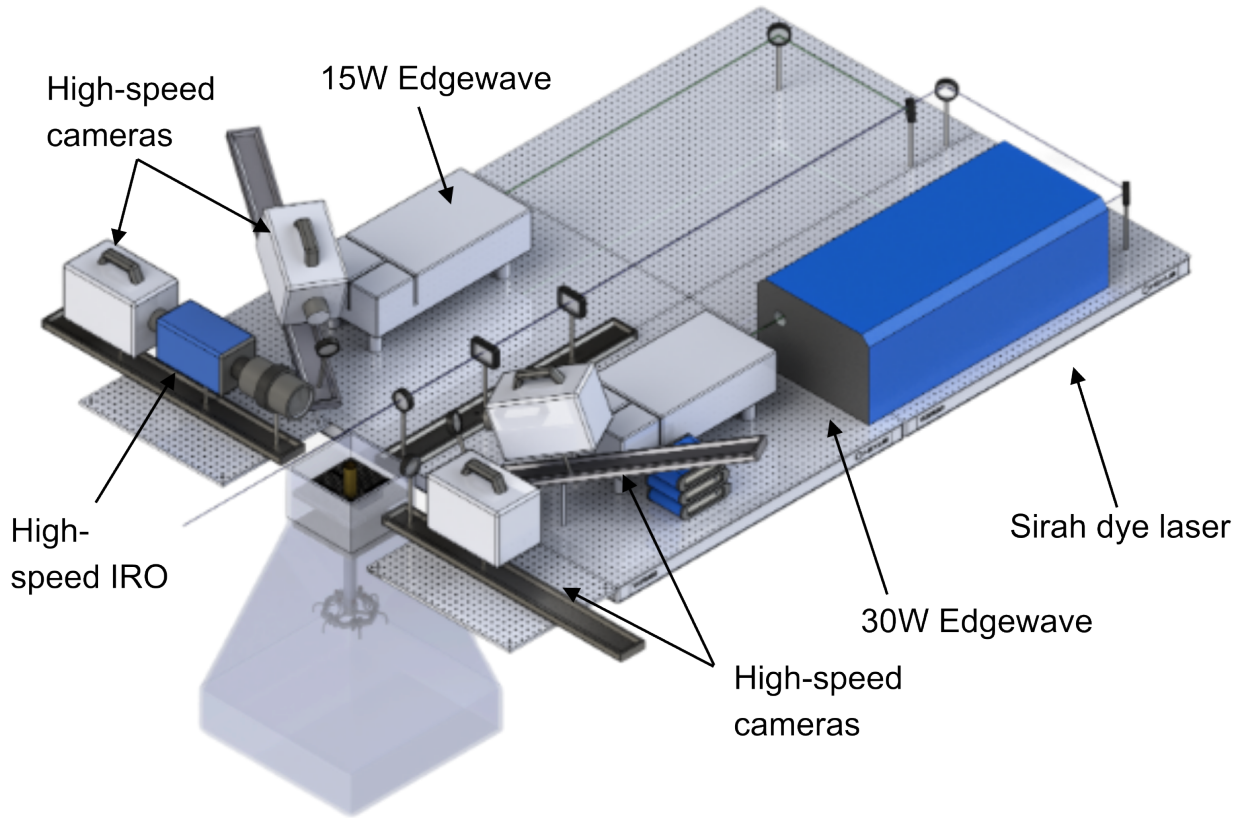


Figure 6.2: Experimental setup of the high-speed OH-PLIF and Mie scattering of droplets.

The same optical setup is used to collect OH-PLIF as shown in Chapter 4. All cameras are set with an acquisition rate of 5 kHz to ensure time resolved flame extinction and re-connection are captured alongside droplet tracking. Calibration images are taken before, during and after the experiment to correct for variations in camera background, intensifier flat field, and laser sheet profiles. A total of 50000 images are taken on each camera in sets of 5000 images for 10 seconds of real time data to ensure enough instability events are recorded for statistical convergence. Similar image pre-processing is applied as previously shown in Chapter 4 Figure 4.2.

6.1.2 Camera calibration and droplet matching

The three droplet Mie scattering cameras are calibrated using a single plane pinhole grid that is traversed in multiple locations in depth (z). A combination of OpenCV [206] and MyPTV [207] are used to calculate the intrinsic and extrinsic camera parameters for all cameras, with sub-pixel errors. MyPTV is used to perform droplet matching (triplet ray matching) of all three cameras with a maximum matching error of 80 microns per droplet. Droplet tracking was attempted, however, due to the striations in the beam profile in the depth direction (z), droplets occasionally “disappear” due to movement into regions of low beam power, this skews/corrupts the tracking data statistics towards higher numbers of low time frame trajectories. Even with the aid of the track stitching algorithm in MyPTV, the tracking statistics are still heavily influenced by the beam striations, therefore any form of droplet tracking will not be presented in this chapter. For qualitative observations of droplet movements in the flame front, the OH camera is mapped onto the single Mie scattering camera on the opposing side. Both cameras have been de-warped using a grid calibration plate applying a 3rd order polynomial geometric transformation [188], resulting in an RMS mapping error of less than 1 pixel over the whole image. The de-warped images have an approximate window size of 45 mm (height) by 45 mm (width) with a resolution of 23.6 pixel/mm. Though the camera pixel resolution ($42 \mu\text{m}/\text{pix}$) is not enough to resolve individual droplet sizes in space, individual scattering events from a single droplet generally saturate a single pixel (or

more), resulting in light from the single droplet “bleeding” into adjacent pixels, which shows as up as a larger scattering event on the camera sensor/image.

6.2 RESULTS AND DISCUSSION

6.2.1 Reaction zone quenching and inhibition

The increased spatial and temporal resolution of the simultaneous high-speed images of OH-PLIF and Mie scattering of droplets allow for a better phenomenological understanding of flame front extinction. Local extinction events of Flames 1 to 3 are shown in Figure 6.3. Each image window is cropped to 30 x 30 mm in lab space coordinates and is positioned above the burner exit plane with the reaction zone positioned at approximately the image centre for visual clarity. The exact position of the image windows is illustrated on each figure with distances relative to the burner lip. The air side is populated with droplets on the left of the images, with the fuel side separated by the flame front on the right side of the image. The first sequence/row of images shows Flame 1, with a 0 % concentration of inhibitor in the water mist. In this pure water case, the flame is highly stable as it is far away in flow rate space from its respective blow-off limit (Table 6.1). In all sets of images in Flame 1, no complete flame front extinction is observed to occur, with minimal droplets traversing the entirety of the flame front from the air side into the fuel side. However, as indicated in Figure 6.3 with arrows, a high number of droplets entrained into the reaction zone causes a local reduction in OH signal/area, though not enough to cause local extinction. This local reduction in OH is primarily driven by a combination of thermal quenching and gas phase dilution due to droplet evaporation [20], illustrating the significance and sensitivity of the reaction zone to where (in space) the droplets evaporate. The second row of image sequences shows local extinction caused by the addition of 20% KHCO_3 in the water mist. This is observed as the breaking of a continuous reaction front, resulting in two edge flames. The gap in the OH is seen to propagate outwards over 8 ms, forming a gap of ≈ 12 mm with droplets penetrating into the fuel side. As droplets traverse the flame front, local chemical time scales

dramatically increase due to the release of inhibitor in the high temperature reaction zone. This results in a decrease in the Damköhler number, where below a critical threshold, flame front extinction occurs [126].

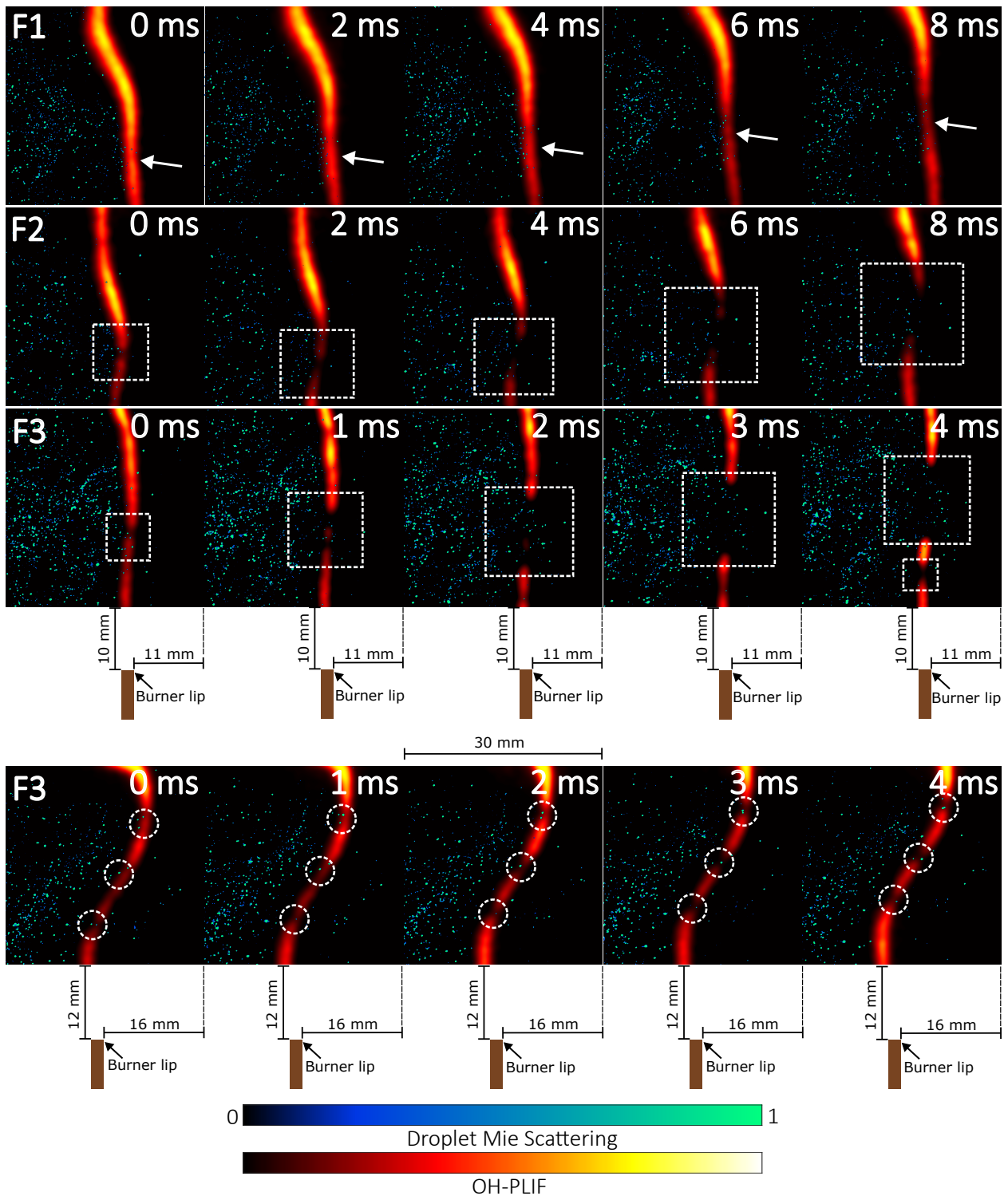


Figure 6.3: Image montages of local extinction events due to droplet evaporation in the flame front, for Flames 1-3 (F1 - F3). Image window size is 30×30 mm with an illustration of where the burner lip is relative to the image window.

The third set of image sequences in Figure 6.3 shows local extinction in the flame front with an increased water mist salt concentration of 40% (Flame 3). The process of local extinction is observed to occur at more than twice the speed in comparison to Flame 2, with the sequence showing a similar size (≈ 12 mm) local extinction hole occurring within 3 ms. Droplets are also seen to impinge into the fuel side once a break in the flame front occurs. These events are observed to occur at a much higher frequency in Flame 3 when compared to Flame 2, as the inhibitor concentration is doubled from 20% to 40%. To further illustrate the impact of increased salt concentrations on chemically induced flame inhibition, the fourth set of images (bottom row of Figure 6.3) highlights three locations in the flame front where individual droplets cause local extinction in the high-temperature reaction zone. This effect is particularly noticeable at 3 ms, as highlighted in the dashed circular region, where single droplets disperse a diffused field of inhibitor, creating temporary gaps of 3 - 4 mm in the flame front. Increasing the concentration of KHCO_3 is shown to significantly enhance the flame suppression properties of individual droplets, where even large individual droplets can cause discontinuities in the flame front.

The flame extinction process of a higher flow rate of water mist (Flame 4) is shown in Figure 6.4. For all sequences, the flame is seen to lift off the burner exit plane as a result of a sufficiently high enough flow rate of water to cause quenching at the flame base. This flow rate maintains the same blow-off regime as Flame 3 (Figure 6.1); however, the method of flame extinction is quite different to that of chemical inhibition. Pure thermal quenching and gas phase dilution do not provide a sufficient loss of sensible enthalpy and/or a reduction in combustion efficiency [92] in the flame to induce extinction in the downstream region of the flame as seen in Flames 2 and 3. This may be because increasing the flow rate of water mist primarily increases velocity rather than instantaneous droplet number density (a small increase). Also, droplet transport into the flame front in a co-flow configuration is primarily through diffusion and entrainment, which is a limiting factor for in-flame droplet penetration. This is specific to this experimental setup, unlike more realistic water misting systems where droplet transport into the flame front is typically dominated by droplet momentum. In all

sets of images for Flame 4, blow-off occurs with the flame base detaching from the burner exit plane at speeds in the order of $\approx 15 - 35$ cm/s until conditions favour flame propagation.

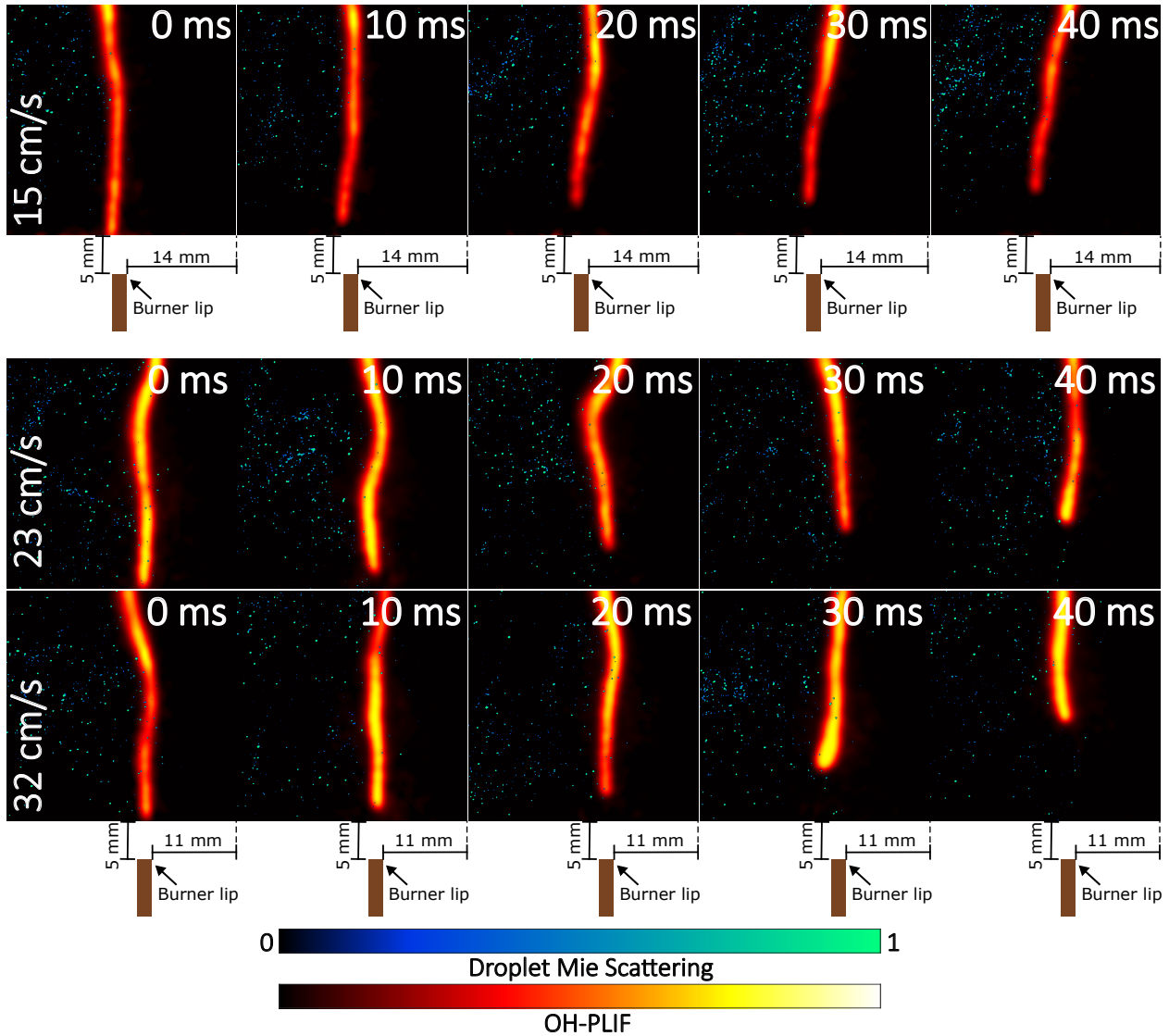


Figure 6.4: Flame 4 (F_4) image montages of flame extinction (blow-off) for an increased flow rate of water mist. Image window size is 30×30 mm with illustrations of where the burner lip is relative to the image window. Average flame propagation rates shown on the left of the sequence.

6.2.2 Flame front re-connection

Flame re-connection is observed throughout all the high-speed images. Figure 6.5 shows sequences of images that illustrate flame re-connection. Re-connection events are defined as the closing of breaks in the flame front due to local conditions favouring combustion (edge flame propagation) over extinction. The first two rows of images show example characteristics of flame re-connection with two reaction fronts propagating towards each other in the order 80 cm/s as shown in flames 2 and 3. There are two mechanisms that constitute hole re-connection: (i), local premixing of the fuel and oxidiser where an extinction front may then transition to an ignition front and propagate inwards filling the hole [208][209]. (ii), when local conditions favour flame propagation rather than extinction due to a reduction in droplet density or inhibitor concentration. A combination of both mechanisms can be generalised by an increase in the Damköhler number as the reaction time scales decrease, favouring re-connection.

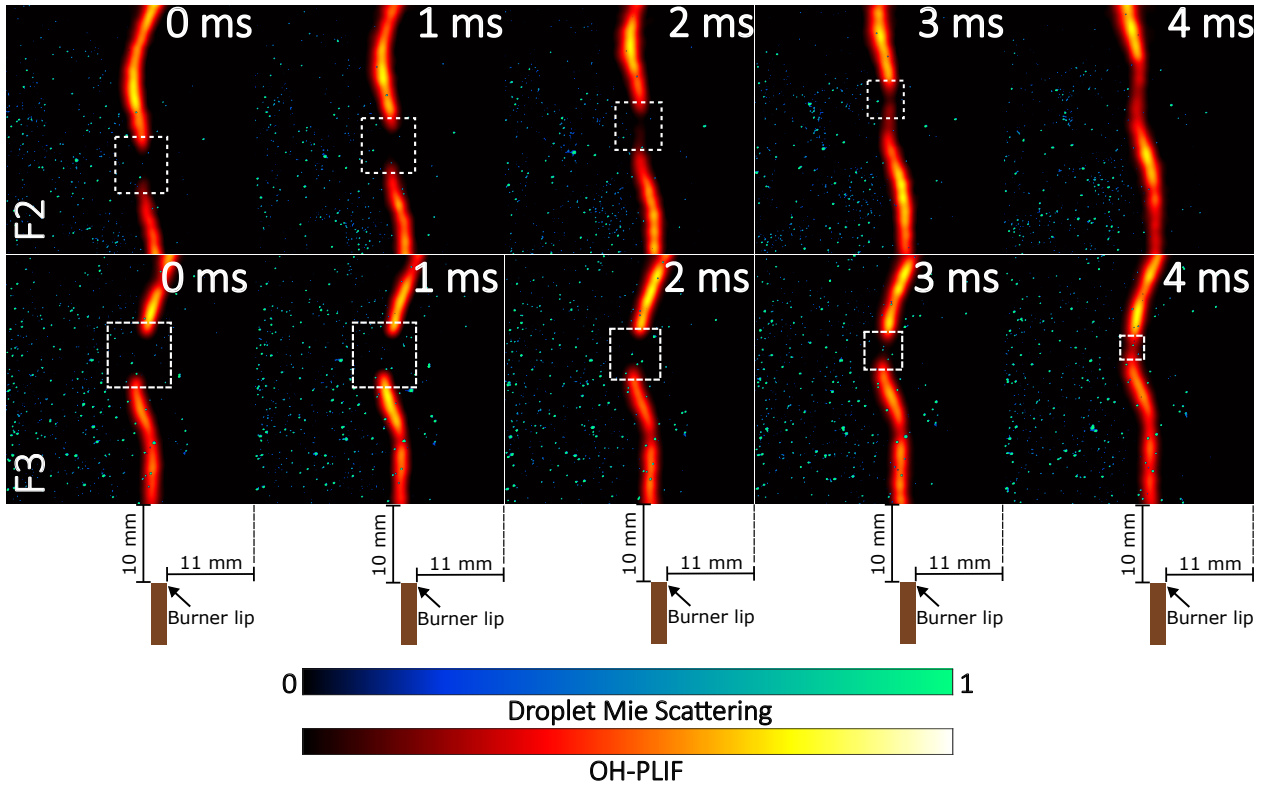


Figure 6.5: Image montages of flame re-connection for Flames 2 and 3 (F2 and F3) with an image window of 30×30 mm. Illustrations show where the burner lip is relative to the imaging window.

