HOST UNIVERSITY: Lund University

FACULTY: Faculty of Engineering

DEPARTMENT: Division of Fire Safety Engineering

Academic Year 2019-2020

FACTORS INFLUENCING THE GENERATION OF CARBON MONOXIDE IN FIRES PARTIALLY SUPPRESSED THROUGH WATER MIST APPLICATION

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Master thesis submitted in the Erasmus+ Study Programme

International Master of Science in Fire Safety Engineering

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Abstract

Fires in the built environment typically consist of diffusion flames with inefficient mixing of fuel and oxygen, resulting in a degree of incomplete combustion and the generation of carbon monoxide. Fire suppression systems, used to control the growth and spread of fire, influence the combustion reaction process. Water droplets interacting with the gas phase chemistry of fire interrupt combustion processes and promotes generation of carbon monoxide.

Past research into mist suppression primarily focuses on optimal droplet size for heat release rate reduction, and notes a significant increase in carbon monoxide concentrations with this approach. The aim of this experimental study was to contribute to the knowledge of the interaction of water droplets on the gas phase chemistry of fire and assess the factors that influence the generation of carbon monoxide.

The experimental set-up was designed to minimise the effect of the mist spray on the heat release rate of the fires. Laboratory-scale fires, having heat release rates of 40-70 kW, and consisting of gaseous, liquid and solid fuels, were subjected to mist suppression sprays. The sprays applied consisted of droplets having characteristic diameters (D_{v50}) of 163-287 µm, and water flow rates of 1.5-3.5 L/min. The concentration of carbon monoxide produced by fires subject to mist suppression increased by up to 250%, with minor reductions to the heat release rate.

This study represents a proof of concept to a currently largely under explored phenomenon. The findings indicate a need for closer examination of how water sprays influence toxic species production. The results raise uncertainly on the applicability of typical applied species yields when fires are partially suppressed through fine water sprays. It is recommended that fire safety engineers consider the adoption of more conservative safety factors where it could be anticipated that the suppression systems would not result in extinguishment.

IMFSE Master Thesis Declaration

This form has been developed in the context of the unforeseen circumstances due to Covid-19, necessitating a reduction of practical project work (whether it be laboratory based, computational, or fieldwork) during the master thesis semester. It acts as a record of the impact on the master thesis. The form has been completed by the student and verified by the supervisor.

Name: Haydn Lewis

Work completed

All items of wholly, or partially completed work must be listed, indicating the percentage completion for each task.

- 36 x lab-scale tests utilising a single liquid fuel (heptane).
- 36 x lab-scale tests utilising a single gaseous fuel (propane).
- 2 x lab-scale tests utilising a solid fuel with liquid fuel ignition source (acrylonitrile butadiene styrene and heptane).
- A number of trial and error experimental test set-up concepts.
- 1 week of laboratory work with the final experimental set-up was conducted.
- Literature review not affected by Covid-19 pandemic.
- Data analysis not affected by Covid-19 pandemic, except for that listed below.

Work not commenced

Any items of outstanding work that have not been started should be listed here.

- 22 x lab-scale tests utilising a solid fuel with liquid fuel ignition source (acrylonitrile butadiene styrene and heptane) utilising different nozzles and operating pressures.
- The opportunity to re-test outlier or unexpected results to confirm results observed was lost due to the Covid-19 pandemic.

Declaration

To the best of our knowledge, this form is an accurate record of the project status on 20 June 2020.

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Supervisor: Nils Johansson

Acknowledgements

First and foremost, I would like to express my thanks to my thesis supervisor Dr Nils Johansson. From the initial moment I approached Nils with the idea of researching this topic, his interest and encouragement in transforming the idea from a concept into a formal research question and methodology was invaluable. The guidance and support Nils provided throughout all stages of this process were invaluable to the completion of this work.

The knowledge and experience that Dan Madsen was able to impart on the laboratory and experimental set-up aspects of this study is greatly appreciated. Dan's thoughts regarding the practical aspects of this study greatly contributed to the quality of work undertaken.

I would also like to thank Prof. Tarek Beji, Dr Ricky Carvel and Dr Haukur Ingason for their guidance whilst this research question was still in its infancy. Tarek, Ricky and Haukur were the first researchers who validated the concept that I was developing and provided initial suggestions which formed the foundation for my work going forward.

Thank you to my IMFSE classmates, the management board and everyone else involved with this program for this amazing experience. This really has been a unique and inspiring two years largely due to what everyone associated with the program brings to it.

I am indebted to my family for the opportunities and support you have provided me over the years. This accomplishment would not have been possible without them.

Lastly, I would like to thank my partner, Alana, for the trust she put in me to uproot our lives in Sydney and move to Europe for two years to undertake the IMFSE program. I am incredibly thankful for the belief she has had in me, and the sacrifices that she has made throughout this big adventure.