Flame 4, however, as previously mentioned, exhibits more of a blow-off phenomenon (Figure 6.4) rather than local extinction of the flame front as seen in the previous Flames 2 and 3. The blow-off process is highly stochastic (as shown in the previous chapter), oscillating around the burner exit plane. Figure 6.6 shows two sets of high-speed images presenting flame re-connection/propagation of a lifted flame. The first row of images shows a flame edge propagating towards the burner rim. The propagation rate is estimated to be 20 cm/s which may be affected by out-of-plane motion, where the dashed lines show the approximate location of the edge flame as it propagates towards the burner exit plane. Another example is shown in the second row of Figure 6.6, where the flame front, initially at 0 ms, hovers in a highly lifted position. At 2 ms, re-connection occurs into the plane of the laser sheet (out-of-plane propagation). The flame remains lifted above the burner exit plane, and at 2 ms, it further propagates towards the burner rim in a manner similar to the previous sequence at

a constant velocity, however, at a much higher estimated velocity of approximately 50 cm/s. The axial flow velocity of fuel and oxidiser ahead of the edge flame is unknown due to the stagnation point that forms above the burner rim (thickness 2.5 mm); however if accounting for the flow velocity of fuel (20 kW Figure 3.3, 0.6 m/s) and oxidiser (Figure 5.3 assuming droplets approximate air side co-flow velocities, 0.5 m/s), the absolute flame propagation speed is ≈ 1.1 m/s. This is much greater than the stoichiometric laminar flame speed of methane/air, which is ≈ 35 cm/s [210]. This higher flame speed could result from many factors such as an increased level of turbulence due to enhanced mixing ahead of the edge flame (caused by droplet momentum and the burner rim). Edge flames are also known to travel at higher speeds [211] and flame propagation into compositionally stratified mixtures can also achieve flame speeds higher than that of the stoichiometric laminar flame speeds [212]. The propagation speeds have high degrees of variability on a case-by-case basis, as there are multiple mechanisms that may vary with time (in the order of milliseconds or less). These include flame quenching (droplet density), local flow field turbulent intensities, and in/out of plane propagation/extinction.

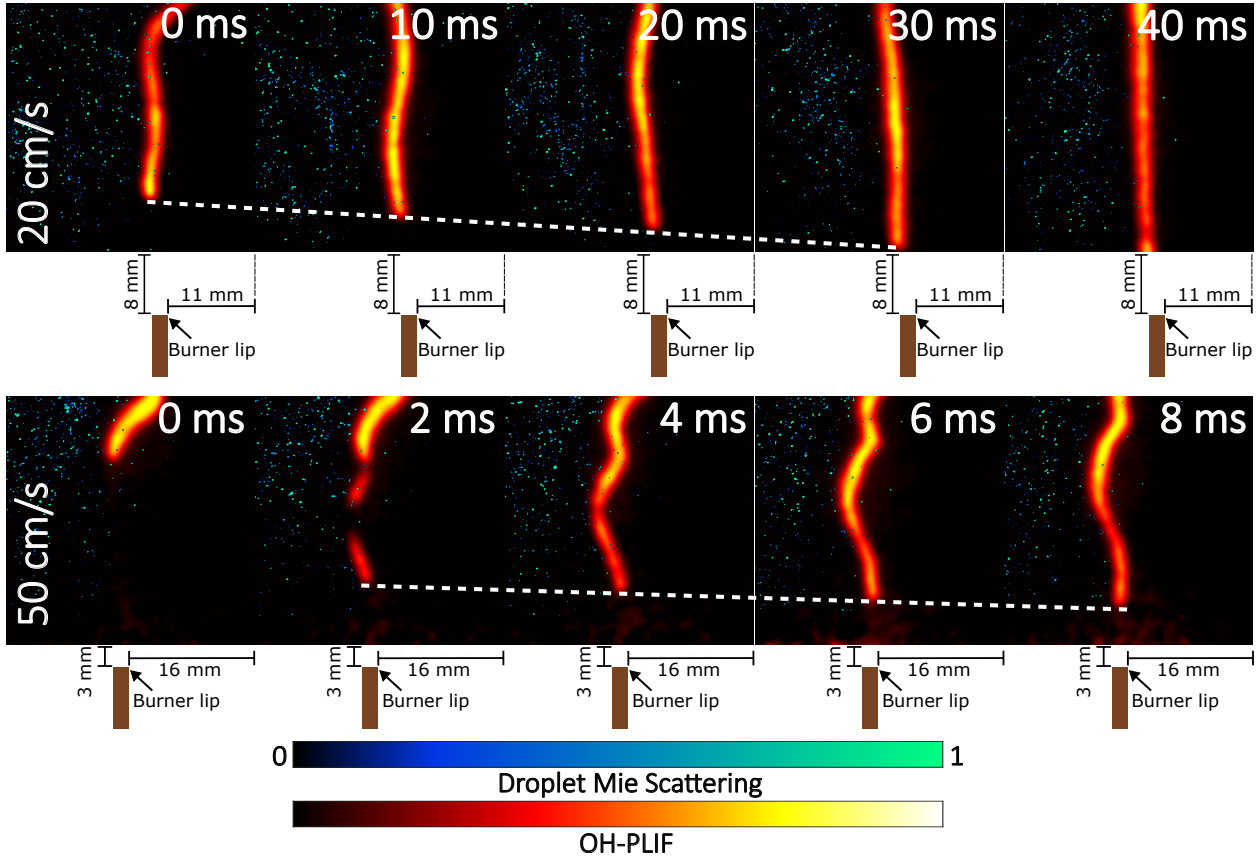


Figure 6.6: Image montages of flame re-connection for Flame 4 with an image window of 30×30 mm. illustrations show where the burner lip is relative to the imaging window. Average flame propagation rates shown on the left of the sequence.

6.2.3 Explosive droplet fragmentation

Interestingly, with an increase in salt concentration, a phenomenon known as “droplet fragmentation” can be observed in individual droplets further downstream (not seen in pure water). Figure 6.7 shows a high-speed sequence of rapid, explosive droplet fragmentation occurring at $\approx 60 - 90$ mm downstream of the burner exit plane. A single droplet (circled) is observed at 0 ms in close proximity to the high-temperature reaction zone (approximately 2 mm away). In the next frame, at 0.2 ms, the droplet expands into multiple fragments. This is confirmed at 0.4 ms, where multiple fragments are observed moving in all directions, expanding outward from the original droplet position. These fragments are measured to reach

speeds of up to 4.2 m/s, significantly higher than the mean flow field velocity of 0.5 m/s. Droplet explosions are observed quite frequently at downstream locations of the burner exit plane, though they primarily occur in smaller droplets that are difficult for the cameras to detect. The explosive break-up of heated droplets has been previously observed and studied in the literature, such as the explosive disintegration of two-component droplets [213][214][215] (flash boiling) and droplets with particle inclusions [216]. The primary driver for explosive droplet fragmentation observed here is believed the latter, caused by crystal growth inside the droplet from supersaturation (due to droplet evaporation). The presence of salt crystals may have enhanced radiation absorption [217], where it is possible to have vapour formation on the inside of the droplet on the crystal/water boundary, causing a buildup of internal pressures. This is perhaps why droplets are only seen to “explode” in the downstream regions on the flame and not near the exit plane (as shown in Figure 6.3) as this gives droplets more time to increase their internal temperatures. This explosion phenomenon has also been previously shown to play a role in the enhanced suppression of pure water [216]; however, its significance in the overall contribution to flame suppression in this study is unknown. Also, note that rapid droplet fragmentation also increases the spatial dispersion of KHCO_3 which may have beneficial effects on flame suppression.

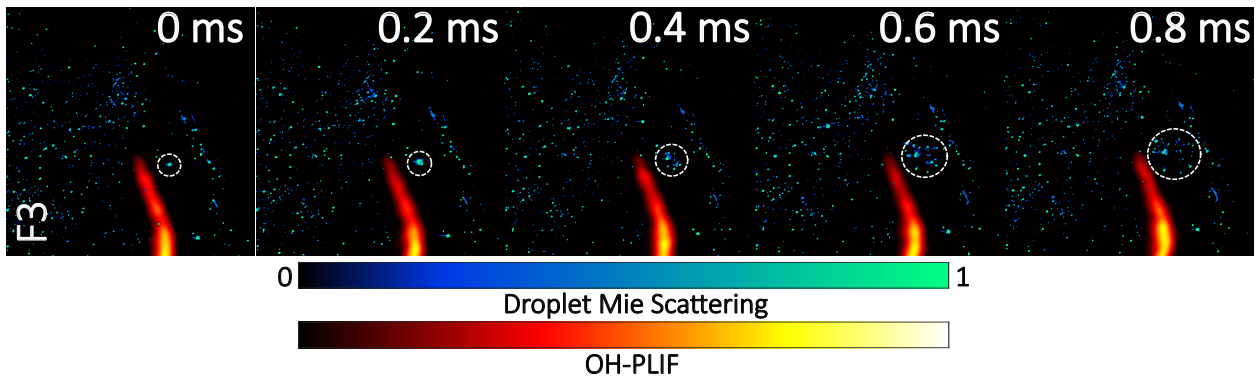


Figure 6.7: Image montages of droplet explosions in a 30×30 mm window (Flame 3) at 60 - 90 mm downstream of the burner exit plane.

6.2.4 Time history of flame front extinction

The process of flame front quenching and inhibition is primarily influenced by droplet transport into the high-temperature reaction zones. To observe this process temporally, Figure 6.8 shows a time history of the total OH area (black) and droplet density (blue) in a 30 x 30 mm window. The OH area is defined as the sum of all pixels within a binarised OH image (image process as shown in Chapter 4 Figure 4.2), where peak OH counts range between 200 and 1000 counts above background depending on the flame. Droplet density is defined as the total number of droplets identified within the binarised OH region normalised by the total OH area. The combination of both series of temporal statistics illustrates the high negative correlations between the size of the reaction zone and the number of droplets within that reaction zone. The first row, Figure 6.8a presents a time history for a one-second real-time sample (5000 images) of Flame 1. The OH area oscillates around 150 mm² with minimal deviation from the mean, indicating that the flame is highly stable (well below the stability limit shown in Figure 6.1). The red arrows illustrate example instances where a decrease in the OH area correlates with an increase in droplet density. The red shaded regions further highlight extreme negative correlations in both directions, where an increase in OH area corresponds to a reduction in droplet density, and vice versa.

The second row, Figure 6.8b shows the time history of Flame 2. The inclusion of an inhibitor is observed to reduce the overall mean OH area of the flame through the radical recombination of KOH, with increased deviations from a mean of ≈ 100 mm². When the OH area dips below 75 mm², in most cases, there is a breakage in the flame front as shown previously in Figure 6.3. The correlations between OH area and droplet density are very similar to those of Flame 1, where the increased droplet density in the reaction zone drives local extinction. The third row, Figure 6.8c shows Flame 3, where an increase in inhibitor concentration to 40 %, further reduces the mean OH area to approximately an average of 80 mm² with major deviations to the mean. Similar instances of high negative correlations between OH area and droplet densities are highlighted in red. However, interestingly, for this

sample, there is also observed a long-term correlation where a “slow” decrease in OH area corresponds with a “slow” increase in droplet density (red arrows). This eventually leads to complete extinction where the OH area drops to 0 mm² with subsequent events of rapid flame re-connection and/or out-of-plane motion. Both long-term and short-term correlations observed are driven by different phenomena. The long-term decrease in OH area is a result of either preferential entrainment or atmospheric draft, as these motions are relatively slow. This drives an increasing number of droplets into the flame front, reducing the OH area over a longer period of time. The short-term oscillations between OH area and droplet density, as highlighted by the red boxes in all the flames, present a competing phenomenon between thermal quenching, radical scavenging, and a form of chemical recovery. As droplets evaporate, local combustion is inhibited. However, once the droplets fully evaporate (as the gas phase temperatures are still relatively high), chain branching combustion reasserts itself (flame propagation), leading to an observed increase in the OH area (concentration and/or gas phase temperatures).

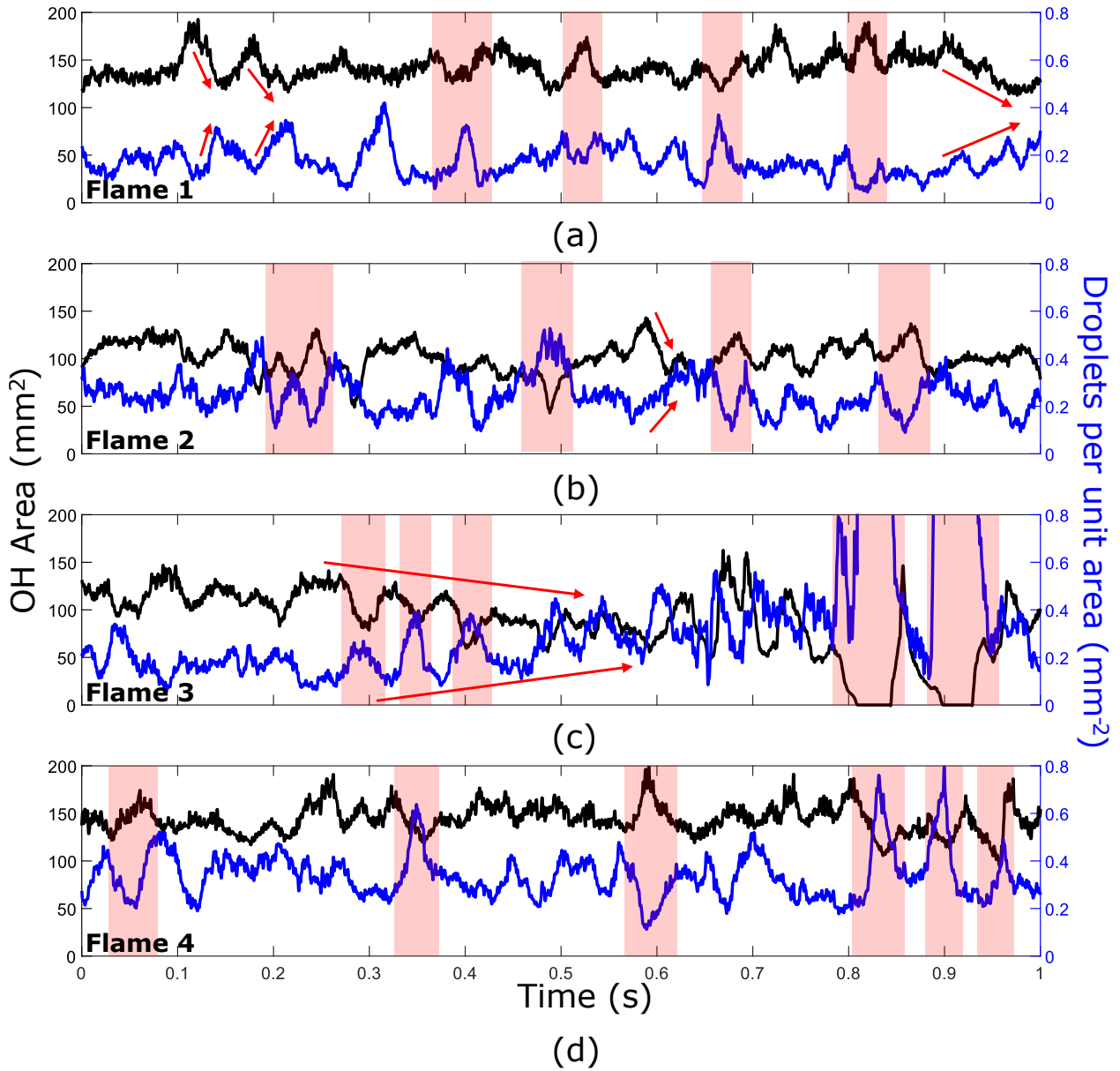


Figure 6.8: Example time histories of OH area and droplets per unit OH area (droplet density) for Flames 1-4.

The last row, Figure 6.3d shows Flame 4, the pure water case with increased flow rate, which once again is in the same stability regime as Flame 3. Interestingly, the mean OH area is almost identical, if not slightly higher (higher deviations and mean) than that of Flame 1, the pure water case with a lower flow rate of water mist. This is primarily due to an

expansion in the thickness of the reaction zone from partial premixing. As shown previously in Figure 6.4, the primary mechanism of flame extinction is thermal quenching of the flame base, which lifts the leading edge off the burner exit plane. The region below the leading edge is now partially premixed, as the fuel and air are given increased residence times for diffusion. This leads to an increase in the reaction zone thickness upon re-connection [218] as shown in Flame 4 of Figure 6.5. Increasing droplet momentum may also enhance turbulent mixing between the fuel and oxidiser, leading to a wider reaction front.

6.2.5 Reaction zone thinning and breaking

Fluctuations in OH area is a combination of both the number of breakages in the flame front (length) and the thickness of the reaction zone (width). To delineate between the effects of local extinction and reaction zone thinning, these quantities are separated and shown in Figure 6.10. Flame 4 is not presented here as the boundary conditions are fundamentally different due to the increase in the flow rate of water mist. Figure 6.9a shows the processing technique/procedure used to calculate the OH FWHM along the flame front. The pre-processed OH image (as shown in Chapter 4 Figure 4.2) is skeletonised where at each point along the skeleton, the OH intensity is extracted along an interrogation line that is projected perpendicular to the skeleton's local curvature (green line on Figure 6.9a). This provides a Gaussian-like profile of OH intensity, which is used to estimate the FWHM OH thickness at that given point as shown in Figure 6.9b. This is completed for the entire set of high-speed images to obtain a distribution of reaction zone thickness.

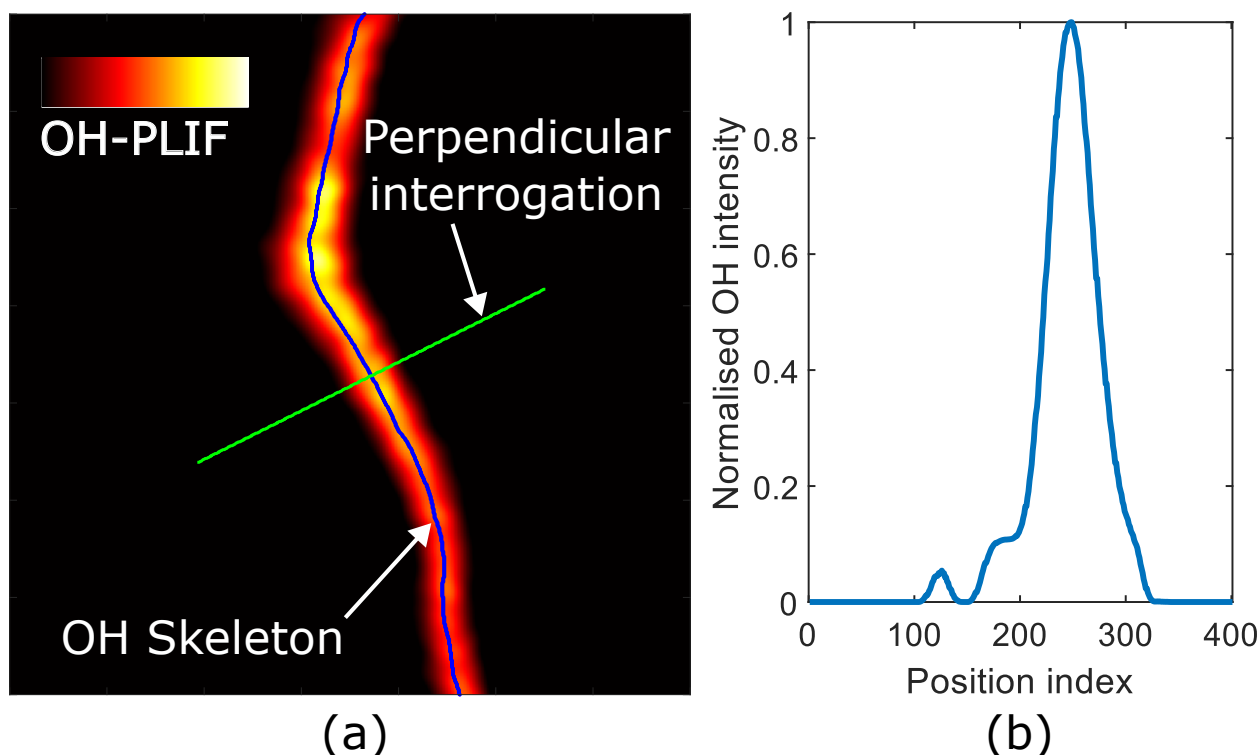


Figure 6.9: Processing technique for OH FWHM (Full Width Half Max), (a) skeletonised OH image with an example single point interrogation of OH intensity along a line perpendicular to the local OH curvature, (b) Normalised OH intensity extracted along the interrogation line used to calculate the OH FWHM.

Figure 6.10a presents the average number of breaks in the reaction zone from the 50000 images taken for each of the Flames 1 - 3. At a constant flow rate of water mist, the average number of breakages seen in each image frame in the flame front increases exponentially with increasing inhibitor concentration, driving the flame to complete extinction. Figure 6.10b shows the average FWHM (full width half maximum) OH thickness of Flames 1 - 3. The average thickness of the reaction front is shown to steadily decrease with an increase in inhibitor concentration, driven purely by the process of radical pool depletion. This is further validated with kinetic modelling performed in Cantera using a methane/air opposed flow diffusion flame at varying strain rates as shown in Figure 6.10c. The GRI3.0 mechanism is modified to include the kinetic model of potassium-containing species [129][219], where

species transport is estimated by analogy or empirical correlations. Table C.1 lists the potassium transport properties used in the laminar flame calculations. A stoichiometric air-to-fuel mixture is used, where N_2 on the air-side is substituted with increasing mole fractions of KOH. KOH is deemed appropriate as an input due to the assumption of rapid thermal decomposition of $KHCO_3$ at low temperatures [139]. With increasing mole fractions of KOH, the OH thickness (FWHM) decreases steadily, showing very similar trends to the experiment. Interestingly, there seems to be a plateauing effect, whereby above a certain concentration of KOH, the effective reduction in reaction zone thickness decreases, as seen in the laminar flame calculations. This is possibly due to a saturation effect. Numerous studies have previously reported this effect [136][163][154] where there is an optimal concentration for inhibition. Rosser et al. [220] noted they observed that the catalytic recombination cycle depends on radicals being reduced from super-equilibrium concentrations to their equilibrium levels. This establishes an upper limit for the inhibitor concentration to achieve maximum effectiveness. Beyond this threshold, any further addition of the inhibitor merely acts as a diluent and/or heat sink for the flame, functioning thermally rather than chemically. The main difference between the experiment and the simulation is that the experiment includes fine water droplets that also quench the flame front. The inhibitor is also not uniformly distributed on the air side, which is not accounted for in the laminar flame calculations. The exact mole fraction of inhibitor in the reaction zone is unknown in the experiment, making the comparison qualitative.

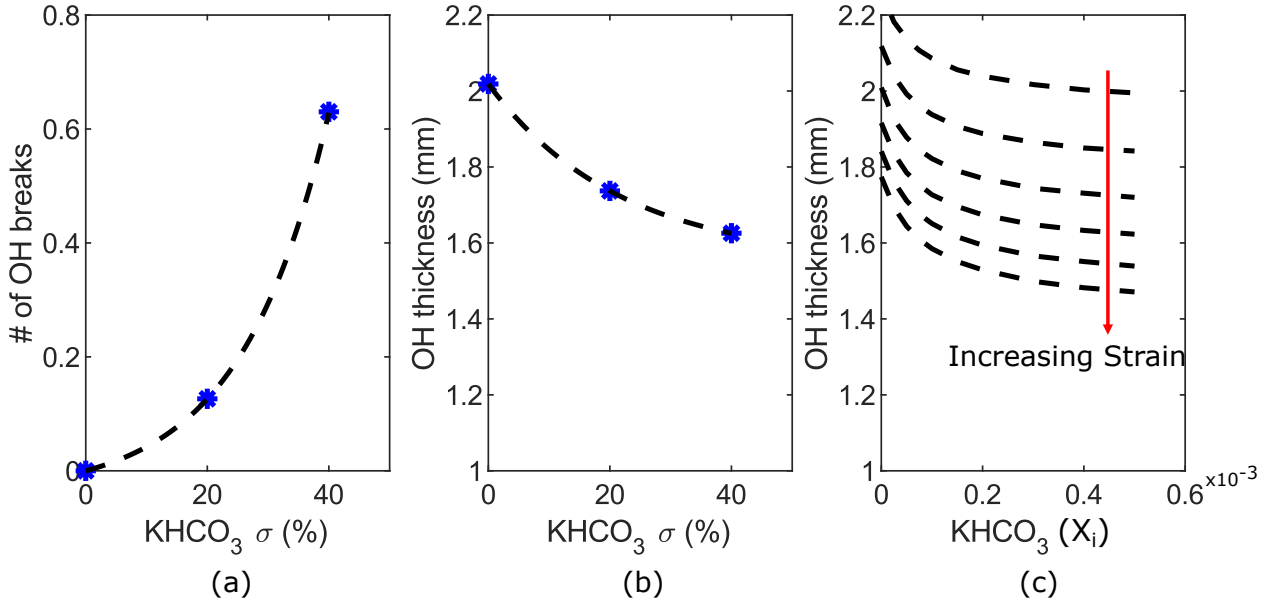


Figure 6.10: Ensemble statistics for Flames 1-3 of (a) average number of breaks in the OH layer per frame, (b) average OH FWHM, (c) laminar flame calculations of OH FWHM at varying strain rates.

6.2.6 Flame width and droplet evaporation

In all the image sequences of flame extinction and re-connection (Figures 6.3 and 6.5), there seems to be a sharp decline in the total number of droplets very close to the flame front. This is due to droplet evaporation from a combination of both flame radiation and the near-flame air-side gas phase temperature profiles. To observe droplet evaporation, distributions of reaction zone width (image processing shown in Figure 6.9) and droplet positions with respect to the centre of the reaction zone (OH skeleton) are shown in Figure 6.12. This is effectively a dimension reduction of the high-speed images by reducing the 2D image (3D for droplets) into a one-dimensional plot of droplet penetration depth. Figure 6.11 shows the processing procedure for calculating droplet positions in 3D space relative to the flame front. Figures 6.11a and b show an example pre-processed image of Mie scattering and OH-PLIF. The Mie scattering image is first binarised and then morphological algorithms such as watershed and regionprops are applied to single out individual droplets and therefore, centroid locations

on all three cameras (Figure 6.11c does not show the use of watershed which can separate connected droplets). Once droplet positions are mapped into 3D lab space coordinates (using MyPTV) and the OH image is skeletonized (Figure 6.11d), the droplets are then conditioned on the flame front such that the Euclidean distance from each individual droplet to the nearest skeletonised OH reaction zone is identified as shown in Figure 6.11e. The droplets are further conditioned to $\pm 250\mu\text{m}$ in the depth direction (where the OH laser sheet sits at $z = 0\text{ mm}$) to ensure each droplet is within the OH plane.

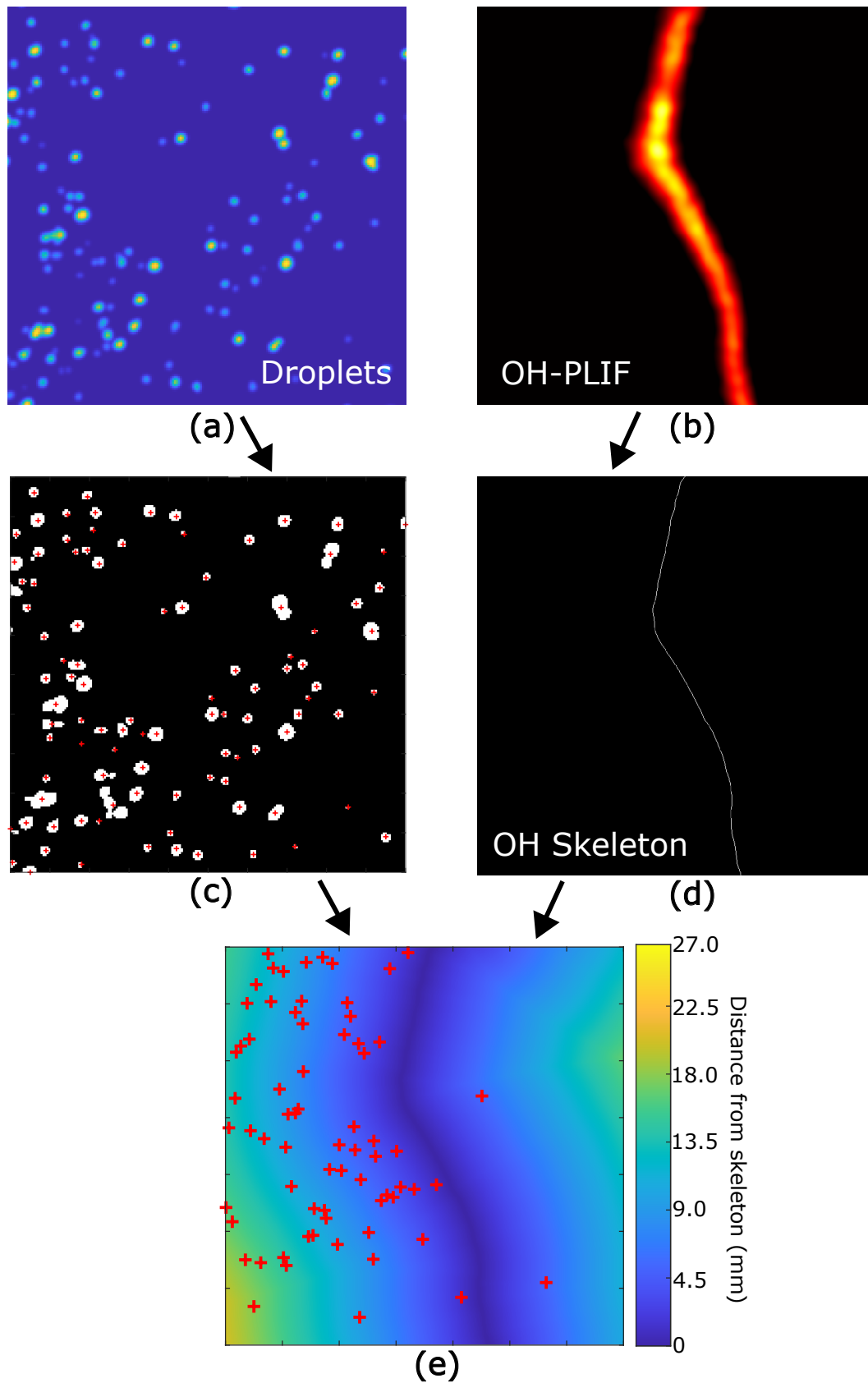


Figure 6.11: Processing procedure for droplet positions. (a) pre-processed Mie scattering of droplets, (b) pre-processed OH-PLIF, (c) droplet centroid positions in 3D lab coordinates using MyPTV, (d) skeletonised OH image, (e) droplet positions relative to the OH skeleton in 3D space.

The OH FWHM PDFs present the probability density functions of the reaction zone on the lean and rich sides of the flame, where the average OH width was presented previously in Figure 6.10b. This is combined with a droplet number distribution to illustrate droplet penetration from the air to the fuel side of the flame. Each row of Figure 6.12 illustrates an ensemble of 50000 images (10 seconds) of their respective Flame cases, with PDFs of the reaction zone boundary (FWHM) overlaid onto droplet distances/locations. Figure 6.12a shows laminar flame calculations are performed for increasing strain rates ($15 - 30 \text{ s}^{-1}$) to show approximate gas phase temperature profiles with respect to peak OH concentrations matched with the experimentally obtained OH width. This is only performed on Flame 1 as there is no inhibitor present (unknown KOH concentrations in the reaction zone for the other cases). On the air side, droplets are seen to uniformly populate the spatial domain for positions greater than $\approx 4 \text{ mm}$ from the centre of the flame sheet, and gas phase temperatures from the laminar flame calculations are also shown to be approximately at/near ambient temperatures (300 K), suggesting that very little evaporation occurs at this distance. This is followed by a rapid decay in droplet density approaching the flame front. This drop in density is observed in all flames and is the result of two effects: (i), the natural decay in the number of droplets in the flow field on top of the burner due to the fact that no droplets leave the burner exit plane, as measured in the previous chapter (Figure 5.3). (ii), droplet evaporation from flame radiation and increased gas phase temperatures. Interestingly, the droplet distribution continues to decay steadily even in the reaction front, where one would assume a dip in the reaction front would be seen.

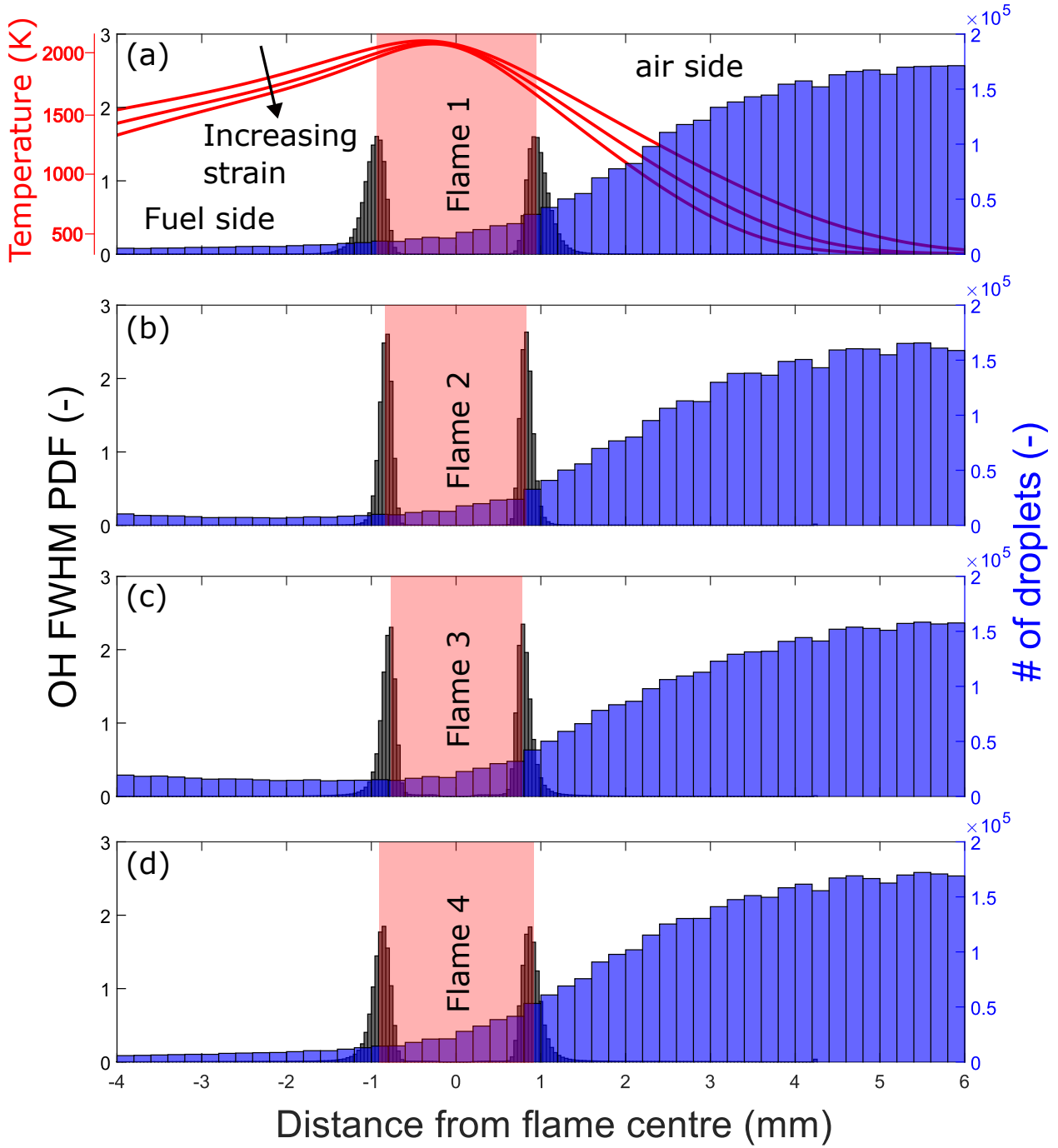


Figure 6.12: Distributions of OH FWHM and droplet locations with respect to the skeletonised centre of the nearest flame front at 10 - 40 mm above the burner exit plane for, (a) Flame 1 pure water with gas phase temperatures obtained from laminar flame calculations for strain rates $15\text{-}30\text{ s}^{-1}$ (no potassium mechanism), (b) Flame 2 20% KHCO_3 , (c) Flame 3 40% KHCO_3 , (d) Flame 4 pure water increased flow rate.

The temperature profiles show steadily increasing gas phase temperatures from 300 K to peak temperatures at 2100 K, corresponding to a steadily decreasing droplet number density. Assuming the D^2 law applies where a droplet lifetime correlation is shown by Equation 6.1 (ignoring radiation), along with ideal conditions in a quiescent environment at 1800 K, large droplets ($40\ \mu\text{m}$) may survive for periods in the order of 10 ms (50 frames) [221]. Depending on local droplet velocities, 10 ms is enough for larger droplets to traverse the width of the flame front without undergoing complete evaporation, as shown previously in Figure 6.3. The caveat here is that the evaporation rate constant “ k ”, depends on numerous factors [123] such as temperature, pressure, turbulence, and more, making this a very broad approximation. Interestingly, Lentati et al. [222] previously conducted experiments on water mist suppression on counter-flow diffusion flames which unveiled optimal droplet sizes, dictated by both a transport and evaporative time scales. It was shown that $20\ \mu\text{m}$ droplets or smaller evaporate extremely quickly in the hot mixing region of the flame, similar to what is qualitatively observed in the high speed images presented herein.

$$D^2 = D_0^2 - kt \quad (6.1)$$

With increasing inhibitor concentrations (Flame 2 and 3), there is an increase in the total number of droplets penetrating from the air side into the fuel side. This effect is caused by a combination of local extinction zones in the flame sheet, which act as low-temperature pathways for droplet transport to the fuel side (Figure 6.3), and the thinning of the reaction layer, which reduces the time a droplet spends in the high-temperature reaction zone (Equation 6.1). As a result, smaller droplets can traverse the flame front since droplet lifetimes increase in a lower temperature environment. The mean width of the reaction zone is illustrated by the red-shaded region. Once again, as shown previously in Figures 6.8 and 6.10, there is a steady decrease in OH width for Flames 1-3 with increasing concentrations of inhibitor. Flame 1 shows a very broad PDF of OH width, which is attributed to the lack of inhibitor resulting in a spatially thick reaction zone. As shown previously in Figure 6.3, as droplets traverse the flame front, the reaction zone undergoes significant thinning due to gas

phase cooling and dilution. The periodic fluctuations in droplet density within the flame front broaden the PDFs. With the addition of the inhibitor (Figures 6.12b and c), the OH width PDFs are significantly thinner, which suggests that the gas phase inhibitor KOH is sufficiently distributed throughout the whole length of the reaction layer. Flame 3, on the contrary, has a slightly broader OH width PDF, though the mean width is lower than that of Flame 2. This is possibly caused by increased premixing as more breaks form in the flame front, giving increased residence time for partial premixing between fuel and oxidiser. Such that when re-connection occurs, a thicker flame front is formed. With increasing concentrations of inhibitor and therefore breaks in the flame front, more droplets are seen to penetrate into the fuel side of the flame. Flame 4 (Figure 6.12d), however, shows an increase in OH width greater than that of Flame 1 (Figure 6.12a) at 2.1 mm with a similarly broad PDF. This has been explained in Figure 6.8 as a result of partial premixing due to flame lift-off, resulting in an increase in turbulent and diffusive mixing of fuel and oxidiser at the burner exit plane.

6.3 CONCLUSIONS

This chapter presented simultaneous high-speed OH-PLIF and Mie scattering of droplets with extremely high temporal and spatial resolutions. This has allowed for the identification and tracking of individual droplets, both spatially and temporally, as they traverse the flame front. Various phenomena are observed with respect to flame extinction and re-connection, conveying the importance of experimentally resolving near-field droplet/inhibitor transport in the high temperature reaction zones. The key findings of this chapter are as follows:

- Pure water mist suppression (Flame 1 and 4) shows no events of local extinction caused by breakages downstream of the burner exit plane. Flame 1 only shows local reductions in OH signal due to thermal quenching, whereas Flame 4 exhibits lift-off of the flame base rather than local flame front extinction as observed in the potassium salt cases (Flame 2 and 3).
- An increase in inhibitor concentration at a constant flow rate of water mist shows

an exponential increase in the presence of breakages in the flame front. At high concentrations of salt, large droplets can individually cause small extinction zones in the OH layers.

- Flame re-connection is observed in the flames with inhibitor (Flame 2 and 3), where gaps in the flame front close due to edge flame propagation, driven by local conditions that favour combustion over extinction. Flame 4 primarily exhibits flame re-attachment to the burner due to partial premixing upstream of the flame front, showing highly stochastic in and out-of-plane motion with a high variability in flame propagation speeds.
- A strong negative correlation is observed between the OH area and droplet density for all the flames. A decrease in OH area correlates with an increase in droplet density and vice versa, highlighting the sensitivity and importance of gas phase cooling, specifically within the flame front.
- For a constant flow rate of water mist with increasing concentrations of inhibitor (Flame 1-3), there is a steady decrease in the reaction zone thickness. This effect is purely due to the presence of KHCO_3 depleting the pool of free radicals, with similar effects observed in laminar flame kinetic calculations with inhibition due to KOH.
- Ensemble droplet positions relative to the flame front show a continuous stream of droplet diffusion and evaporation, moving from the far field towards the centre of the burner. With increasing inhibitor concentrations, more droplets are seen on the fuel side due to increased droplet transport through breakages in the flame front.

These results demonstrate the importance of experimentally resolving the near-field interactions of gas phase cooling through water mist droplets. This enables a deeper phenomenological understanding of droplet transport and penetration into the flame front and the effects of the addition of inhibitor (KHCO_3). Therefore, this work provides valuable measurements of flame structure and flame droplet interactions, which builds a platform for future quantitative

measurements to help further develop and validate numerical models in water mist fire suppression.

Chapter 7

Ferrocene as a Water Mist Additive

This chapter delves into the development of new methods for dissolving and/or dispersing ferrocene into water mist. The advantages of ferrocene over proven flame suppressing agents such as KHCO_3 and NaHCO_3 is that not only does it have greater suppression efficacy on a molar basis [140][150], but it is also a non-corrosive and non-conductive suppressing agent. The inhibition efficacy of ferrocene as an additive in water mist has rarely been assessed in literature for canonical flames representative of a fire, primarily because ferrocene is not soluble in water, posing a significant challenge. This chapter explores various methods to incorporate ferrocene into a water mist suppression system. The efficacy of these complex aqueous ferrocene blends is directly compared using the same experimental setup as in the previous chapters, enabling a comparative study of ferrocene's inhibition performance against water and alkali metal salts.

7.1 EXPERIMENTAL SETUP

7.1.1 Water misting system design

The layout of the water misting system and fire burner is identical to that of the previous chapters. However, the water supply system is changed in this case from a gear pump to a nitrogen pressurised chamber, as shown in Figure 7.1. This allows for easy decontamination of the water lines and supply chambers, as the following experiments use non-trivial solvents and solutes.