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Nomenclature

A	s^{-1}	Pre-exponential constant in reaction rate
$\mathrm{A_f}$	m^2	Fuel area
D	m	Diameter
Da	-	Damköhler number
$\mathrm{D_{v10}}$	m	10% volume percentile diameter
$\mathrm{D_{v50}}$	m	Volume median diameter
$\mathrm{D_{v90}}$	m	90% volume percentile diameter
$\mathrm{D_{v99}}$	m	99% volume percentile diameter
d_d	m	Droplet diameter
E_a	J/kg or J/mol	Activation energy
f	-	Fuel mass fraction
f	-	Probability density function
k	s^{-1}	Reaction rate constant
$k\beta$	m^{-1}	Material constant for liquid fuels
M	g/mol	Molecular weight
$\dot{m}_e$	kg/s	Exhaust mass flow rate
$\dot{m}_f$	kg/s	Fuel mass flow rate
$\dot{m}_{ox}$	kg/s	Oxygen mass flow rate
$\dot{m}''_{\infty}$	$kg/(m^2s)$	Limit burning rate of a liquid
$\dot{Q}$	kW	Heat release rate
$\dot{Q}*$	-	Dimensionless heat release rate
R	J/(kg.K) or J/(mol.K)	Gas constant
r	-	Stoichiometric ratio
T	K	Temperature
ΔU_d	m/s	Relative particle velocity
We	-	Weber number
w_{ox}	-	Mass percentage of oxygen in ambient air
Y_i	-	Mass fraction of species *i*
y_i	-	Yield of species *i*
ε	-	Excess factor
ϕ	-	Equivalence ratio
ρ_l	kg/m^3	Liquid mass density
σ	N/m	Surface tension
τ_{chem}	s	Characteristic chemical time scale
τ_{flow}	s	Characteristic flow time scale
$\tau_{t,\mathrm{I}}$	s	Integral turbulent time scale

1. Introduction

This chapter begins with a brief description of why the study of toxic species production through combustion, in this case carbon monoxide production, is of such importance to the field of fire safety engineering. It introduces the concept that the water sprays of fire suppression systems, utilised within the built environment to control the growth and spread of fire, can interrupt the combustion reaction processes and significantly increase the generation of products of incomplete combustion. The study undertaken within this thesis aims at contributing to the knowledge of the interaction of water droplets on the gas phase chemistry of fire and the resulting rate of generation of carbon monoxide. This chapter concludes with an explanation of the methodology adopted and limitations considered within this study.

1.1. Background

Diffusion flames, such as those typically associated with fires occurring in the built environment, are categorised by the inefficient mixing of fuel and oxygen. The interior of a diffusion flame is always under-ventilated due to lack of oxygen availability within the reaction zone. This process provides a source for products of incomplete combustion (1). It is well known that the generation of carbon monoxide (CO) is a major by-product as a result of the molecular diffusion of fuel and oxygen within the region of combustion of common fuel sources.

Carbon monoxide is an asphyxiant which leads to anaemic hypoxia through an accumulated dose taken up by occupants within a fire/smoke compartment (2). Inhaled carbon monoxide binds itself to haemoglobin in red blood cells results in a "lowered oxygen delivery capacity of the blood" (1), leading to a reduced level of physical and mental performance, which significantly increases the likelihood of an individual succumbing to the effects of fire. Historical fire records show that carbon monoxide exposure is the "dominant toxicant in fire deaths" accounting for approximately two-thirds of fire deaths within enclosures (1, 3, 4).

Where occupants are provided appropriate means to egress from a 'typical', compartmentalised fire scenario, carbon monoxide dose is not generally a limiting tenability criterion assuming occupants are awake and alert. However, the risk of carbon monoxide dosage limits being exceeded increases substantially in scenarios where occupants are present within the same environment as the fire gases for prolonged periods of time as a result of an extended egress conditions; the most extreme of which would be the act of egressing from a road or rail tunnel fire scenario, or if occupants were inhibited from reaching a place of safety.

The chemical species produced through combustion are a function of the following (5):

- The fuels involved,
- "The model of combustion (flaming, smouldering ...),
- The availability of air, and
- The addition of chemical agents to retard" (5).

Gottuk and Lattimer (4) also note that the thermal environment and fluid dynamics involved are key factors in the chemical reaction processes of combustion, influencing the species that are produced.

Fire suppression systems are a key fire safety design measure utilised within modern built environment structures that, when activated, can significantly influence the processes of combustion chemical species production. The continual advancement towards bigger, more complex and safer buildings/infrastructure has resulted in the increased prevalence of fire suppression systems within prescriptive-based design codes and performance-based fire safety engineering assessments, with the intent to limit the growth and spread of potential fires (6). However, to date the influence of fire suppression systems on the mechanisms of combustion in terms of the production of chemical species is relatively under-researched.

Suppression of fire by water is a complex physio-chemical process, involving a number of competing mechanisms, all of which have not yet been fully understood. Rasbash, one of the earliest modern authorities on the interaction of water and fire, observes "It is probably safe to say that since mankind first made use of fire, they made use of water to control it. Apart from rhetorical quotations, very little has come down to us from these aeons of time" (7). While our level of understanding of the processes involved has improved in recent times, there is still a degree of detail that remains unknown.

A number of fire dynamics research projects have been undertaken over recent years, detailed within Section 2.2.3, that indicate an increase in carbon monoxide concentration produced from fires subject to sustained water suppression without extinguishment. In other words, if the properties of the applied water spray(s) are not appropriate to cause extinction of combustion, the application of water droplets within the fire environment can “affect the pathway of oxidation” (5) and promote the generation of products of incomplete combustion, including carbon monoxide.