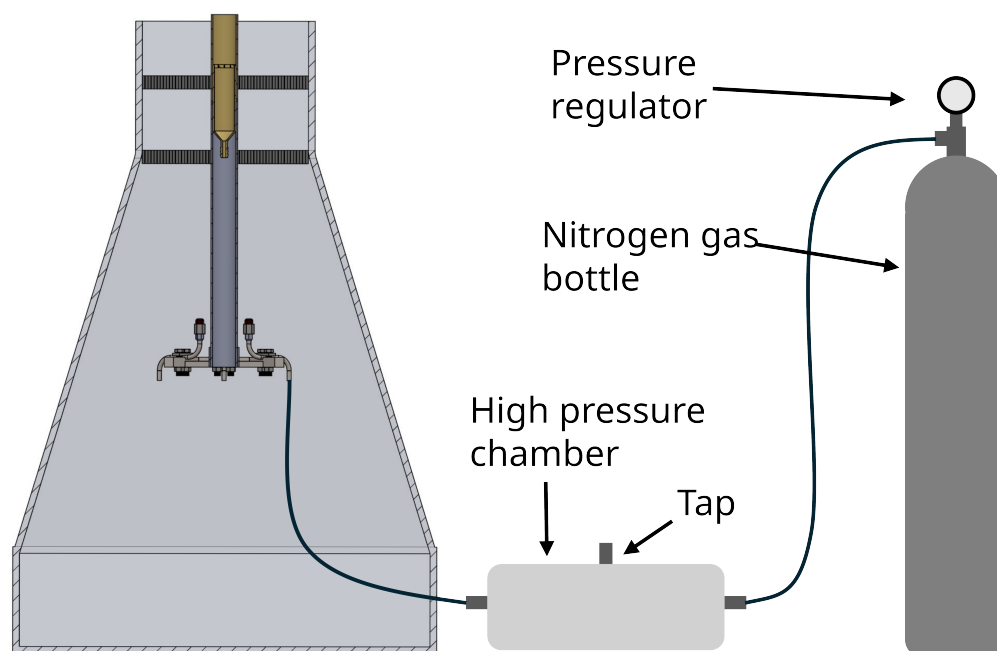


Figure 7.1: Water mist setup.

The pressure chamber is filled with the solution of interest where the flow rate of the water mist is controlled by two pressure regulators, one to control the nitrogen bottle pressure, and another to regulate the chamber pressure. The two-step decrease in pressure allows for accurate controllability of line pressure without the need for a mass flow controller. A pressure gauge is placed at the nozzle line inlet identical to the experiments conducted in the

previous chapter, to maintain and identify the same operating conditions produced in the previous experiments. The experimental procedure for obtaining extinction delay times and stability limits are also identical to the previous chapters (Chapter 5 Figure 5.6). Due to the hydrophobic nature of Fc (ferrocene), its implementation as a homogeneously dispersed additive in water is non-trivial. However, there have been many attempts in several different fields of research utilising different methods to create an aqueous solution of ferrocene, some of these methods are attempted herein and are detailed in the following sections.

7.2 AQUEOUS DISPERSION OF FERROCENE

7.2.1 Anti-solvent precipitation

Anti-solvent crystallisation is a technique commonly used in pharmaceuticals and chemical processing to produce fine micro/nano-sized particles. This process primarily consists of bringing a dissolved solution to supersaturation via the addition of an anti-solvent [223][224]. This is followed by the rapid formation of nuclei and further crystal growth of the solute. To produce the nano-sized Fc (ferrocene) particles, a similar setup is adapted to that of Koshiba et al. [25]. Figure 7.2 shows the experimental setup procedure for the production of nano-sized Fc particles in aqueous suspension. A solution of Fc dissolved in ethanol and/or acetone is placed in a burette and dripped into an ultrasonic bath (or mixing tank) filled with water. The ultrasonic bath is kept on during the whole process. The flow rate of the burette was varied between 2 - 10 ml/min, no visual difference in the suspended solution was observed between the different flow rates. Ethanol and acetone are chosen as solvents as both alcohols are completely miscible in water and are capable of dissolving ferrocene. Water acts as the anti-solvent where the alcohol forms a homogeneous solution with water, forcing Fc to crystallise out of solution.

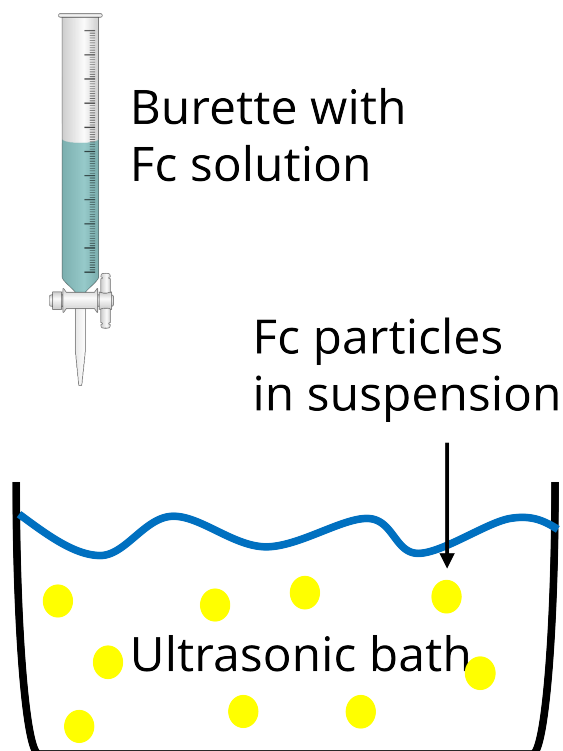


Figure 7.2: Anti-solvent crystallisation setup of nano-sized Fc particles using a water-filled ultrasonic tub.

Table 7.1 shows the different solvents and concentrations (C) of Fc (ppm mass/mass basis) used to assess suppression efficacy. Solvent concentrations are on a volume basis, where 10 % means that the aqueous dispersion of Fc contains 10 % solvent by volume (e.g. 1 L of water has 100 mL of solvent). The maximum concentration of Fc achievable was 1500 ppm with acetone, as the solubility of Fc in acetone is almost three times more than in ethanol. Increasing the amount of Fc shifts the balance of particle formation to crystal growth rather than the formation of nuclei, resulting in visibly larger particles of Fc. Larger particles cannot pass through the nozzle orifice, causing Fc to collect in the water lines. No measurements were taken to determine the particle size distributions, as the results of suppression efficacy are inconclusive regardless of the preparation method. Also note, that the visibility of the dispersion of suspended ferrocene particles starts to settle after 3 - 4 hours. Images of the

aqueous solution are shown in Appendix D Figure D.1.

Table 7.1: Solvent (ethanol and acetone) and ferrocene concentrations

Solvent	Solvent concentration %	C (ppm)
EtOH	10	100
EtOH	10	200
EtOH	10	500
EtOH	5	100
EtOH	5	200
EtOH	5	500
Acetone	1	100
Acetone	1	200
Acetone	1	500
Acetone	1	1000
Acetone	1	1500

7.2.2 Water-soluble host-guest inclusion

Ferrocene cannot dissolve in water as the Fc molecule is symmetric and therefore, has low polarity resulting in weak interactions with water molecules. However, attempts at solubilising non-polar substances in aqueous solution is a highly researched area in pharmaceuticals and other areas of interest, such as ferrocene battery electrolyte research [225]. One method commonly used to solubilise a compound not soluble in water is host-guest inclusion. This method involves using a host molecule (β -cyclodextrins variants) as a carrier of Fc which can then be dissolved in water. β -cyclodextrins is an extremely large cone-shaped [226] molecule that contains a hydrophobic cavity [227] and a hydrophilic shell. The hydrophobic cavity attracts the Fc molecule and “contains” it inside the β -cyclodextrin (β -CD), and because the outer shell is hydrophilic, the inclusion complex (Fc + β -CD) is also soluble in water. Initial tests found that the inclusion complex of Fc + β -CD is barely soluble in water, however,

2-Hydroxypropyl- β -cyclodextrin (HP- β -CD), a modified version of the standard β -CD, allows for a much higher effective solubility of Fc in water [225], with concentrations upwards of 0.3 mol/L of Fc in water.

The preparation method of the Fc HP- β -CD inclusion complex is simple, dissolve the desired amount of the host molecule in water until a homogeneous solution is formed. Then directly add at most 1/3 by moles (Fc to HP- β -CD) [225] of Fc into the homogeneous solution, stir and mix until all the Fc is included. Considering the total mass and volume of HP- β -CD added to the water is quite large, both the viscosity and surface tension of the solution will change depending on how many free water molecules are available. Viscosity and surface tension measurements in previous studies [228] have shown an exponential increase in fluid viscosity with increasing concentrations of HP- β -CD, with the surface tension remaining rather consistent. The viscosity dictates the solubility limit of the inclusion complex. SaCouto et al. showed that at 50 % concentration by weight, the fluid viscosity of HP- β -CD in water increases exponentially [228]. Given the increase in viscosity, the atomisation properties of the nozzle will also change with increasing concentrations of HP- β -CD. To ensure a pseudo similar droplet mist environment for fair comparisons in experiments, the solution is doped with an anti-foaming agent (dimethylpolysiloxane) to help maintain similar misting properties as the previous chapter by reducing the surface tension to assist droplet atomisation [229]. Table 7.2 shows a complete list of the concentrations tested for the inclusion complex. One set of stability limits without Fc (only HP- β -CD) and another set of stability limits with Fc, this is to isolate the effect that HP- β -CD has on suppression efficacy. Images of the aqueous solution are shown in Appendix D Figure D.2.

Table 7.2: Concentrations of HP- β -CD and Fc used in the test cases

HP- β -CD (g/L)	Fc (g/L)
0	0
32.6	1.44
48.5	2.15
64	2.83
123	5.45

7.2.3 Water soluble ferrocene derivatives

The solubility of Fc in water can be modified by chemically modifying one or two of the cyclopentadienyl rings with a chemically active group to increase its polarity and therefore ability to form hydrogen bonds with water, or to convert the molecule into a salt, allowing it to form ionic bonds with the counterions in water. Examples include converting pure ferrocene into a salt such as ferrocene trimethylammonium chloride [230] or ferrocene trimethylammonium iodide [231][232], or to append different functional groups such as a carboxyl group which can improve ferrocenes solubility in aqueous base [233]. This study will use ferrocenecarboxylic acid as the water soluble ferrocene derivative because of its availability and relatively low cost compared to other ferrocene derivatives. Experiments showed that ferrocenecarboxylic acid (FcCOOH) is barely soluble in pure water, but when paired with a strong base (NaOH), its solubility in water increases dramatically [233]. In the presence of a strong aqueous base, FcCOOH forms a carboxylate salt (FcCOO⁻Na⁺) allowing for dipole interactions that keep the molecule in aqueous solution. The preparation method is as follows: simply mix a ratio of 1:1.05 by moles of FcCOOH to NaOH in water and stir until fully dissolved (the higher concentration of NaOH ensures most of the FcCOOH converts to its corresponding carboxylate salt). Using pH strips, the solution was tested to have a slightly basic pH of approximately 8 depending on the amount of NaOH dissolved. Table 7.3 shows the concentrations of FcCOOH and NaOH used in this study (Note: Solubilities of

other derivatives, specifically ferrocene methanol and ferrocene dicarboxylic acid were also tested with results shown in Appendix D Figure D.3, however, no suppression tests were performed on these derivatives).

Table 7.3: Concentrations of NaOH and FcCOOH used to produce different solutions of ferrocene in water, used to assess suppression efficacy

NaOH (mol/L)	FcCOOH (mol/L)
0	0
0.01	0.01
0.05	0.05
0.1	0.1
0.2	0.2

7.2.4 Boundary condition verification

To assess the change in spray atomisation due to the change in fluid viscosity from the addition of HP- β -CD, PDA measurements (same setup as in Chapter 5) were conducted on a single spray nozzle at a constant flow rate and pressure with two concentrations of HP- β -CD. One concentration at 0 g/L and another at 136 g/L with and without the anti-foaming agent (dimethylpolysiloxane) to illustrate the change in droplet field statistics (changes in viscosity and surface tension via the addition of HP- β -CD). Figure 7.3 shows both the axial velocities and d_{32} droplet diameters at 20 mm downstream of the nozzle exit plane. The flow rate is kept constant at 25 mL/min which is for reference, 150 mL/min for six nozzles as shown in Chapter 5 Figure 5.4. Figure 7.3a shows droplet statistics for pure water, the axial velocities range from 1.8 m/s near the centre of the hollow cone to 5 m/s near the wings, while the d_{32} droplet diameters range from 22 μm near the centre of the hollow cone to 60 μm at the wings. Figure 7.3b shows droplet statistics for an aqueous solution of 123 g/L of HP- β -CD with 0.5 mL/L of anti-foaming agent. Droplet velocities are very similar to that of pure water and the d_{32} follows a very similar profile with a slightly broader range of

droplet diameters, d_{32} ranging between 20 - 65 μm . Figure 7.3c shows droplet statistics for an aqueous solution of 123 g/L of HP- β -CD. Both the axial velocity and droplet d_{32} profiles are significantly higher than the other cases, this is due to the increased viscosity of the solution. The PDA measurements show that the inclusion of the anti-foaming agent assists in the nozzle atomisation process, ensuring that the droplet field stays relatively similar between the different concentrations of HP- β -CD.

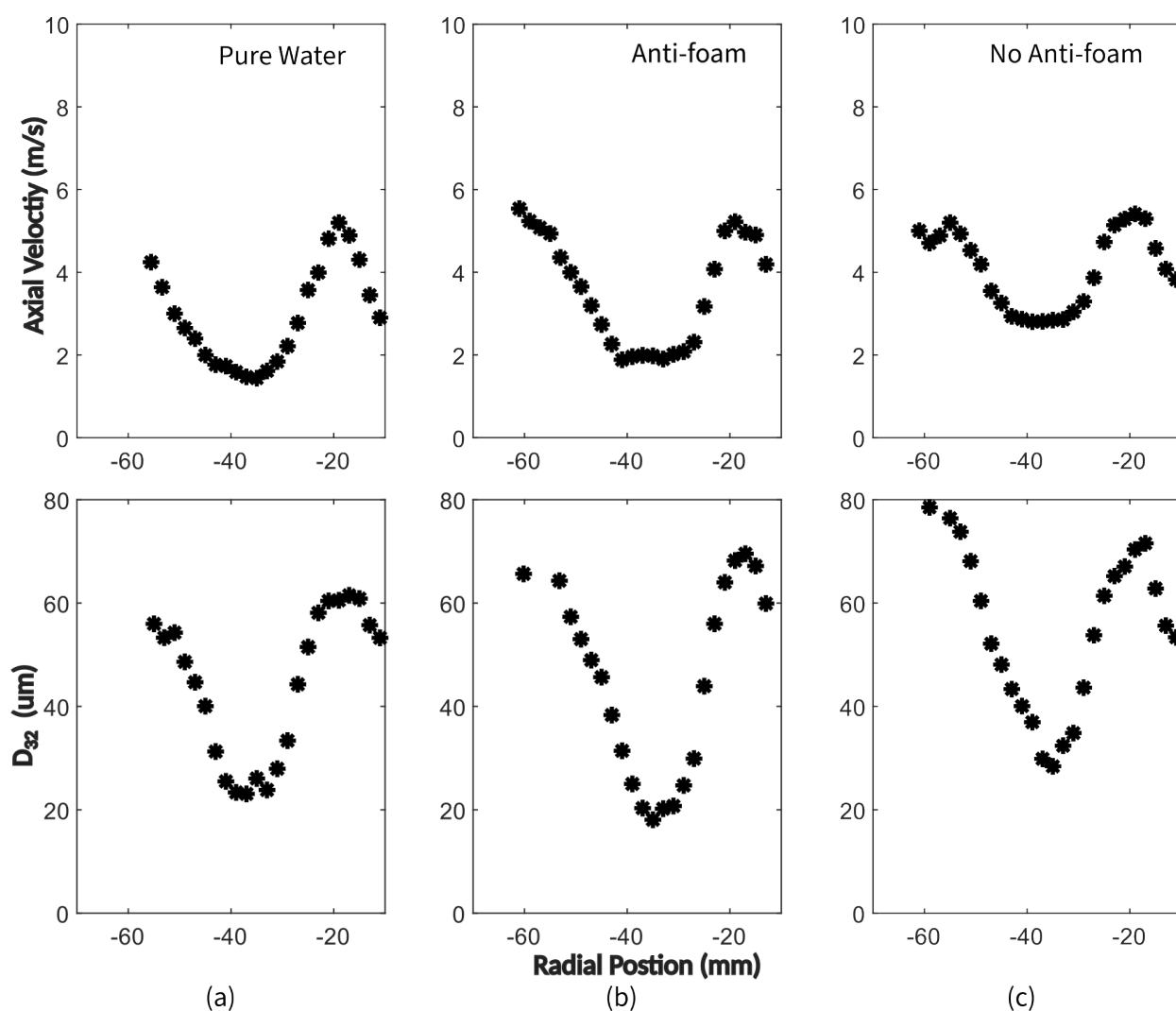


Figure 7.3: PDA measurements of droplet velocity and D_{32} diameter distributions of: (a) pure water, (b) aqueous HP- β -CD with anti-foaming agent, (c) aqueous HP- β -CD no anti-foaming agent.

7.3 RESULTS AND DISCUSSION

7.3.1 Suppression stability limits

Stability limits are produced for all the methods and concentrations of aqueous dispersion of ferrocene in water presented in the previous sections. Figure 7.4 shows the suppression performance of different methods of incorporating Fc in water. Please see Chapter 5 Figure 5.7 for reference to suppression efficacy with respect to KHCO_3 and NaHCO_3 . The process of obtaining flame stability limits for all the test cases in this chapter is identical to the previous chapters (Chapter 5 Figure 5.6), using an average extinction time to extrapolate the asymptotic stability limit using Equation 5.1 (stability boundary where extinction time is infinite). Figure 7.4a shows the flame stability limits of varying concentrations of HP- β -CD in water and the stability limits of the Fc HP- β -CD inclusion complex. Pure HP- β -CD shows a reduction in suppression efficacy compared to that of pure water, resulting in an increase in the flow rate of water mist required for flame suppression with increasing concentrations of HP- β -CD. The inclusion of Fc as the guest molecule shows a reduction in the flow rate of water mist required for suppression compared to pure HP- β -CD. However, the overall suppression efficacy even with the inclusion of Fc is less optimal than pure water.

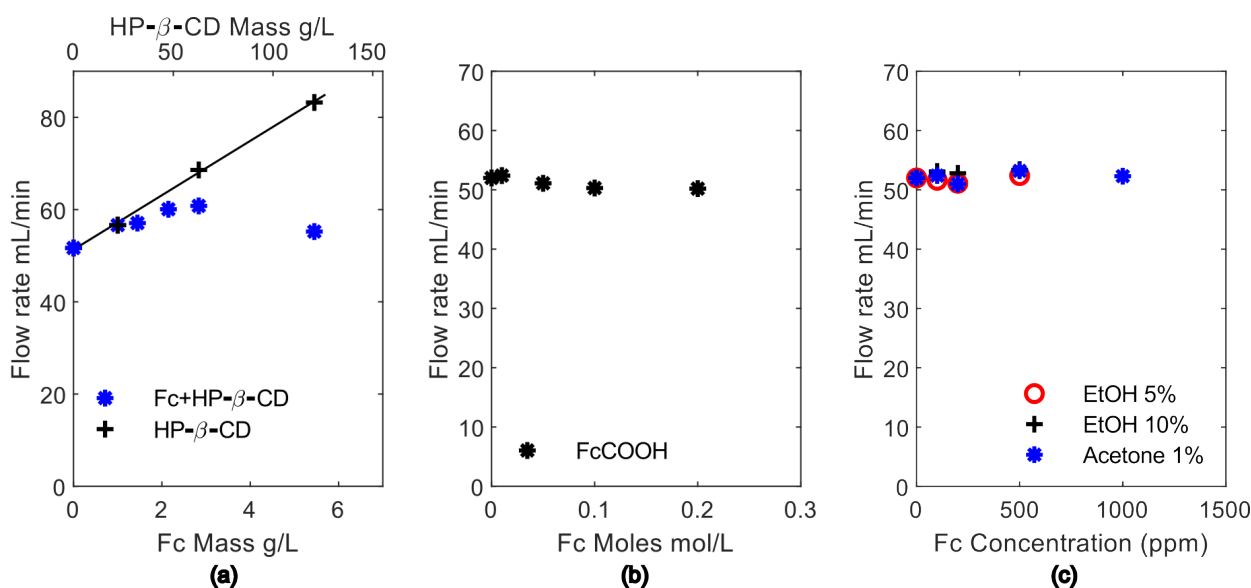


Figure 7.4: Flame stability limits of the different methods of suspending/dissolving Fc in water mist, (a) host-guest inclusion, (b) water soluble Fc Derivative, (c) Anti-solvent precipitation.

This reduction in suppression efficacy (increased flow-rate requirements) is attributed to the gaseous products released in the thermal decomposition of HP- β -CD. The thermal decomposition process of HP- β -CD has previously been measured [234], showing a 92% loss of mass in TG analysis up to temperatures of 614K where a char residue is observed. The decomposition products of the more well known β -CD has been measured using chromatography, which has identified combustible pyrolysis products such as toluene and many more [235]. The pyrolysis products are unfavourable when it comes to flame suppression as they effectively introduce more fuel into the flame front upon droplet evaporation and then thermal decomposition. Ferrocene itself seems to inhibit this process as seen by the drop in flow rate requirements on the stability map, but not significant enough as the molecular weight of HP- β -CD ($\approx 1400\text{g/mol}$) is almost an order of magnitude greater than that of Fc ($\approx 186\text{g/mol}$). Per molecule of the inclusion complex, more flammable pyrolysis products are released per mole of Fc, ultimately resulting in enhanced combustion. For a viable inclusion complex, a host molecule needs to have a high enough solubility whereby more than 1/3 by moles of Fc can be included in the solution. A potential candidate is β -cyclodextrin

polymer (β -CDP), where a 1:1 ratio of Fc per unit of β -cyclodextrin was achieved [236]. This effectively triples the amount of Fc that can be “dissolved”, while also reducing the molecular weight (atoms) of the host molecule (β -cyclodextrin-polymer has a 20% lower MW than HP- β -CD per unit cyclodextrin). However, β -CDP cannot be purchased off the shelf in large quantities (expensive), and the synthesis procedure is non-trivial [236].

Figure 7.4b shows the stability limits for the Fc derivative FcCOOH. The overall trend is flat with arguably a small reduction in the flow rate of water required to achieve suppression. This small reduction is believed to be a contribution from the sodium hydroxide rather than FcCOOH. At 0.2 moles of FcCOOH (46 g/L), the expectation is a major increase in suppression efficacy, one that’s greater than KHCO_3 according to the elemental inhibitor rankings [140]. However, little to no improvement is seen in suppression efficacy. This is possibly due to the thermal decomposition pathway of FcCOOH, even though the bulk of the molecule remains very similar to pure Fc, appending a function group to one of the cyclopentadienyl rings may reduce the thermal stability of these rings causing multiple branching decomposition pathways that don’t release atomic iron (whereas pure Fc releases atomic iron). The thermal decomposition of FcCOOH is different from that of Fc as shown in previous studies [237], where FcCOOH does not sublime like Fc, instead leaving behind iron oxide residues at higher temperatures. The decomposition products are therefore assumed to be varying forms of iron oxides that are unfavourable when it comes to radical scavenging and therefore flame inhibition.

Figure 7.4c shows the stability limits for pure Fc in water, suspended through anti-solvent precipitation. Regardless of the type of solvent used, concentration and/or ppm of Fc, there is no observable change in suppression efficacy. These results are juxtaposed to recent results in literature [167][25], suggesting that this area of research needs more data to come to a reasonable conclusion of enhanced suppression through ferrocene. No observed enhancement in suppression is possibly the result of two factors, one being the inclusion of the solvent which acts as a fuel, therefore reducing the effectiveness of any enhanced suppression provided by Fc. Two, the low concentrations of Fc that can be suspended in water due to the limitations

of the solubility of Fc in the solvents used. At these low ppm levels, there are not enough Fc molecules to produce an observable effect on flame suppression. Inhibitor rankings [140] suggests that Fc on a molar basis, is three times more effective than that of KHCO_3 , which suggests that a molar concentration of at least 0.1M of Fc is needed to observe any significant improvements on flame suppression according to the results in the previous chapter (Figure 5.7a). 0.1M of Fc is equivalent to 18000 ppm which is an order of magnitude above the concentrations achievable using anti-solvent precipitation which may be the reason for the absence of enhanced suppression.

7.4 CONCLUSIONS

Ferrocene has the potential of being a truly viable non-corrosive and non-conductive excellent fire suppressant, however, the difficulty of its implementation in water mist is currently the greatest obstacle. This chapter presents the limits of three different strategies for achieving a homogeneous solution of ferrocene in water, with their respective flame stability limits. The results unfortunately show no enhanced suppression which could be a contribution from many different parameters. Key findings in this chapter are as follows:

- Anti-solvent precipitation, though is able to produce extremely small particles of pure ferrocene in temporary suspension in water, the maximum concentration is limited to ≈ 1000 ppm due to the solubility of ferrocene in the solvent (Ethanol and Acetone). With such low concentrations of ferrocene, no enhanced inhibition was observed.
- The host-guest inclusion method allowed for very high concentrations of ferrocene to be “dissolved” in water, however, the host molecule HP- β -CD enhanced flame combustion due to the combustible products formed through thermal decomposition, therefore the net effect of inhibition due to ferrocene is negated. However, the results do show enhanced suppression relative to pure HP- β -CD without ferrocene.
- A ferrocene derivative, ferrocene carboxylic acid (FcCOOH) was observed to be highly soluble in an aqueous base. However, no enhanced inhibition was observed. The

modification of the ferrocene molecule changes the thermal decomposition pathway which may produce undesirable decomposition products leading to no enhanced suppression.

Though no overall enhanced suppression was observed, the different methods presented provide further insight into what is required to achieve enhanced suppression with ferrocene. Pure Ferrocene is a key component as its thermal decomposition leads to desirable iron inhibition molecules. Host-guest inclusion shows promise, however, improvements need to be made with careful selection of a host molecule such as β -CDP which may provide higher solubility of ferrocene while also reducing the total addition of host molecule by mass. The findings in this chapter will be greatly beneficial for future attempts/works in producing a powerful water mist additive for fire suppression.

Chapter 8

Conclusions

The findings of this thesis provide a thorough analysis of a canonical laboratory scale turbulent buoyant diffusion flame with varying levels of fuel turbulence, alongside flame suppression through a chemically enhanced water mist-laden co-flow. The first experimental campaign investigated flames with varying levels of fuel-turbulence using 250 Hz high-speed simultaneous imaging of OH-PLIF and Mie scattering of soot. Flame characterisation was performed, looking at how flame structure develops with turbulence and observing a flame pinch-off phenomenon. A second experimental campaign characterises flame suppression through a chemically enhanced water mist-laden co-flow, comparing suppression efficacy between different inhibitors at different concentrations. Boundary conditions were mapped with PDI alongside high-speed 400 Hz simultaneous imaging of OH-PLIF and Mie scattering of droplets. The imaging provided the first insights into flame droplet interactions, crucial for model validation. The third experimental campaign builds upon the previous, with an increase in temporal and spatial resolution of OH-PLIF and Mie scattering of droplets, with attempts at 4D PTV (not presented in this thesis). The increased resolutions allowed for time resolved observations of flame inhibition caused by droplets traversing the flame front. The last experimental campaign looks at incorporating a new novel fire suppressant, ferrocene, as an additive in water mist. Different methods of creating a homogeneous solution of ferrocene

in water are trialled with their relative suppression performance presented on stability maps. The following conclusions and observations are drawn from the work presented in this thesis.

- A characterisation study is performed on the Sydney buoyant fire burner. Exit plane velocity profiles at varying levels of fuel turbulence are measured through LDV, which showed that by the inclusion of the turbulence generating plate, exit plane velocity fluctuations increase from 0.135 – 1.813 m/s. DSLR images show that the change in flame structure near the burner exit plane is purely a result of the inclusion of the perforated plate and not the change in HRR.
- The structure of buoyant flames with increasing levels of fuel-turbulence is revealed through the simultaneous high-speed imaging of OH-PLIF and Mie scattering of soot. These images show that the angular orientation of the flame sheet in the near-field along the vertical axis increases with increasing fuel-turbulence. Puffing instabilities align closely with empirical models, but give an increasingly flat spectral response with increased fuel-turbulence. Pinch-off instabilities commonly associated with pool fires have been observed to take place at the flame neck due to lateral air entrainment, quenching the flame front.
- A new experimental setup studying the chemically enhanced water mist suppression of fires is characterised by PDA, measuring droplet distributions, flux and velocities. Flame stability maps of NaHCO_3 and KHCO_3 are created showing relative suppression performance between different inhibitors and concentrations. Initial high-speed simultaneous images of OH-PLIF and Mie scattering of droplets show the upstream flame structure and how breakages in the flame front occur with increasing salt concentrations. Overall suppression efficacy follows $\text{KHCO}_3 > \text{NaHCO}_3 > \text{H}_2\text{O}$.
- The process of flame extinction and re-ignition is more closely observed by increasing the temporal and spatial resolution of the simultaneous high-speed images of OH-PLIF and Mie scattering of droplets. For a given constant flow rate of water mist, with increasing concentrations of inhibitor, an exponentially increasing number of breaks are

observed in the reaction zone, alongside a steadily decreasing OH width. A decrease in OH width is also seen in laminar flame calculations.

- Highly resolved temporal and spatial simultaneous imaging of OH-PLIF and Mie scattering of droplets have shown that OH area and droplet density are highly inversely correlated, indicating a competing phenomenon between droplet evaporation and OH intensity (area) across all the flames studied. The ensemble of droplet positions relative to the flame front shows a decrease in the number of droplets approaching the high-temperature reaction zones. This decrease highlights droplet evaporation and their penetration from the air side to the fuel side.
- Multiple methods were attempted to include ferrocene as an additive in a water misting system. Host-guest inclusion showed the most promising outcome of potentially being a viable solution of including ferrocene in water. However, no enhanced suppression was observed, and this requires further research in the selection of host molecule, as HP- β CD (host) was shown to enhance combustion, negating the suppression enhancing effects of ferrocene.

Chapter 9

Recommendations

The work from this thesis is focused on developing experimental datasets for model validation of buoyant fires with varying levels of fuel turbulence and chemically enhanced water mist fire suppression. However, throughout each stage of experimentation, there were many other avenues of interest that could have been taken, requiring further investigation. Some of the ideas recommended for further studies are briefly outlined below:

- The flames studied with varying levels of fuel-turbulence had either a fixed plate recess distance of 75 mm or no plate at all. The turbulence levels were controlled by a combination of the perforated plate and the fuel flow rate. An interesting area of study would be to fix the HRR of the flame and only alter the recess distance, keeping the fuel flow rate constant. However, this may require the extension of the burner housing to allow for larger recess distances. This would be supplementary to the study performed in Chapters 3 and 4.
- PIV on the various flames would be useful in obtaining velocity fields and therefore local strain rates. This would produce a complimentary data set to Chapter 4.
- Brief radiation measurements were conducted on some of the flames which observed a reduction in radiative fraction for flames with increased turbulence (Appendix A.5).

This was not further pursued, but a worthwhile study to perform for future work as it unveils interesting phenomena of turbulence-radiation interactions. Alongside radiation, axial and radial thermocouple temperature measurements of flames with varying fuel-turbulence would also supplement the experimental dataset.

- PDA measurements of water mist fire suppression were primarily performed to characterise the boundary conditions. It would also be interesting to conduct PDA measurements simultaneously with the high-speed imaging of OH-PLIF and Mie scattering of droplets to obtain in-situ droplet size distributions in the flame front. However, this will require a different Mie scattering collection system, as the PDA utilises 532 nm for droplet sizing. Also, downstream measurements of droplet distributions were briefly performed in this thesis, it would be interesting to conduct a rigorous mapping of droplet distributions along the axial length of the flame.
- Simultaneous OH-PLIF and PTV were attempted, but as mentioned previously, the results are not presented in this thesis due to experimental issues. PTV is of great interest as it can resolve droplet Lagrangian statistics and droplet lifetimes in the presence of the flame front. To achieve this, improvements need to be made to the existing diagnostic setup, as shown in Chapter 6. This will require a Mie scattering beam with exceptional stability and uniform beam profiles in the depth and planar directions. This future study could potentially produce distributions of droplet evaporation rates, which would be crucial for model development and/or validation.
- Finally, further investigation into aqueous dispersion of ferrocene through host-guest inclusion using different host molecules to develop an unprecedented water mist fire suppression additive. This will require a screening of all available host molecules capable of encapsulating ferrocene with the ability to dissolve in water without significantly enhancing flame combustion. A potential candidate is β -cyclodextrin polymer, which unfortunately cannot be purchased off the shelf, and has to be synthesised in large quantities.

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Appendix A

Supplementary Data on All Flames

A.1 DSLR IMAGES

This section presents supplementary data for the flames studied in Chapter 3 and 4. Figure A.1 shows example instantaneous DSLR images of the burner exit plane for all the flames (10 - 40kW) with and without the turbulence generating plate. This shows that the flame structure is fundamentally altered by the presence of the perforated plate and not by an increase in HRR.

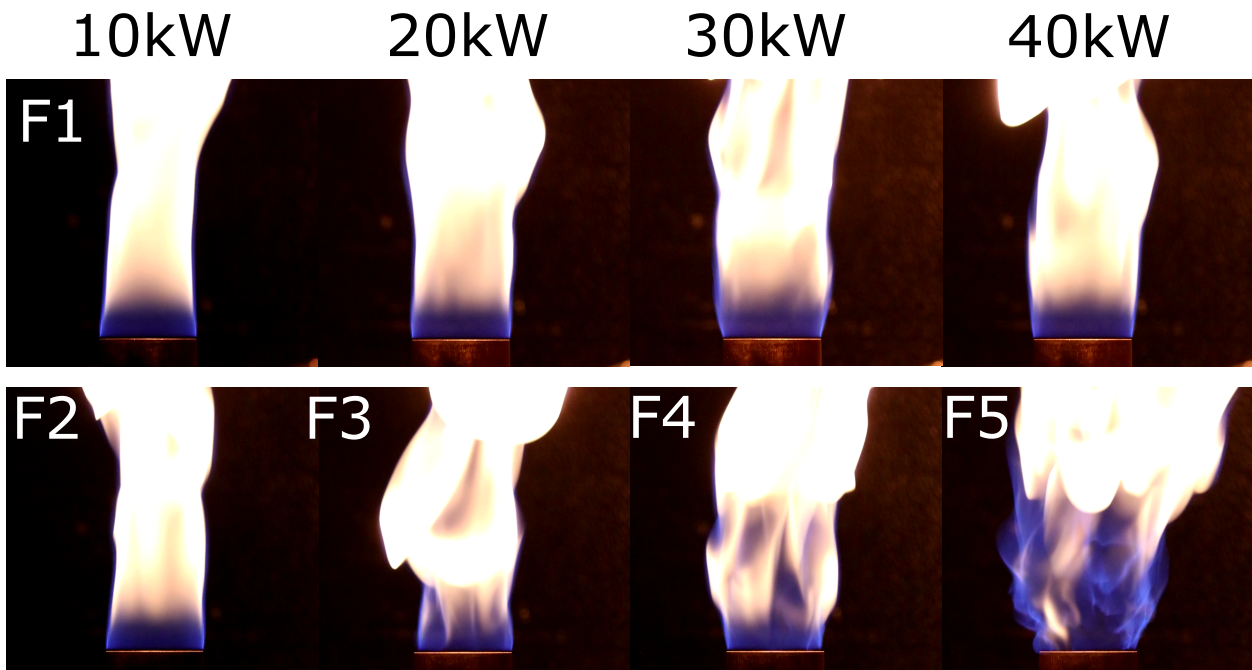


Figure A.1: Instantaneous DSLR images of all the flames 10 - 40kW at the burner exit plane. Top row, no turbulence generating plate, bottom row with the inclusion of the turbulence generating plate.

A.2 SIMULTANEOUS HIGH-SPEED OH-PLIF AND MIE SCATTERING OF SOOT

Figure A.2 to A.5 show simultaneous high-speed OH-PLIF and Mie scattering of soot images for the different flames (10 - 40 kW) without the turbulence generating plate. Each set of stacked images is independent of one another, the colour scales follow that of Figure 4.4, where they have been normalised for viewing clarity.

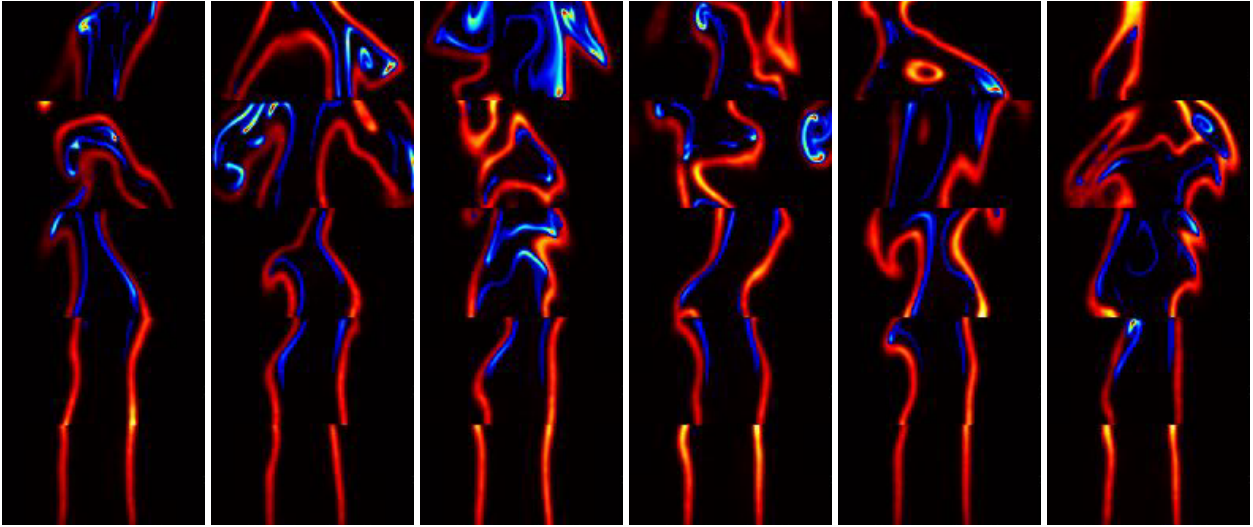


Figure A.2: Superimposed instantaneous images of a 10kW no plate flame using OH-PLIF and Mie scattering of soot. Height above burner: 0 - 250 mm.

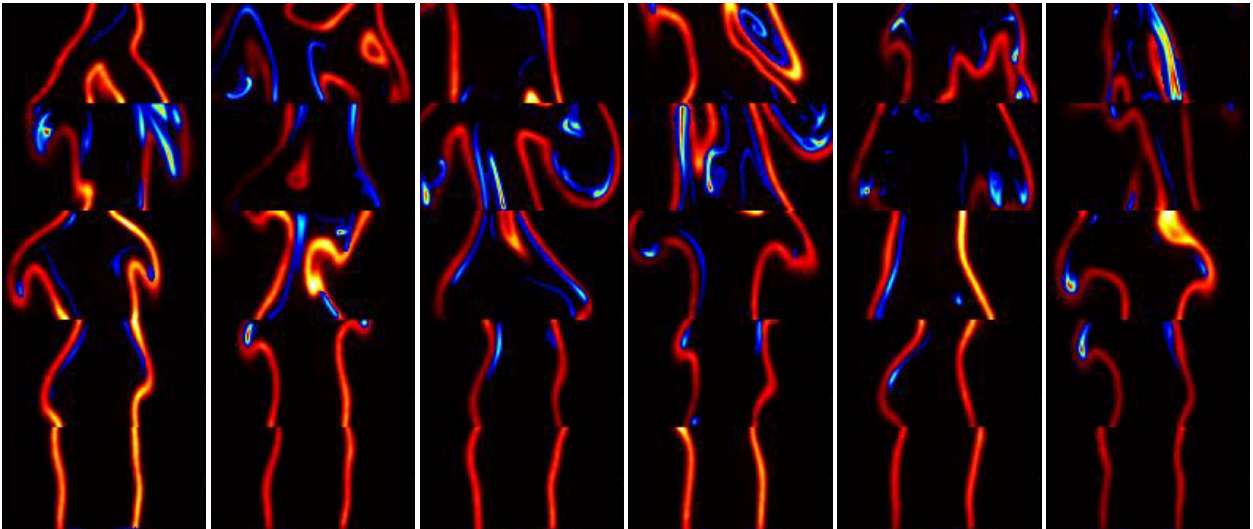


Figure A.3: Superimposed instantaneous images of a 20kW no plate flame using OH-PLIF and Mie scattering of soot. Height above burner: 0 - 250 mm.

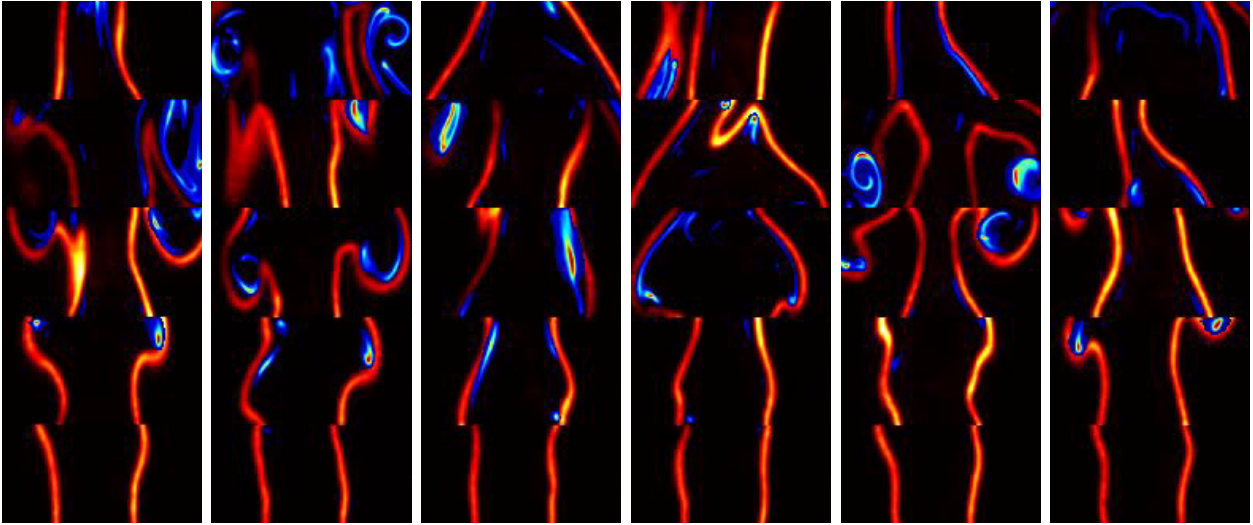


Figure A.4: Superimposed instantaneous images of a 30kW no plate flame using OH-PLIF and Mie scattering of soot. Height above burner: 0 - 250 mm.