It is generally believed that fire suppression does not worsen the effects of the fire environment as long as the size of the fire is sufficiently reduced. Li et al. found that “fire suppression does not cause significant adverse effects in cases (where)… the fire size has been reduced to less than 40% of that in the free burn test” (8). However, other studies have shown “an increase in CO yield of about 20 times” (or 1900%) accounting for the reduced heat release rate (HRR) (9).

1.2. Aim and Objective

The research work undertaken during this thesis aims to contribute to the knowledge of fires subject to suppression by water; specifically, the interaction of fine water droplets on the gas phase chemistry of fire and the interruption of the combustion chemical process and resulting generation of carbon monoxide. It is not the intention of this work to oppose the use of fire suppression systems within infrastructure or the built environment. Rather, the intention is to further understanding of the factors influencing gaseous species production as a result of suppression by water sprays.

The objective of this thesis is to experimentally assess the factors which influence the rate, and significance, of carbon monoxide generation within partially suppressed fires. The main factors to be considered are:

- Water droplet size within a water spray,
- Rate of water applied through a spray,
- Fuel type (gaseous, liquid, or solid), and
- Heat release rate of the fire.

Once trends in the data were identified, an investigation of fundamental gas phase fire chemistry and heat transfer was undertaken to identify the phenomena which may be responsible for the results obtained.

1.3. Methodology

The following methodology has been developed in order to achieve this objective:

i. Undertake a literature review of existing studies investigating the influence of water suppression on fire, including studies focusing on the effectiveness of combustion and suppression mechanisms more broadly.
ii. Design and construct laboratory-scale experiments utilising the knowledge gained through reviewing relevant literature.
iii. Conduct the experiments and analyse the consistency and trends of the products of combustion within the exhaust hood.
iv. Compare the results obtained with the phenomena identified in the literature review and draw conclusions as to the key influential factors responsible for carbon monoxide generation within partially suppressed fires.

1.4. Limitations

The limitations for this study consist mainly of time and practical simplifications made when designing and constructing the experimental apparatus. During the project, these time constraints were amplified due to the university access restrictions implemented as a result of the COVID-19 pandemic. As a result of the experimental time limitations of this project, tests involving gaseous and liquid fuels were prioritised over solid fuel tests as the combustion of gaseous and liquid fuels provide a more uniform and repeatable set of data that is more readily suitable for comparison.

Other general limitations of the experimental set-up, and hence the results obtained, within this study include:

- Relatively small, laboratory-scale test fires being tested,
- Two types of water mist pressure energy atomiser nozzles being incorporated,
- A relatively narrow range of system testing pressures, and hence sprays having a limited range of water flow rates and characteristic droplet sizes.

Tests were only able to be undertaken with a single gas (propane) and a single liquid (heptane) fuel, again due to experimental time limitations. It was initially intended to also investigate how different fuels of the same state, but differing hydrocarbon chain lengths and typical combustion product yields, influenced the results obtained.

As a standardised experimental set-up does not exist for this type of research, there was an inherent trial and error process involved in the design of the test apparatus. Due to this, cost and complexity simplifications were made throughout the process to minimise the potential wastage of resources during this proof of concept.

2. Literature Review

A literature review was undertaken to find all existing analogous experimental studies and studies of suppression/species production mechanisms that would inform the direction taken with this project. A comprehensive literature review was undertaken in Lund University's LUBsearch. LUBsearch is a search engine across Lund University Libraries' collections and databases covering "200 databases and more than 78,000 e-journals" (10) including Web of Science and Scopus. The breadth of databases used demonstrate that the results of the literature review represent good coverage of available peer-reviewed literature.

2.1. Methodology

In order to be comprehensive in the literature review process, the structure shown within Figure 1 was followed. The literature review was conducted by first defining a keyword string to identify all relevant literature within the databases. The results were then progressively filtered until only relevant literature remained. All literature found manually from the concept stage of this thesis topic until commencement were also incorporated within the process. This manually identified literature was obtained through periodical LUBsearch and Google Scholar searches utilising preliminary keywords as well as general academic reading on the subject. Another iteration of this literature search was undertaken through reviewing the referenced literature within all documents deemed relevant to the topic.

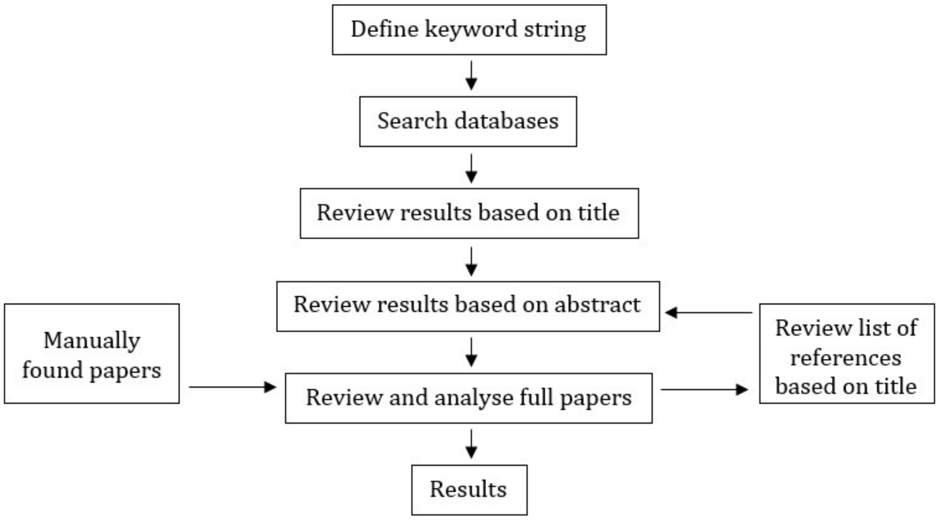

Figure 1 – Comprehensive literature review process

The keyword string was defined by identifying three conceptual buckets of keywords relevant to the topic; being fire, suppression and toxicity. All terms or synonyms appropriate to these buckets were identified and Boolean operators were utilised to capture all literature which included reference to each bucket. The keywork search string utilised is shown within Figure 2.