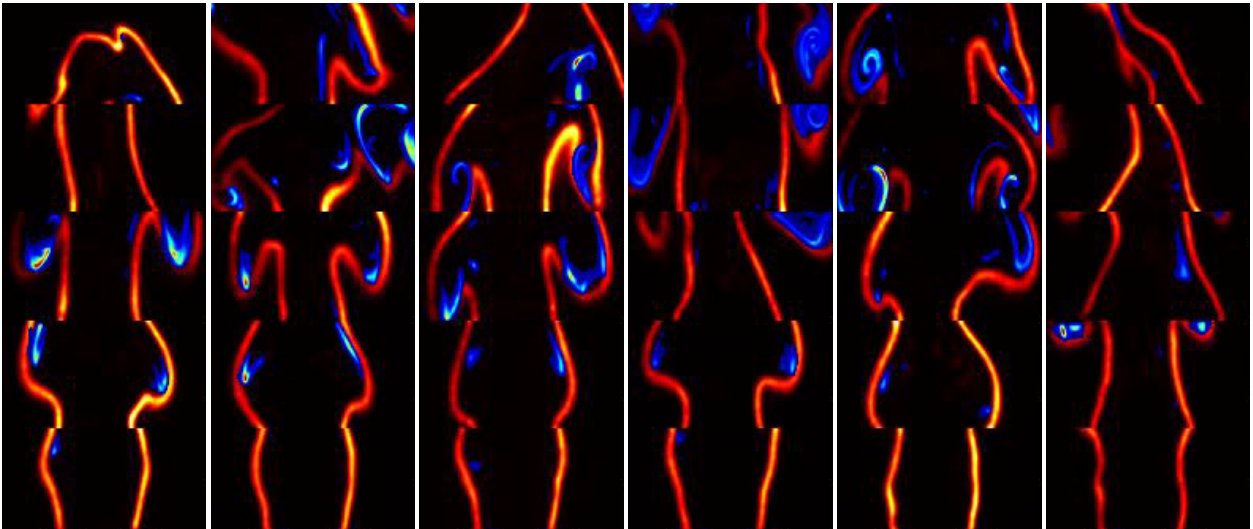


Figure A.5: Superimposed instantaneous images of a 40kW no plate flame using OH-PLIF and Mie scattering of soot. Height above burner: 0 - 250 mm.

A.3 LDV MEASUREMENTS

Figure A.6 presents the LDV measurements of the burner exit plane with no turbulence generating plate. This shows standard parabolic velocity profiles indicative of laminar pipe flow with extremely low levels of turbulence (RMS).

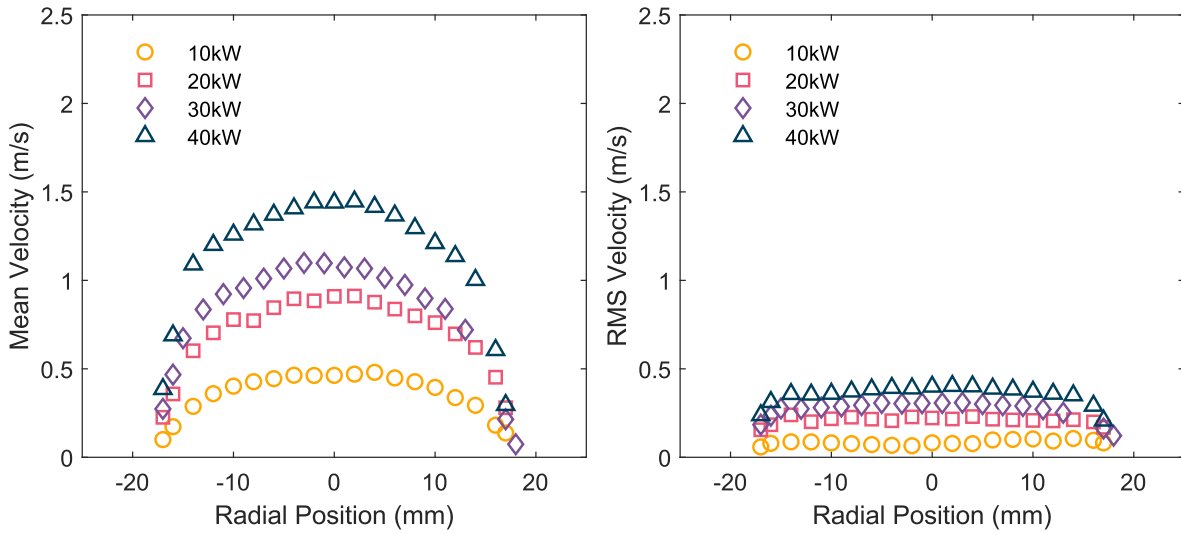


Figure A.6: LDV measurements of burner exit plane mean and RMS velocities for flames without the turbulence generating plate.

A.4 FLAME PUFFING/FLICKERING

In the upstream regions of the flame, two sets of instabilities, at two distinct frequencies, have been identified in both the high-speed OH-PLIF and DSLR images. Figure A.7 presents the spectral responses of the four flames without the turbulence generating plate (10 - 40 kW). Near the burner exit at 0 mm, there is a minor spectral response in all flames for an oscillating flame width at approximately 10 Hz. This suggests that fluctuations in the flame width occur very early on in the diffusion dominated regime of the flame. Interestingly, there is a pronounced reduction in peak magnitudes with decreasing HRR, this suggests that

the oscillations in flame width are initially driven by a Kelvin-Helmholtz type instability caused by the fuel flow rate. With increasing axial distance towards the necking region, in all the flames, a second frequency response is observed at 6 Hz. This is the classical puffing phenomenon observed in buoyant fires driven by the long term buoyancy driven Rayleigh Taylor (RT) instabilities. The two frequency responses appear to be a combination of flame flickering and classical RT instabilities, as shown in previous studies by Hu et al. [238] and Sato et al. [239, 240].

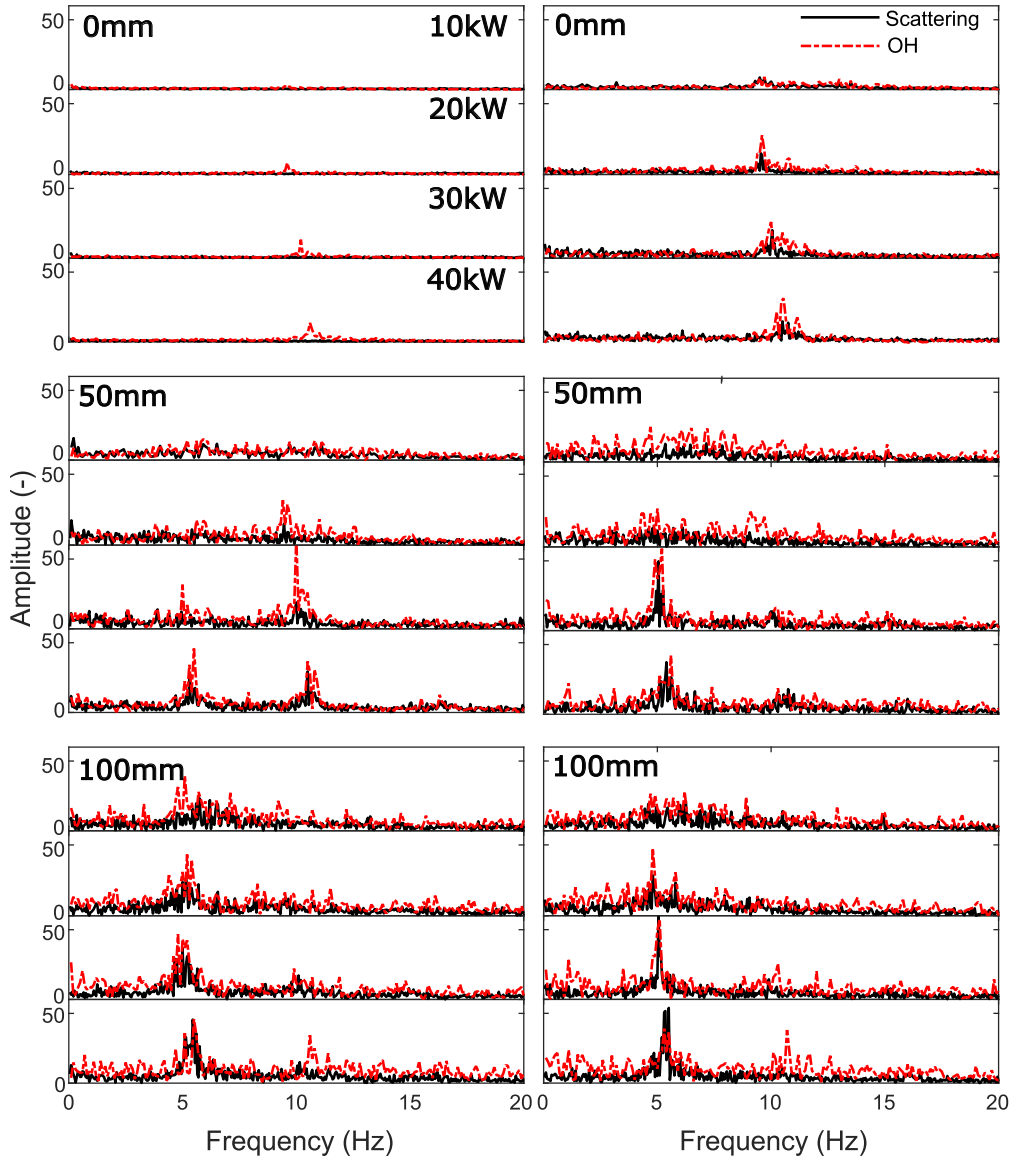


Figure A.7: Spectral responses of all the flames without the turbulence generating plate (10-40kW). Flame width is marked by OH-PLIF and soot intermittency through Mie scattering.

The time histories of OH width and soot Mie scattering are shown in Figures A.8 and A.9. Figure A.8 shows flame instabilities at an axial distance of 75 mm down stream of the exit plane. The oscillations seen are clearly periodic, with extremely high correlations between flame width and soot Mie scattering. At 175 mm (Figure A.9), the period of the oscillations has doubled, from 6 Hz to approximately 11 Hz.

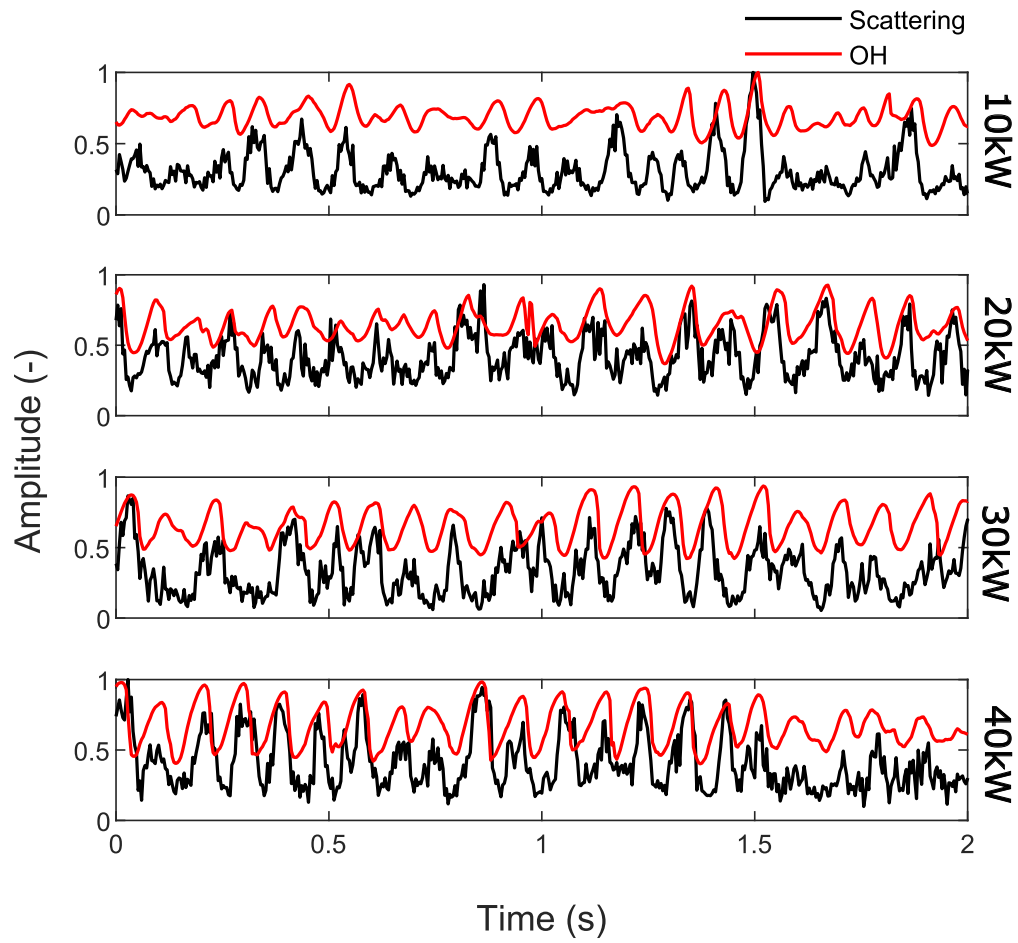


Figure A.8: Time history of flame width (OH) and Mie scattering of soot at an axial location 75 mm above the burner exit plane.

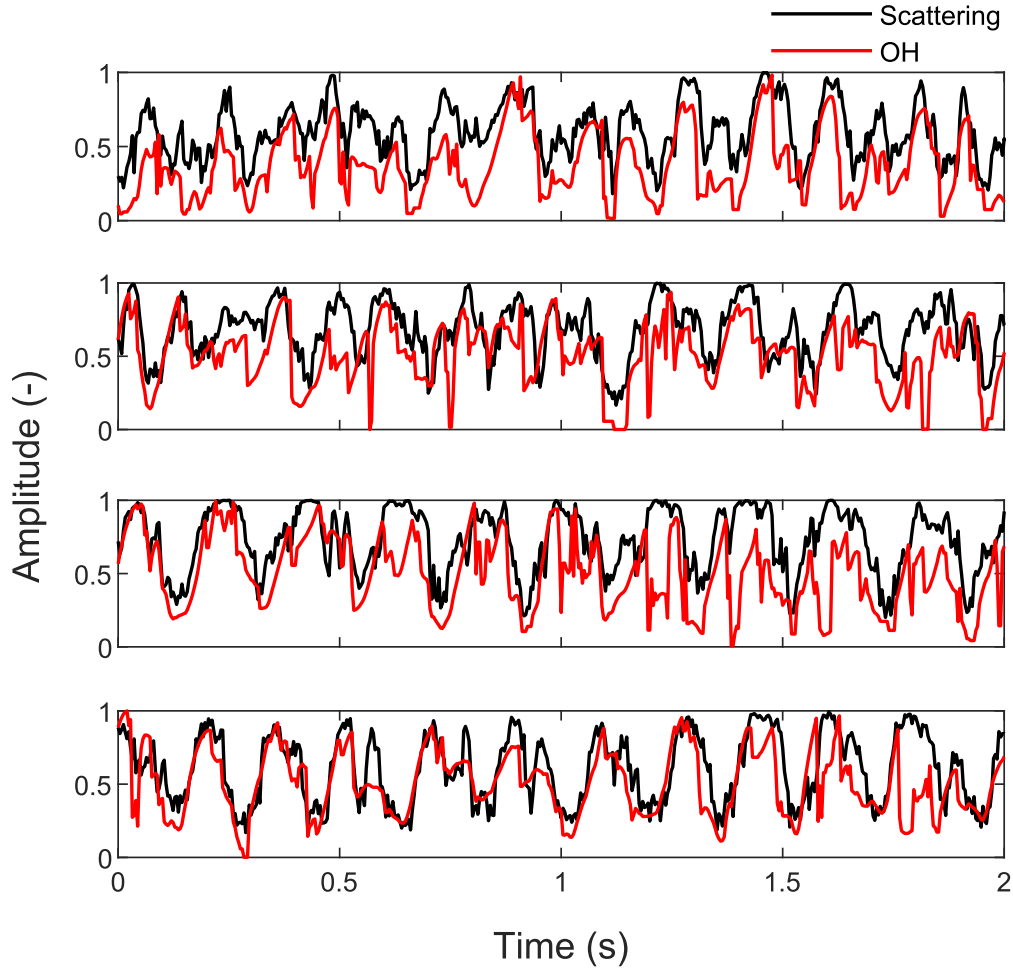


Figure A.9: Time history of flame width (OH) and Mie scattering of soot at an axial location 175 mm above the burner exit plane.

Figure A.10 plots generally the Strouhal (St) number against the inverse Froude (Fr) number for puffing and flickering frequencies for 10 - 40 kW flames without the turbulence generating plate. The Fr and St number are defined in Equation A.1 and A.2 respectively. The power law fitting exponent for the puffing instability is 0.558 which is extremely close to existing literature [197][198]. The flickering frequency fitting exponent of 0.451 is similar to that found by Sato et al. [240], where they identified two regions, one of 0.41 and the other of 0.5.

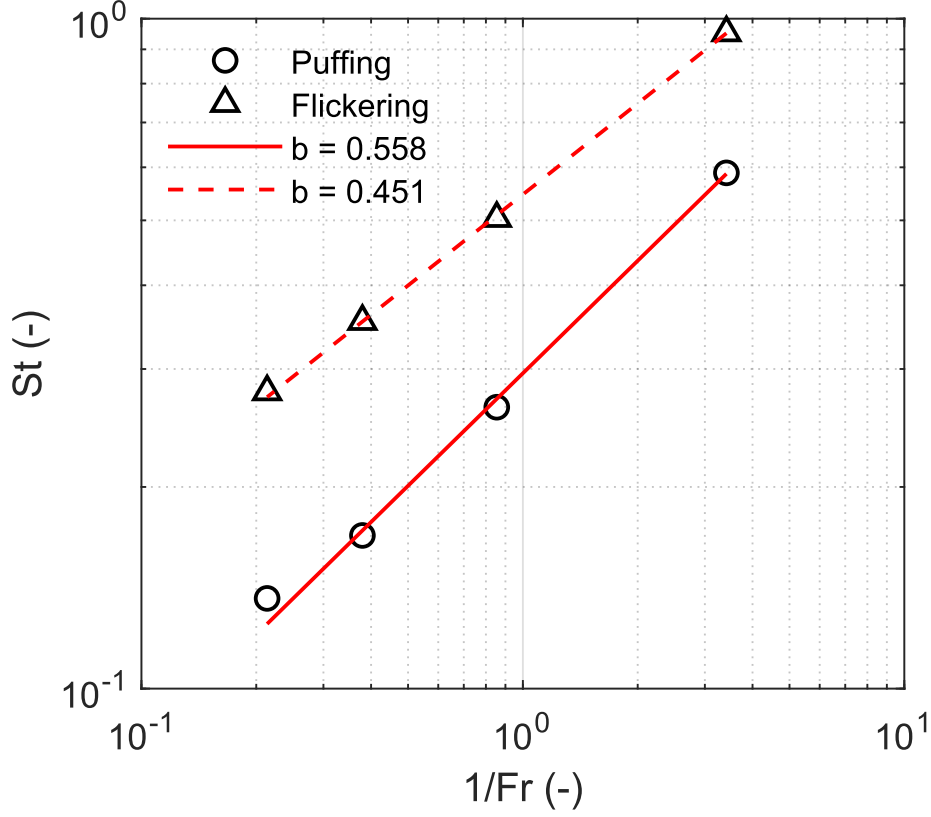


Figure A.10: Scaling relationships between the Strouhal number and the inverse Froude number. Two instabilities, one for classical puffing (0.558) and another for short-life Rayleigh Taylor instabilities (flickering, 0.451).

$$Fr = \frac{V^2}{gD} \quad (\text{A.1})$$

$$St = \frac{fD}{V} \quad (\text{A.2})$$

A.5 TURBULENCE RADIATION INTERACTIONS

To reconstruct the total radiative power of the flame, a multipoint source method is incorporated [52]. The flame is discretised into 24 point sources and the slit radiometer is used to measure the radiative output at each point source location as shown in Figure A.11. The

diagram below shows an example traverse using the slit radiometer. A laser power meter is placed inside a tube with a 2 mm slit installed at the front of the tube to produce a slit radiometer. The slit radiometer is placed on a traverse mechanism with the sensor 375mm from the burner centre. A bright point source (LED) is used to determine the slit radiometer viewing window by traversing the LED horizontally and vertically to find the FWHM. The x and z sensor viewing windows were then determined to be 310mm and 45mm respectively. A spectrally flat power meter is used to measure the radiative output of the entire flame, the measurement is taken at multiple locations around the flame to confirm flame symmetry and measurement accuracy.

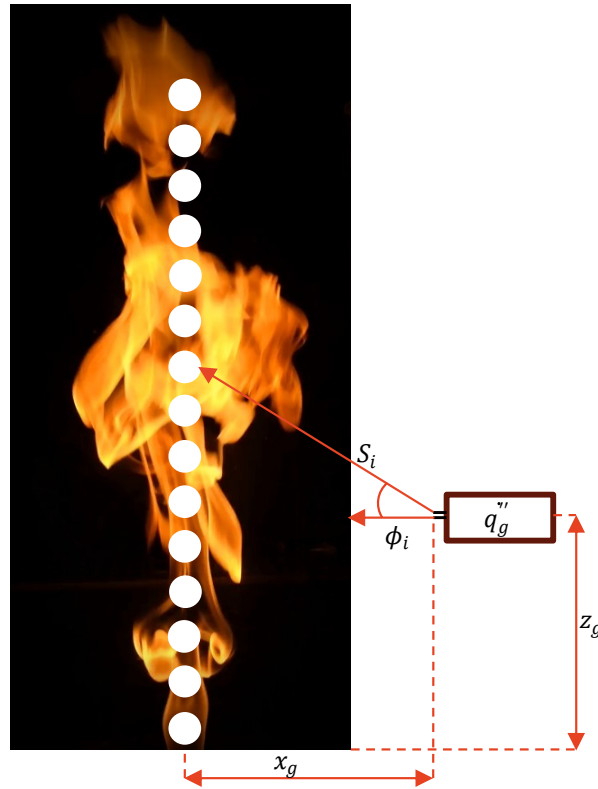


Figure A.11: Measurement method for multipoint source reconstruction of radiative power.