(Fire OR Flame OR Combustion)
AND
(Suppression OR Sprinkler OR Water Mist OR Water Spray OR Extinguish)
AND
(Toxicity OR By-products OR Asphyxiant OR Carbon Monoxide OR Hydrogen Cyanide)

Figure 2 – Keyword search string

This keyword string returned 415 unique potential sources via LUBSearch when searched in the early stages of this project (20 January 2020). Documents were progressively excluded through the PRISMA structure (11), shown in Figure 3. Literature was excluded if it was published in a language other than English, from a field of study not related to fire dynamics, not related to fire suppression, not focused on the link between suppression and species production, or not addressing the mechanisms of suppression, as shown within Table 1.

Table 1 – Exclusion criteria description

Exclusion Criteria	Description
1	Not published in English
2	From a field of study not related to fire dynamics
3	Not related to suppression
4	Not focused on the link between suppression and species production or not addressing mechanisms of suppression

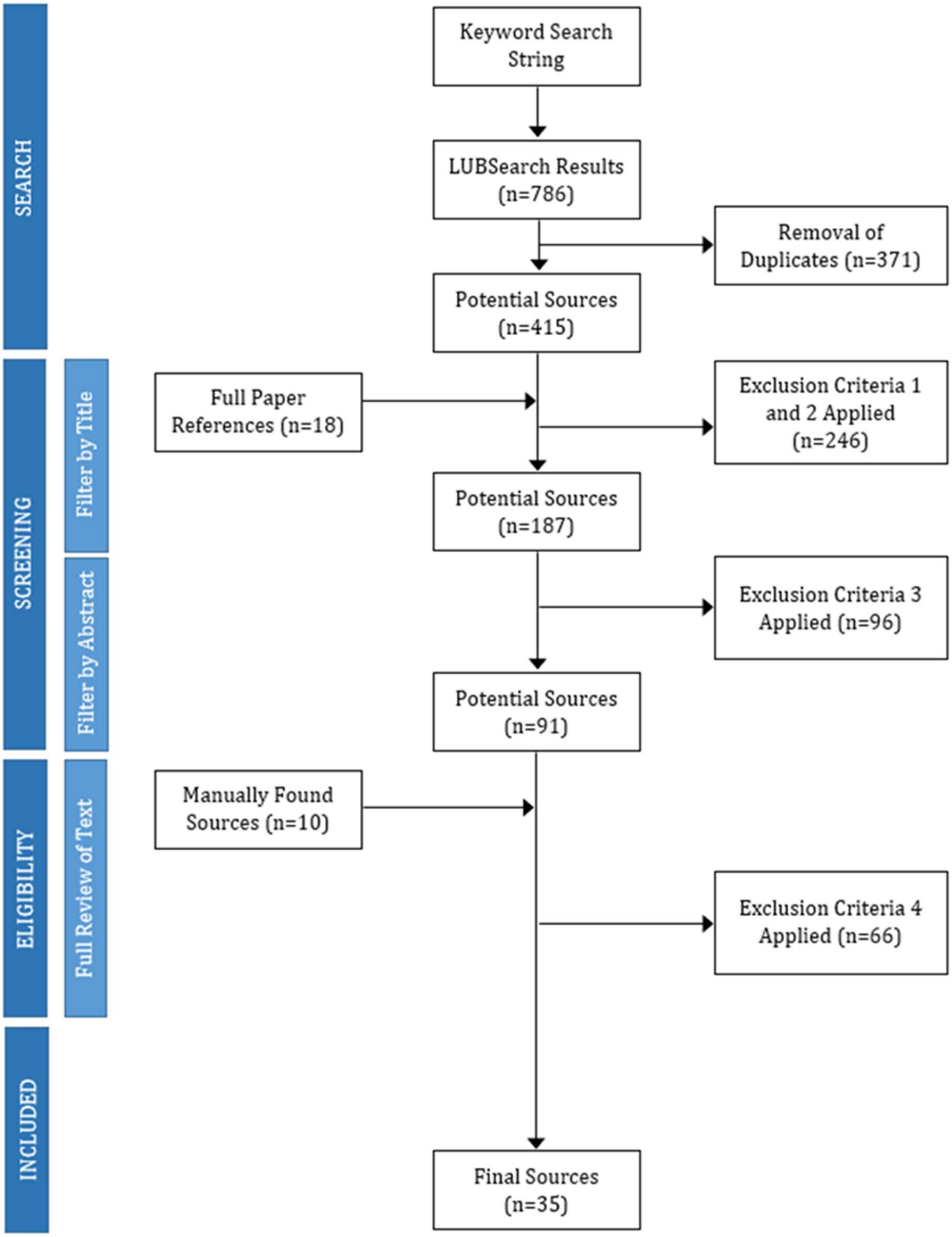

Figure 3 – Literature review source selection

The final sources are summarised within a data extraction table within Appendix A. Analysis was undertaken of the extracted data to identify key concepts and findings within these sources. The synthesis of these findings are described within this literature review.

The keyword search string was repeated on 16 July 2020 to ensure that any relevant, recently released publications were captured. The search returned 24 new unique references, none of which were deemed relevant to this study.

2.2. Results

The intent of the literature review was to identify the mechanisms behind suppression and chemical species production as well as all analogous research undertaken within this field. As a result of analysing the literature, it became clear that a discussion of water spray generation and classification would be beneficial to provide the required context and background for the subsequent discussion of literature. Therefore, the results of the literature review have been organised into three categories:

- The generation and classification of water mist sprays,
- The physical and chemical mechanisms involved in combustion, and
- A review of existing analogous experimental studies identified within literature.

2.2.1. Spray Generation and Classification

The purpose behind all water spray nozzles, whether utilised in conventional sprinkler suppression systems or water mist fire suppression systems, is to "accelerate and disintegrate [atomise] a liquid and to disperse the resulting drops" (12) as a spray. Within the firefighting and fire safety engineering fields, nozzles can be conceptually classified as either:

- Pressure energy atomisers – where water is atomised through its movement through a nozzle, or
- Gaseous energy atomisers – where water is atomised through the rapid movement of a gaseous medium within the nozzle (12).

The generation of a mist through a nozzle creates a spray consisting of many millions of droplets having a distribution of different diameters, known a polydisperse spray (13-15). The droplets produced by fire suppression systems are categorised by a series of characteristic diameters which give the proportion of droplets that fall under a specified size. The significance of droplet size on the interaction of water with fire is detailed within Section 2.2.2.

To draw comparisons between sprays and systems, it is necessary to define a representative size of the distribution referred to as a characteristic diameter. Rasbash notes that “care has to be exercised in deciding on the relevant representative drop size to use since drop size enters into the physical laws that influence the effects of sprays on fires in widely different ways” (7). Two common characteristic diameter definitions are as follows:

- Sauter mean diameter (SMD): “Sum of droplet volumes divided by the sum of the droplet surface areas” (14). The Sauter mean diameter considers the “distribution of volume-to-surface ratio (which is larger for larger droplets)” (15). This characteristic diameter is most applicable to heat/mass transfer and reaction applications since the surface ratio to volume ratio is crucial to these processes.

$$\mathrm{SMD} = \frac{\int_0^\infty f(d_d) d_d^3 d(d_d)}{\int_0^\infty f(d_d) d_d^2 d(d_d)} \qquad \textit{Equation 1}$$

- Volume median diameter (D_{v50}): The diameter at which 50% of a volume of spray is contained within droplets smaller than this size. Whilst not the most directly applicable characteristic diameter based on theory, it is the most commonly reported measure within literature and technical specifications.

It is noted that quantifications of mean/median diameter provide a “measure of the central tendency of the distribution” (12) and not the extreme ends. Therefore, when defining a droplet distribution it is typical to define three volume diameters, for example D_{v10}, D_{v50} and D_{v90}, representing the 10th, 50th and 90th volume percentile respectively (16), which provide additional information regarding the width of the droplet size distribution and characteristics of the spray.

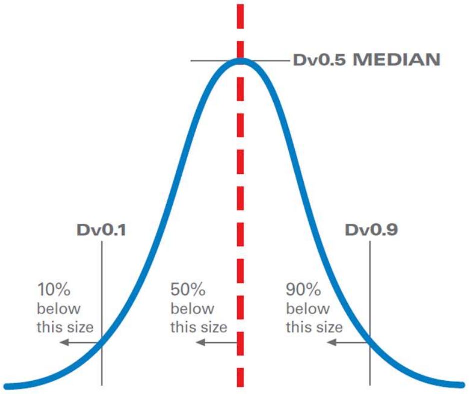

Figure 4 – Illustration of D_{v10}, D_{v50} and D_{v90}
Extracted from (16)

For the purposes of fire suppression, water sprays fall into two broad categories; conventional sprinkler systems and water mist systems. NFPA 750, Standard on Water Mist Fire Protection Systems, defines water mist suppression systems as those having a D_{v99} (99th volume percentile) less than 1,000 µm (17), whereas sprinkler systems are those with droplet distributions with volume diameters that fall above that criteria. Conventional sprinkler systems are considered to have a D_{v99} in the "order of 5,000 µm" (14) with typical droplet sizes "between approximately 200 and 3,000 µm" (18), depending on the design of the system .

The NFPA 750 classification of water mist suppression systems is intended to separate the characteristics of performance of these systems from conventional sprinkler systems. However, it is considered that there is a large degree of variation or qualities of performance in fire suppression properties of sprays having a D_{v99} less than 1,000 µm. Therefore, mist suppression systems are further categorised into three classes; Class 1 having D_{v90} less than 200 µm, Class 2 having D_{v90} between 200 and 400 µm, and Class 3 having D_{v90} between 400 and 1000 µm (19, 20). As will be discussed further in Section 2.2.2, the finer mists of Class 1 and Class 2 systems are more suited to applications where high momentum droplets and surface wetting are to be limited, whereas the slightly larger droplets of a Class 3 systems have their application where fuel wetting is acceptable or desired (12).