The radiative weights are calculated using the Equations below. The radiative weights are used as a view factor correction in the reconstruction of total radiative power. $\dot{q}_g''$ is the radiative heat flux measured from the heat flux gauge, $\dot{Q}_r$ is the total radiative power, τ_i is

the transmissivity, S is the distance from the heat flux gauge to a single point source and ϕ is the angle between vector direction S and the horizontal plane. The radiative weights (w_i) are calculated by normalising the single traversed heat flux measurements ($\dot{q}_{sr,i}''$) with the sum of all the traversed heat flux measurements.

$$\dot{q}_g'' = \sum_{i=1}^N \frac{\dot{Q}_r \tau_i}{4\pi S_i^2} \cos \phi_i \quad (\text{A.3})$$

$$w_i = \frac{\dot{q}_{sr,i}''}{\sum_{i=1}^N \dot{q}_{sr,i}''} \quad (\text{A.4})$$

Figure A.12 shows the radiative weightings of the different flames with different turbulence levels (recess distances). With increasing turbulence, peak radiation moves closer upstream towards the burner exit plane.

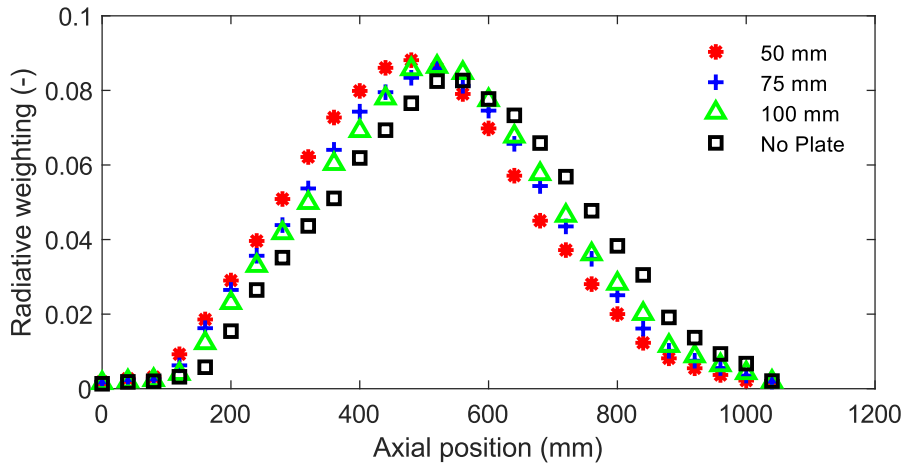


Figure A.12: Radiative weighting from slit radiometer measurements normalised by the total radiative power.

Table A.1 shows the change in the flame's radiative power and radiative fraction by purely modifying fuel-turbulence while maintaining the same HRR. It can be seen that with increasing turbulence levels, there is a steady decrease in the radiative output of the

flame, with the radiative fraction dropping from 33 % to 28 %. This shows how increased turbulence modifies oxidiser transport into the fuel side, either enhancing the oxidation of soot or reducing soot formation through reduced residence times.

Table A.1: Radiative power and radiative fraction with different plate configurations (turbulence levels).

Turbulence configuration	Radiative power	Radiative fraction
No Plate (lowest)	6638	0.332
100 mm	6245	0.312
75 mm	6112	0.306
50 mm	5553	0.278

Appendix B

More Droplet PDA Measurements

B.1 DROPLET FIELD MESH INDEPENDENCE

It is known that droplet field statistics (diameters, velocity and flux) heavily impact suppression performance, therefore the effect of including a mesh screen in the droplet pathway needs to be assessed. PDA measurements are completed for varying mesh positions within the wind tunnel to ascertain both the uniformity and symmetry of the boundary conditions. Figure B.1 on the left shows the axial component of droplet velocities at the wind tunnel exit plane for three axial locations ($y = -10, 0$ and 10 mm). A mesh recess distance of 0 mm (at the exit plane) greatly impacts the exit plane as shown by the divots in the droplet velocity profile. The peaks and troughs come from the interference of the mesh cells. The mesh cells are 19 mm hexagons, which collect a thin layer of water on top of the aluminium mesh surface over a period of time. This thin layer of water traps incoming water droplets, producing a boundary-like profile at the walls of each cell. By recessing the mesh screen from 0 mm to 50 mm, the profiles improve, with the peaks and troughs of velocity and volume flux being less pronounced. Finally, at 100 mm, the profiles are smooth, showing sufficient homogeneous mixing in the downstream position of the mesh screen at the burner exit plane, producing the relevant profiles shown. The 100 mm mesh recess distance is chosen as the

ideal recess for all experimental runs in Chapters 5 to 7.

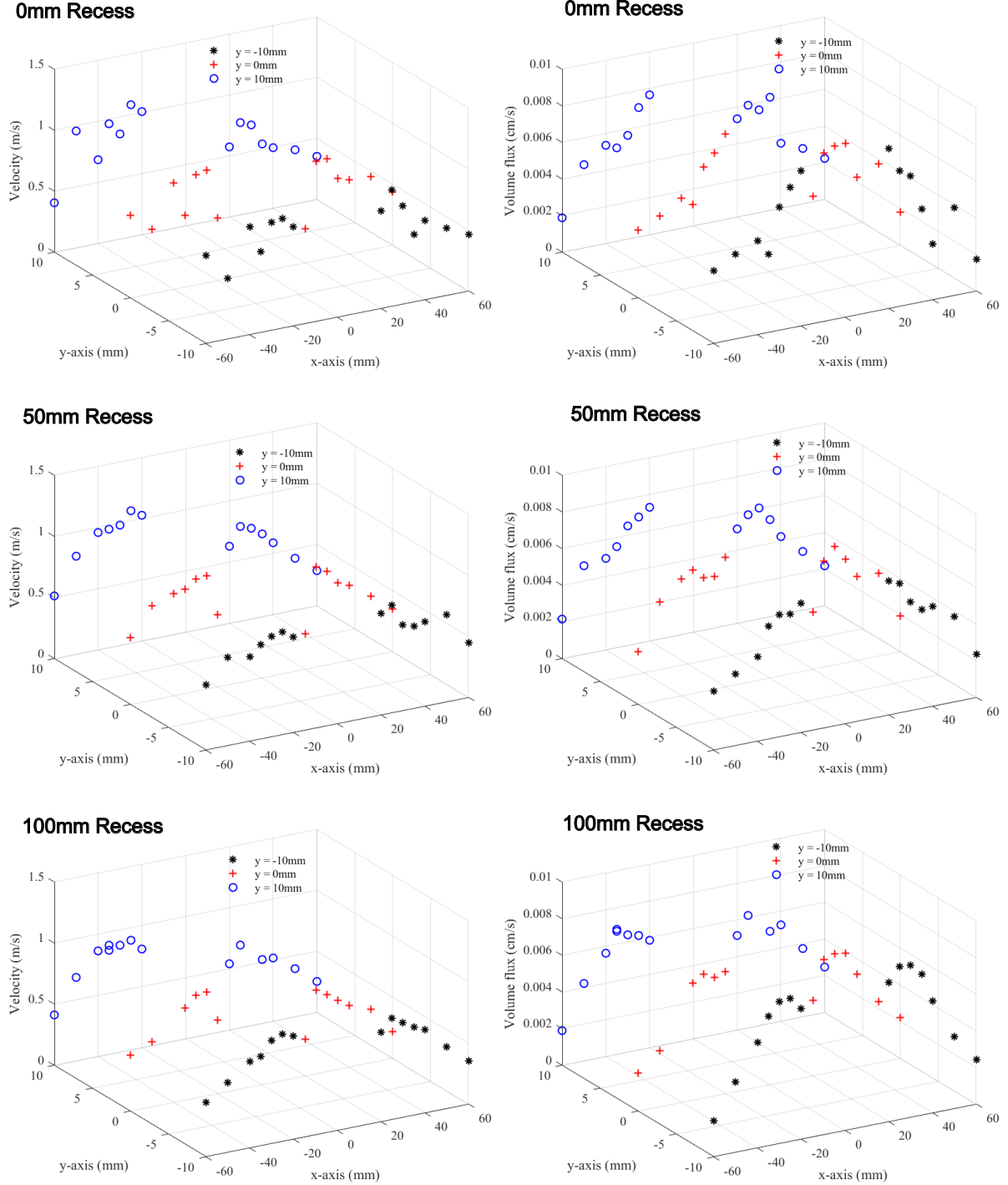


Figure B.1: Flow convergence study looking at variations in velocity and flux droplet fields with mesh recess distances.

B.2 DROPLET EVAPORATION

PDA measurements of radial traverses at select axial locations above the wind tunnel exit plane are shown in Figure B.2 (five axial locations between $z = 0\text{mm}$ and $z = 270\text{mm}$). These measurements are at an exit plane flow rate of 40 mL/min of pure water with a 20kW flame stabilised at the burner exit plane within the stable regime (below the stability limit). The series of figures on the left shows the mean axial component of droplet velocities, while the series of figures in the centre shows the mean radial components of droplet velocities. At the exit plane ($z = 0\text{mm}$), droplets travel primarily vertically with little to no radial components of velocity, as flame entrainment does not affect droplet field statistics at the exit plane. With increasing axial positions at locations near the flame sheet ($x = -20\text{mm}$ to $x = 20\text{mm}$), average droplet velocities monotonically increase from 0.75m/s at the exit plane to upwards of 1.5m/s. The radial components of velocity also increase towards the flame sheet above the exit plane ($y = 60\text{mm}$) but stay rather consistent throughout the length of the flame. The last set of figures on the right shows the volume flux of water mist at different axial locations. Interestingly, the volume flux monotonically decreases from approximately 0.008 cm/s at the exit plane near the flame sheet to effectively 0 cm/s at $z = 270\text{mm}$.

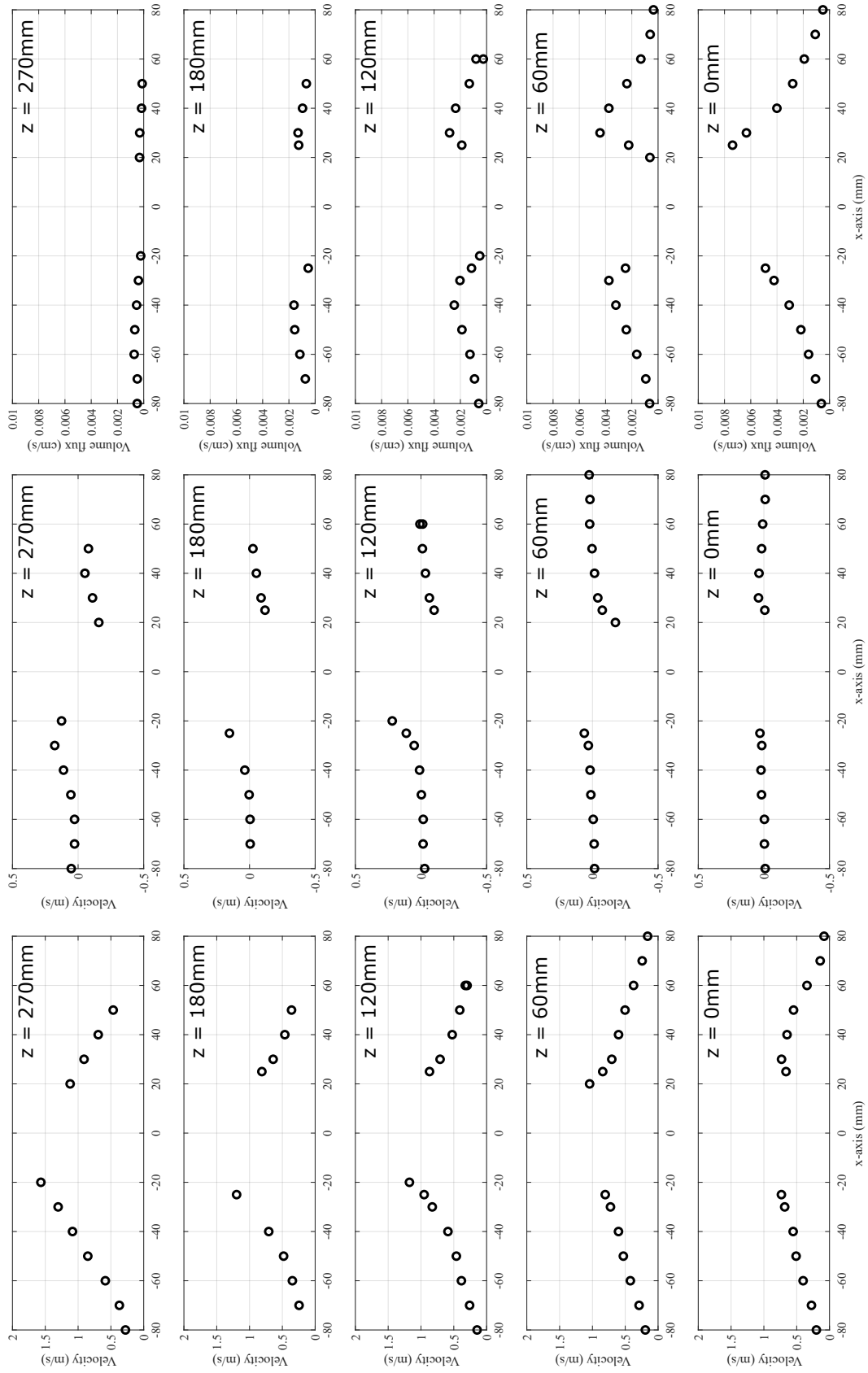


Figure B.2: Droplet axial, radial velocity and flux at varying locations along the flame.

Volume flux, if integrated across the entire exit plane, an effective droplet evaporation rate axially along the exit plane can be estimated. Assuming axial symmetry and that the droplet volume flux profiles follow the decay rate as shown in Figure B.2, the rate of droplet evaporation can be extended to other axial locations without a full 3D exit plane map at downstream locations. The droplet evaporation rate is estimated in Figure B.3, showing an exponential decay in the local presence of water mist droplets with increasing axial locations. At an axial distance of 0mm, there is a maximum water mist flow rate of 40 mL/min at the wind-tunnel exit plane and continuously decreases to 0 mL/min at 270mm above the exit plane. Above 270mm, the flame grows in size as the rest of the fuel undergoes combustion, since all the droplets have evaporated. This is also shown previously in the DSLR images, Figure 5.8.

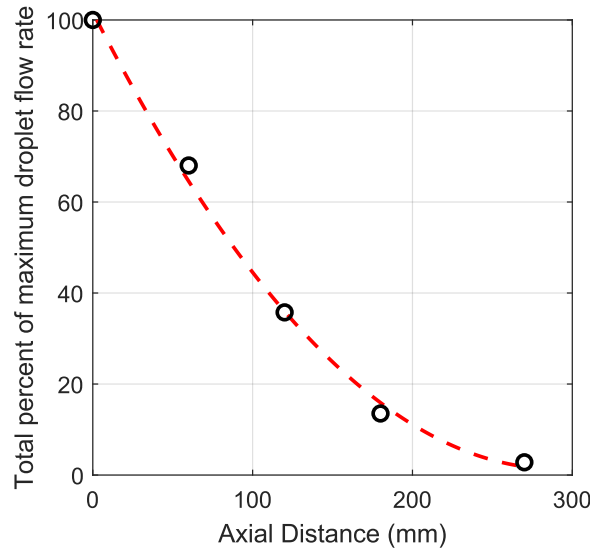


Figure B.3: Total reduction in water mist axially along the flame.

Figure B.4 shows the droplet diameter distributions at varying axial locations along the flame. Interestingly, regardless of axial location, both, the d_{10} and d_{32} droplet diameters remain constant along the flame. This suggests that droplet diameter statistics remain rather consistent throughout the length of the flame as there is not enough time for radiation to cause significant evaporation in this experimental setup.

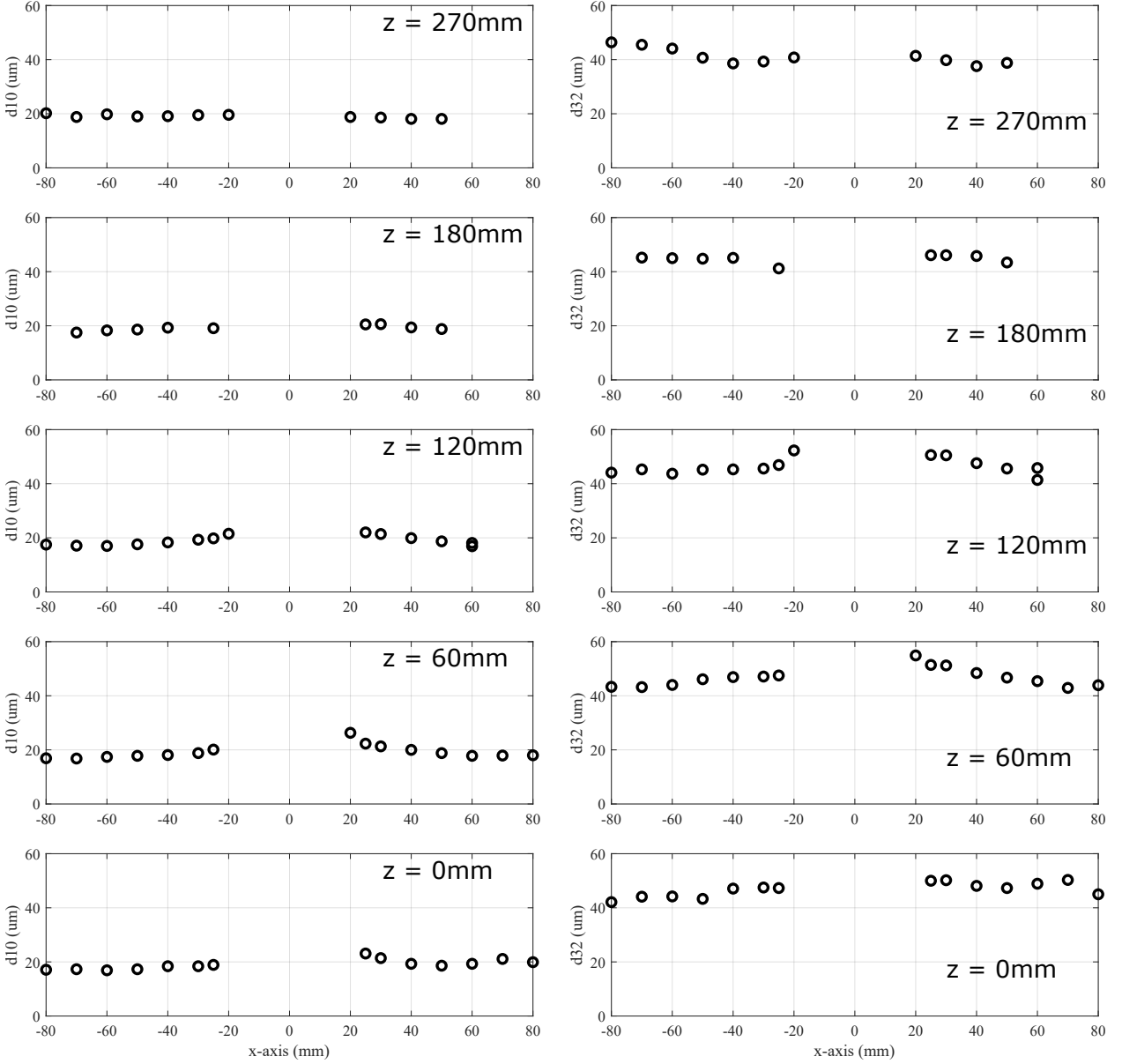


Figure B.4: Droplet distributions d_{10} and d_{32} at varying axial locations along the flame.

PDA measurements were completed at two axial locations along the flame with water mist doped with 60% of the saturation limit of KHCO_3 to identify differences in droplet field statistics with high concentrations of inhibitor. It is commonly known that small additions of salt contribute to a small increase in fluid viscosity, however, these increases in viscosity are minuscule and unlikely to affect droplet atomisation given the nonlinear increases in the

Ohnesorge number. Figure B.5 shows a centre line profile of droplet velocity and volume flux at 0mm and 120mm above the wind tunnel exit plane. The axial and radial velocities are very similar to that of the pure water cases at both $z = 0\text{mm}$ and 100mm . The volume flux is also similar at 0mm, however, at 120mm the volume flux is marginally higher than that of the water mist counterpart. This is primarily due to operating in a different stability regime relative to the extinction limit and the local extinction zones caused by the inhibition of KOH. As local extinction holes start appearing in the flame sheet, the flame surface area effectively decreases, which results in less evaporation of water droplets.