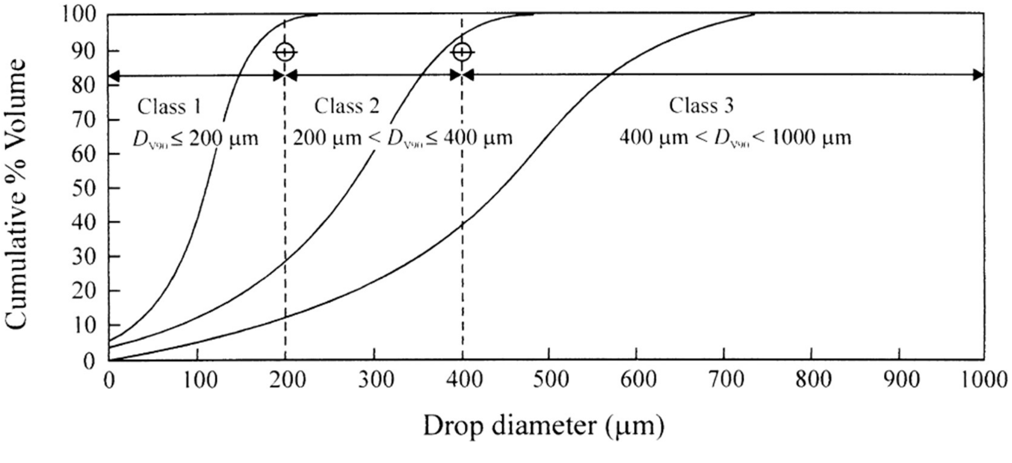

Figure 5 – Definition of mist classification by D_{v90}
Extracted from (19)

2.2.1.1. Variation in Droplet Size as a Function of Distance from Nozzle

Santangelo (21) found that not only do sprays consist of a distribution of droplet sizes, the size of the droplets measured vary as a function of axial distance from the nozzle. It is noted that Santangelo's study utilised a pressure-swirl atomizer nozzle operating at high pressure with characteristic droplet diameters in the order of 20-80 μm. However, the variation of droplet diameters as a function of distance from the nozzle is considered to affect all mist suppression systems. Santangelo (21) reports that in the near-field region to the nozzle, where there is a high density of droplets, the rate of collision and coalescence is high, resulting in larger droplets being present near to the nozzle. In other words, the density of water flux in the near-field region is so great that droplets have not separated sufficiently to have enough free space to atomise and form smaller droplets. The droplets were observed to undergo secondary atomisation as the liquid/gas ratio reduced and the flow-induced forces overcame the surface tension of the droplets. Minimum droplet sizes were seen at around 100 mm from the nozzle. As the distance from the nozzle becomes greater, the velocity of the droplets decreases and the flow-induced forces have a reduced effect. Therefore, droplets are able to interact and coalesce, resulting in an increase to the characteristic droplet diameters recorded (21).

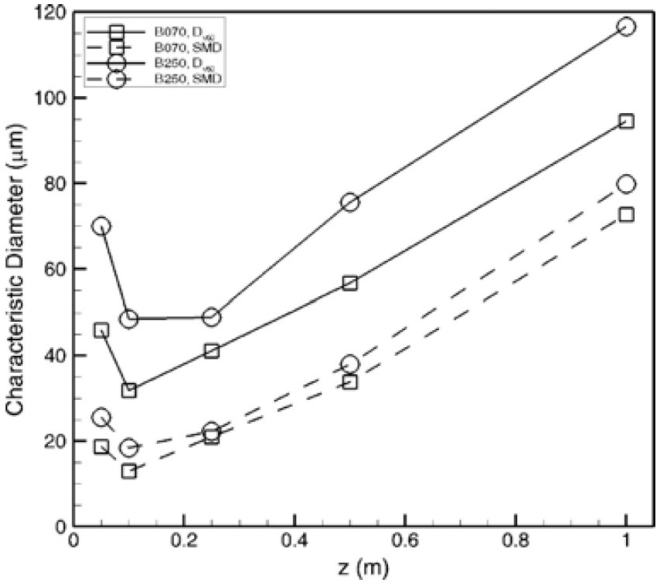

Figure 6 – Characteristic diameters of sprays as a function of axial discharge distance
Extracted from (21)

The Weber number, expressed below, provides a ratio of flow-induced force and surface tension, which is helpful to explain the results observed by Santangelo. Larger Weber number sprays result in larger flow-induced forces leading to droplet breakup or secondary atomisation.

$$We = \frac{\rho_l (\Delta U_d)^2 d_d}{\sigma} \qquad \textit{Equation 2}$$

Merci and Beji state that "the 'relative droplet velocity' ΔU_d is used to characterize the flow-induced forces and the droplet diameter is used as characteristic length scale" (15). Through Equation 2 it can be seen that in the near-field region of the nozzle, the liquid mass density, ρ_l, is high and the relative droplet velocity, ΔU_d, is high. The result of this is that whilst the rate of coalescence is high, the high Weber number will act to force the droplets to undergo secondary atomisation. Whereas, at further axial distances from the nozzle, the droplets would be more dispersed with a lower relative droplet velocity leading to a lower Weber number and reduced secondary atomisation.

2.2.2. Physical and Chemical Mechanisms of Suppression by Water

The physical and chemical mechanisms involved in the suppression of fire by water are complex and numerous. Santagelo et al. found that the "phenomenological characteristics [of water mist suppression] are very complex and not completely understood" (13). Grant and Drysdale (22) report that the following key mechanisms occur due to the interaction of water droplets with the combustion chemical process:

- **Cooling**
    - Cooling of the hot gases and flames – Water droplets reduce the amount of energy available to continue the chain reaction of combustion, and
    - Fuel surface cooling – Water droplets reduce the rate of pyrolysis of solid fuels and the vapour pressure of liquid fuels.
- **Inerting** – Water droplets that evaporate within the flame, produce inert water vapour and displace the oxygen (reduce oxygen partial pressure) required for combustion.
- **Thermal radiation attenuation** – The presence of water droplets attenuates the radiative feedback between the flame and hot surfaces to the fuel slowing the rate of pyrolysis or vaporisation.

- **Inhibiting** – Water droplets are more chemically attractive to the free radicals needed for the combustion process, removing them from the combustion zone and slowing the chain reaction
- **Blanketing** – Water provides an inert, insulating barrier over the fuel surface to reduce the ability for the fuel to vaporise.
- **Flame blow-off** – High extinguishant velocities result in the reactant transport time being shorter than the time required to chemically react, preventing combustion.

Wighus et al. (23) report that the first three of these mechanisms (being cooling, inerting and thermal radiation attenuation between the flame and the fuel) are the key aspects to effective suppression for many common fuels and environments.

Whilst the discharging of water droplets inhibits the chemical process through all of the above mechanisms, there is the potential that the inclusion of water droplets in some circumstances may enhance combustion. Water droplets that have sufficient mass and momentum to penetrate the surface of a liquid pool fire can cause a flare-up as the pooled, vaporising water increases the combustible surface area of the liquid fuel and resulting heat release rate of the fire (24-26). Further, the entrainment of air to the spray flow improves the mixing of fuel and air, potentially increasing the rate of combustion (27, 28).

The sizes, and discharge speeds, of the droplets within water sprays are key variables involved in weighting the potential influence of each physical and chemical mechanism in the combustion process. Conventional sprinkler systems, with their larger water droplets, are more suited to applications prioritising fuel cooling and pre-wetting of fuel, such as typical solid fuels present within compartment fires (12). Droplets that are larger are able to penetrate deeper vertically within the flame structure due to their greater momentum and thermal mass (14). Further, larger droplets are less able to be entrained within a flow and as a result are reliant on the location and direction of their discharge being appropriate to reach the seat of the fire. As noted by Grant and Drysdale, “larger, lower velocity droplets produced by the coarse sprays [of conventional sprinkler systems] were not able to negotiate obstacles” (12) having greater reliance on the properties of droplet discharge.

2.2.2.1. Reaction Chemistry Processes of Combustion

The general chemical reaction process in the field of fire safety and combustion science is the oxidation of a fuel releasing energy to the environment. This reaction process is conceptually viewed as:

$$\text{Fuel} + \text{Oxidiser} \rightarrow \text{Products} \qquad \textit{Reaction 1}$$

Or for the complete combustion of a hydrocarbon fuel in excess air as (15):

$$C_m H_n + \varepsilon\left(m + \frac{n}{4}\right)\mathrm{O_2} + \frac{79}{21}\varepsilon\left(m + \frac{n}{4}\right)\mathrm{N_2}$$

$$\rightarrow m\mathrm{CO_2} + \frac{n}{2}\mathrm{H_2O} + (\varepsilon - 1)\left(m + \frac{n}{4}\right)\mathrm{O_2} + \frac{79}{21}\varepsilon\left(m + \frac{n}{4}\right)\mathrm{N_2} \qquad \textit{Reaction 2}$$

However, it is noted that the single step chemical reactions shown in the two equations above hide the fact that even for the simplest of fuels the reaction process consists of many hundreds of intermediate steps and species (29). For example, Curran et al. found that the "complete reaction mechanism for *n*-heptane oxidation included 2,450 elementary reactions among 550 chemical species" (30). It is considered that the effects of the inclusion of water droplets and vapour within this complex series of elementary reactions can interrupt many stages of this process through both cooling and inerting mechanisms. This interruption ultimately results in products of incomplete combustion, such as carbon monoxide, being present among the gaseous species produced.

Literature shows that the main elementary reactions which result in the formation of carbon monoxide are the oxidation of soot by oxygen (Reaction 3 below), the reduction of carbon dioxide molecules by soot particles (Reaction 4 below) (15) and the oxidation of soot by the hydroxyl radical (Reaction 5 below) (31).

$$\mathrm{C} + \tfrac{1}{2}\mathrm{O_2} \rightarrow 2\mathrm{CO} \qquad \textit{Reaction 3}$$

$$\mathrm{CO_2} + \mathrm{C} \rightarrow 2\mathrm{CO} \qquad \textit{Reaction 4}$$

$$\mathrm{C}_i + {\cdot}\mathrm{OH} \rightarrow \mathrm{C}_{i-1} + \mathrm{CO} + \tfrac{1}{2}\mathrm{H_2} \qquad \textit{Reaction 5}$$

2.2.2.2. Reaction Chemistry Speed

In order for chemical species to react with each other, they must be present within the same location for an appropriate residence time in which to interact. This chemical interaction is best described through the Damköhler number which represents how fast a chemical process is compared to the residence time of the molecular interactions involved (15).