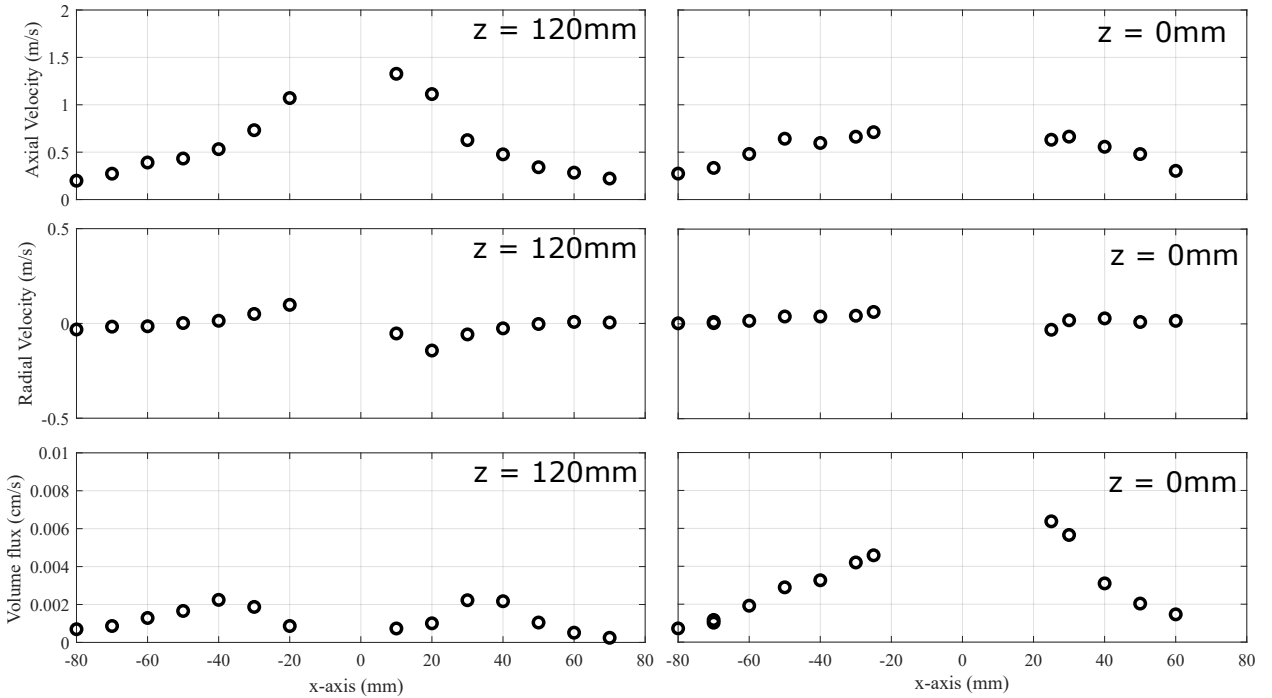


Figure B.5: Droplet axial, radial and volume flux at varying axial locations along the flame for a salt concentration of 60 % KHCO_3 .

Figure B.6 shows profiles of diameter distribution (d_{32} and d_{10}). Compared to the pure water case in Figure B.4, the diameters are almost identical, confirming that the small changes in viscosity and surface tension have little to no effect on droplet atomisation, therefore maintaining equivalent boundary conditions to the pure water case.

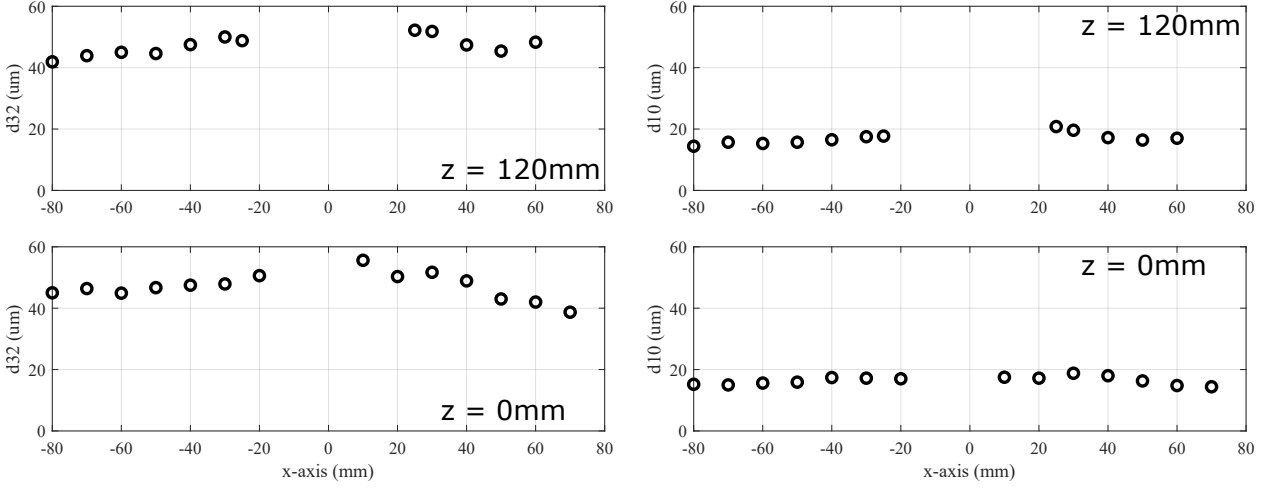


Figure B.6: Droplet distributions d_{10} and d_{32} at varying axial locations along the flame for a salt concentration of 60 % KHCO_3 .

B.3 WIND TUNNEL EXIT PLANE PDA MAPPING

This section shows the full 2D exit plane wind tunnel PDA measurements of droplet velocity, distribution and flux at three flow rates of water mist. The colour scale/map has been smoothed for presentation. As mentioned, the traverse grid resolution is 1 cm, with each point containing an average of 60 seconds of real-time data. The minor asymmetries observed in the exit plane for any of the quantities are due to manufacturing differences between all the nozzles. As the red type KBN nozzles have a spring-actuated pressure mechanism inside, each nozzle may produce slightly different qualities of spray. If future work is to be conducted, it is recommended to use misting nozzles with no moving parts.

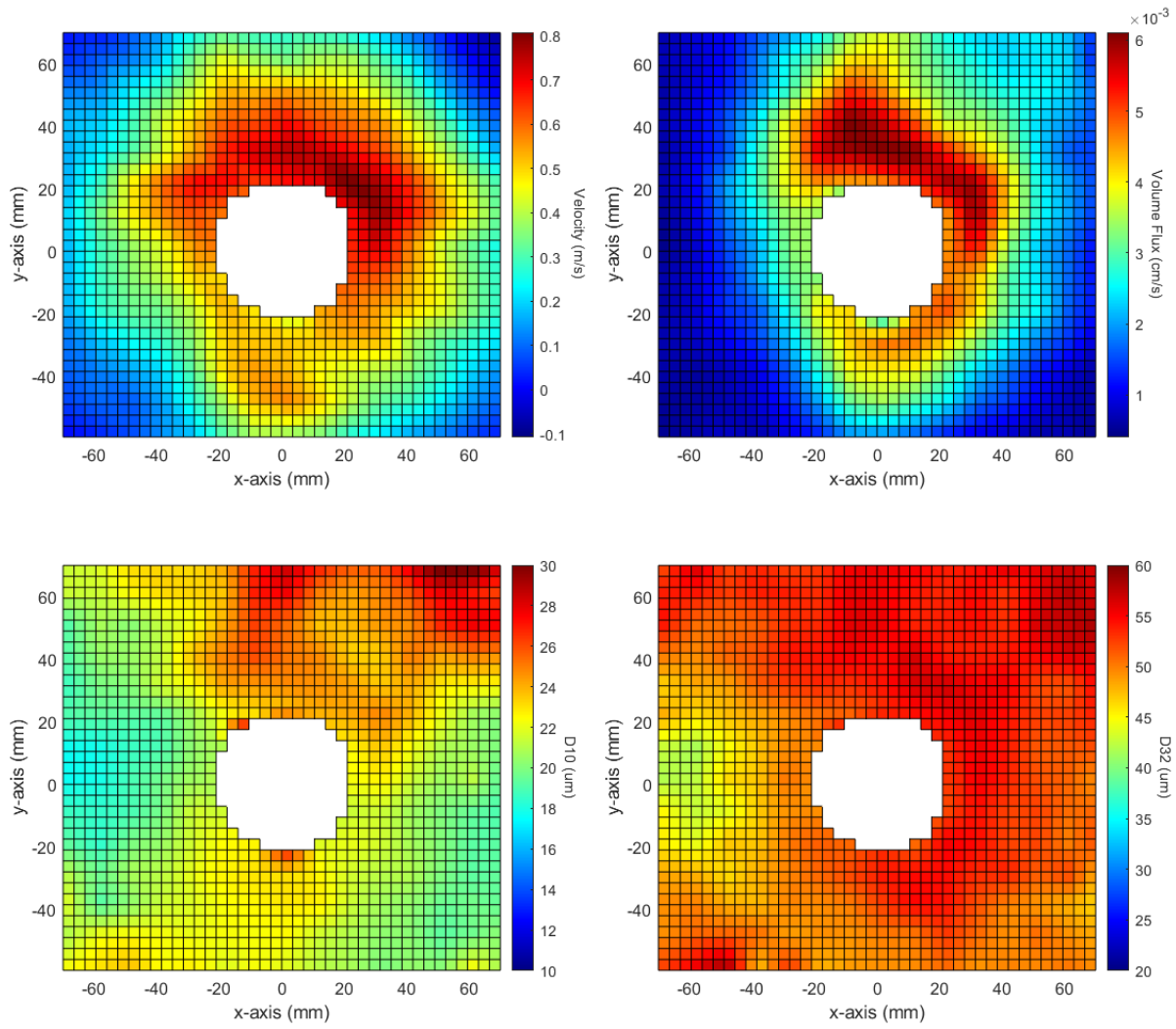


Figure B.7: Wind tunnel exit plane map of droplet statistics at a constant flow rate of water mist of 148 mL/min.

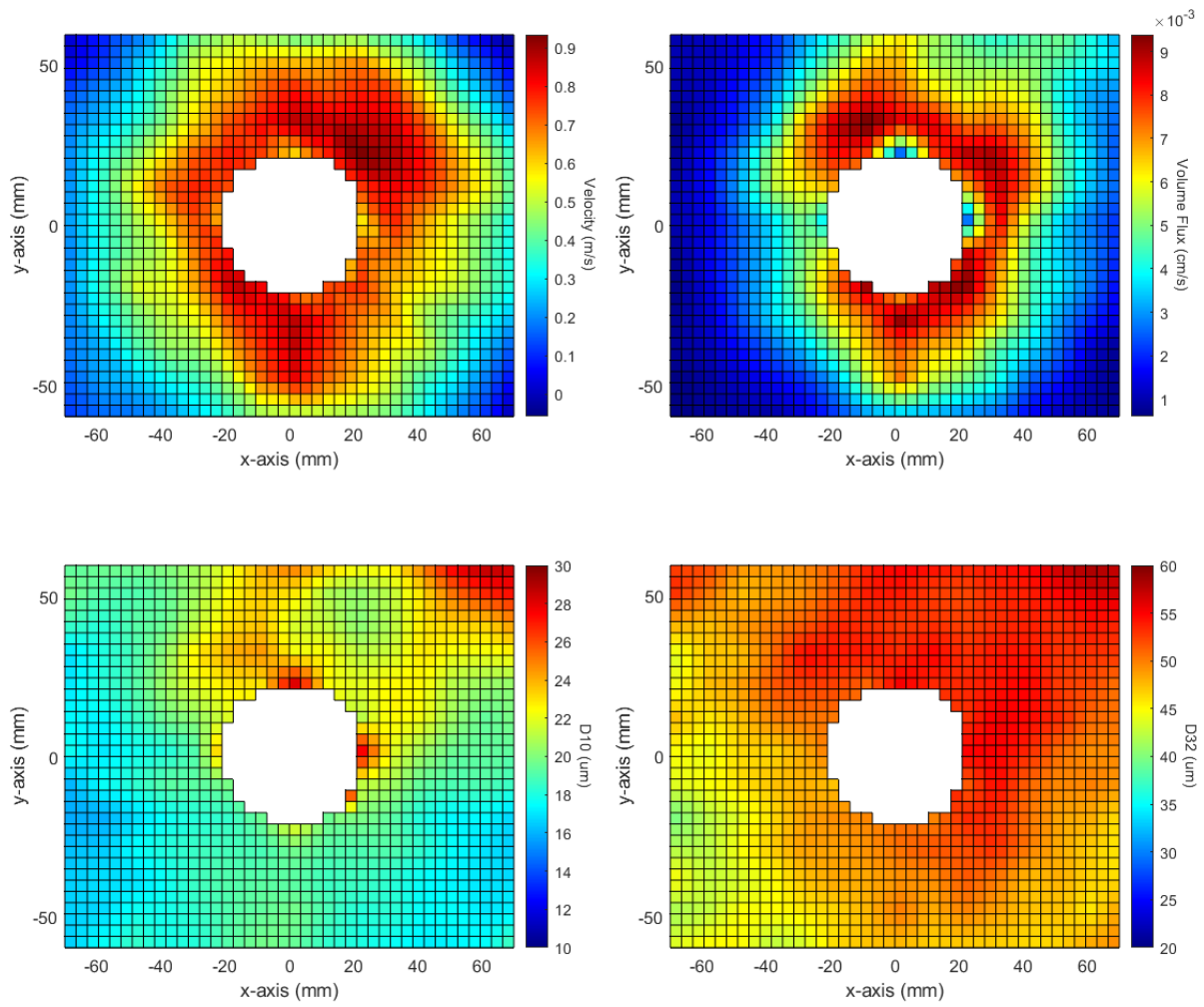


Figure B.8: Wind tunnel exit plane map of droplet statistics at a constant flow rate of water mist of 171 mL/min.

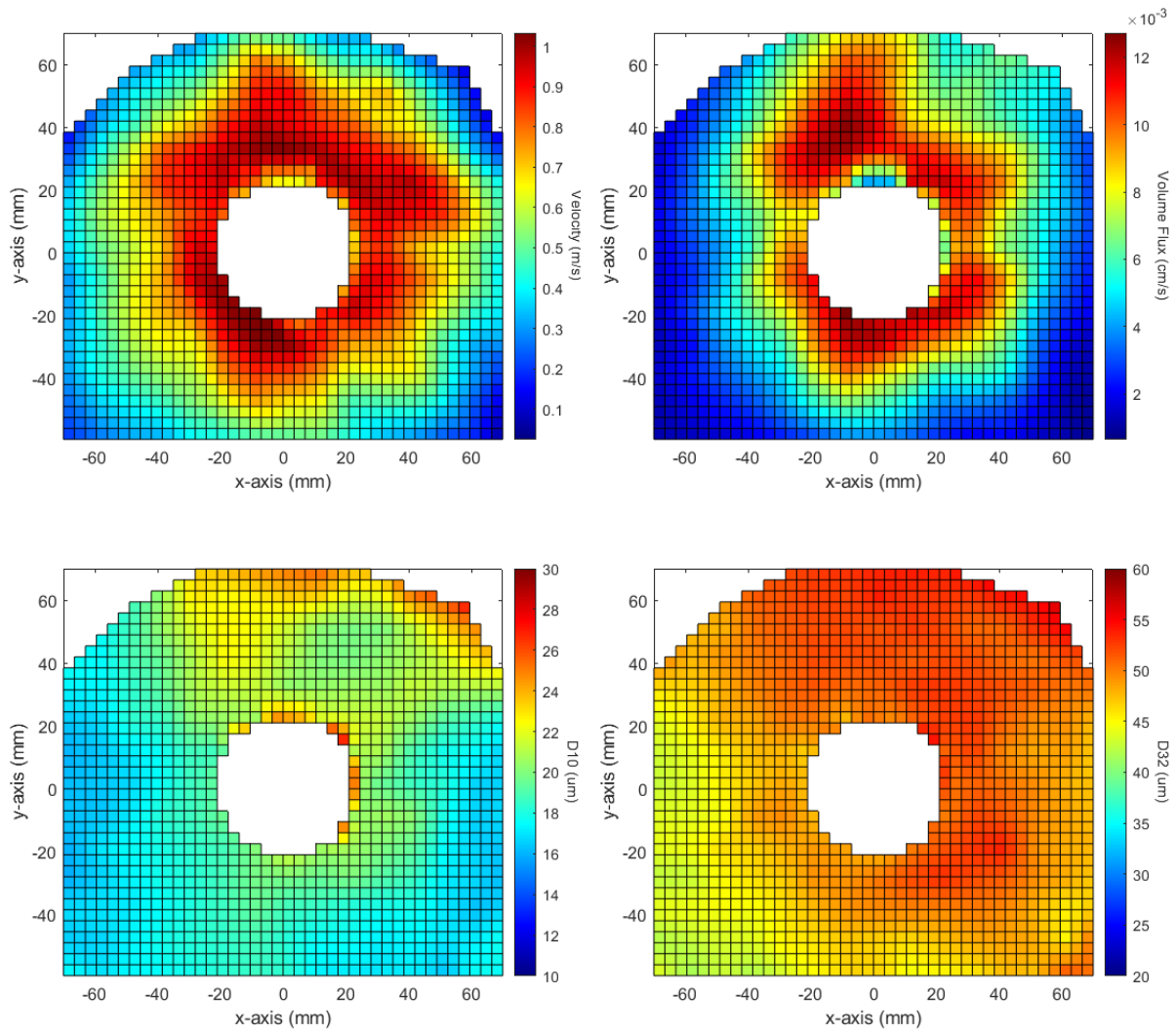


Figure B.9: Wind tunnel exit plane map of droplet statistics at a constant flow rate of water mist of 187 mL/min.

Appendix C

Potassium chemical kinetic properties

Table C.1 shows the list of transport properties estimated for the various potassium molecules used in the laminar flame calculations. The list is estimated from existing literature on similar molecules. Please see the following reference for the list of chemical kinetic equations and thermodynamic properties for the potassium-containing species: [129].

Table C.1: Transport properties of Potassium Compounds, estimated from similar atomic species and molecules.

Compound	Geometry	Well-Depth (ϵ/kB)	Diameter (σ)	Rotational Relaxation
K	Linear	300 K	3.5 Å	1.0
K2	Linear	400 K	4.0 Å	1.0
KH	Linear	350 K	3.8 Å	1.0
KCO3	Non-linear	500 K	4.5 Å	1.0
K2O2	Linear	450 K	4.2 Å	1.0
KO	Linear	400 K	3.9 Å	1.0
KO2	Non-linear	470 K	4.3 Å	1.0
K2O	Non-linear	440 K	4.1 Å	1.0
KOH	Non-linear	410 K	4.0 Å	1.0
K2CO3	Non-linear	510 K	4.6 Å	1.0
KO3	Non-linear	480 K	4.4 Å	1.0
KHCO3	Non-linear	490 K	4.3 Å	1.0

Appendix D

Aqueous Dispersion of Ferrocene

This section of the appendix presents images of the various solutions of aqueous dispersion of ferrocene. Figure D.1 shows images of the nano/micron-sized ferrocene particles in suspension through the use of anti-solvent precipitation. The image on the left shows a low concentration (1000 ppm) of ferrocene as a homogeneously dispersed solution. Whereas if the concentration is pushed above 1000 ppm to 2000 ppm, the image on the right shows the result of a non-dispersed solution of ferrocene in water. Large particles are seen to agglomerate on the edges of the flask.

Dispersed Non-dispersed

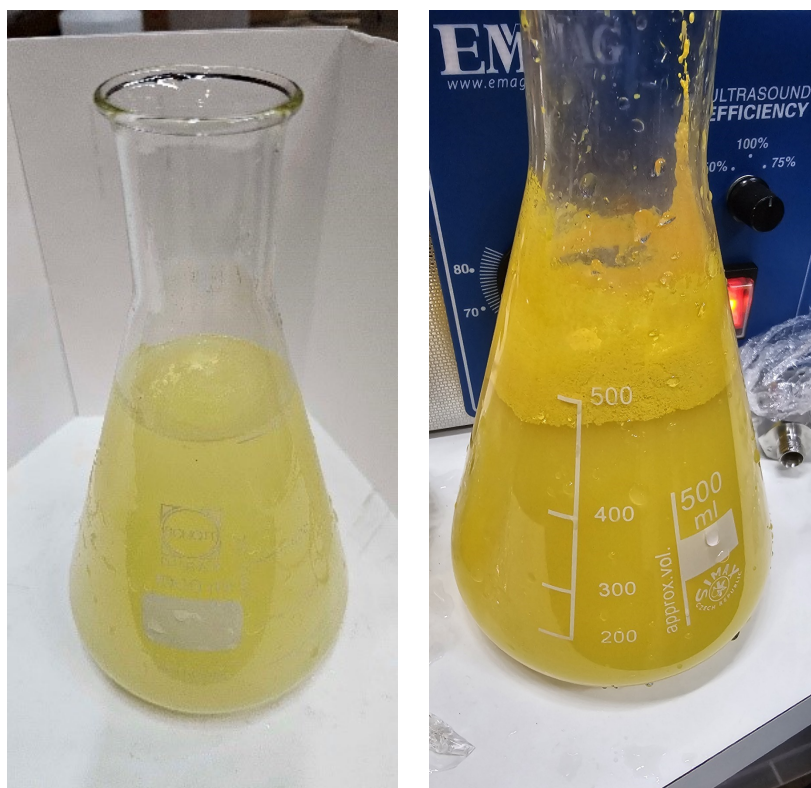


Figure D.1: Images of the aqueous dispersion of ferrocene using anti-solvent precipitation. Left, low concentration fully dispersed/suspended particles. Right, high concentration not dispersed particles.

Figure D.2 shows images of host-guest inclusion of ferrocene at a low and high concentration. As host-guest inclusion is technically a dissolved solution of ferrocene, the solution is now translucent, which confirms that Fc is in solution rather than in suspension.

Low Concentration High Concentration



Figure D.2: Images of aqueous dispersion of the host-guest inclusion complex of ferrocene.

Figure D.3 shows images of the ferrocene derivatives in an aqueous base. Similar to the host-guest inclusion, because these new ferrocenes can dissolve in water, the solution is now also translucent. Ferrocene dicarboxylic acid ($\text{Fc}(\text{COOH})_2$) is also briefly tested for solubility. It was found that dicarboxylic acid has a much higher solubility in aqueous base than that of the carboxylic acid (FcCOOH) counterpart. However, $\text{Fc}(\text{COOH})_2$ is far more expensive to purchase off the shelf than FcCOOH , and is therefore not pursued in this thesis. Ferrocene methanol was also tested for solubility. It was found to be barely soluble, however, much more soluble at elevated temperatures ($60\text{ }^\circ\text{C}$).



Figure D.3: Images of aqueous dispersion of the ferrocene derivatives.