$$Da = \frac{\tau_{\mathrm{flow}}}{\tau_{\mathrm{chem}}} = \frac{\tau_{\mathrm{t,I}}}{\tau_{\mathrm{chem}}} \qquad \textit{Equation 3}$$

The chemical time scale can be seen as relative to the chemical reaction rate shown below.

$$\tau_{\mathrm{chem}} \sim k = A\exp\left(-\frac{E_a}{RT}\right) \qquad \textit{Equation 4}$$

As mentioned above, a significant mechanism associated with the presence of water droplets on combustion is the absorption of large amounts of energy from the flame; through the sensible heat absorbed by increasing the temperature of a droplet and the latent heat absorbed in order to evaporate a droplet. Rasbash reports that “the major useful property of water as an extinguishing agent is its capacity to cool” (7). It can be seen through Equations 3 and 4 that a reduction in reaction temperature results in an increase to the chemical time scale required for molecules to react and a reduction to the Damköhler number, which represents a reduction in the effectiveness of combustion.

Compared to conventional sprinkler systems, the smaller droplets of mist sprays have greater efficiency in absorbing heat from the gas phase and evaporate more readily (22). This greater efficiency is as a result of the typical diameter of droplets created by mist suppression systems being of the same order of magnitude as the flame reaction zone thickness, being approximately 0.1 mm (15). The effect of this is that “water mist systems can interact directly with the reaction zone” (15):

- Increasing the amount of heat absorbed within the flame inhibiting the chain reaction process, and
- Evaporating more readily causing greater levels of oxygen displacement, and reducing the rate of molecular interactions required to oxidise the fuel (32).

In this way, a properly designed water mist suppression system, utilised as a total flooding agent, achieves key acting suppression mechanisms similar to those formerly utilised by halon agent chemical suppressants (23, 33). Although Novozhilov notes that whilst “mist [fire suppression systems] can be considered as a total flooding agent … [its] properties can never match the diffusive abilities of gaseous agents” (34).

In contrast, the droplets of conventional sprinkler systems are significantly larger and “flow through the flames with relatively little interaction” (15), suppressing fires primarily due to the act of surface wetting reducing the rate of pyrolysis (26).

The greater total surface area present within the spray of water mist systems enhances the degree of heat and mass transfer within the combustion gas phase. The extent by which the total surface area of a volume of water droplets increases, and hence the extent by which the proportionality of heat and mass transfer increases, with decreasing droplet size, is illustrated within Figure 7. This calculation has assumed that droplets are considered as solid spheres of water having a single monodisperse size. Whilst external forces such as air resistance can act on droplets distorting their shape, “an isolated liquid droplet in equilibrium assumes a spherical shape since this possesses the minimum surface energy” (12). The spherical, monodisperse droplet assumption is considered appropriate for the purposes this illustration.

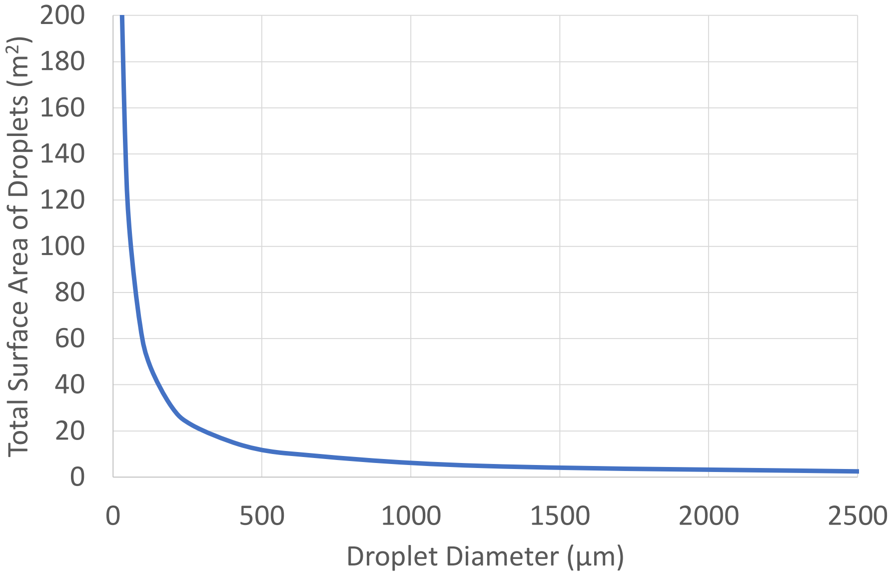

Figure 7 – Total surface area for a monodisperse spray consisting of 1 L of water

2.2.2.3. Practical Application of Physical and Chemical Mechanisms of Suppression by Water

As detailed within Section 2.2.3, many studies on species production during mist suppression found in literature, utilising a diverse range of fuels, report that the measured concentration of carbon monoxide initially significantly increases for a temporary duration, before reducing with time. It is reported by Atreya et al. (35) that a key mechanism behind this short, but significant, increase in carbon monoxide concentration is the chemical enhancement as a result of the increased rate of mixing imposed by the water spray. With increasing water flux, the effects of the inhibiting suppression mechanisms overwhelm this competing process, reducing the heat release rate and consequently the generation of products of combustion. Similar results were also found by Kim et al. (36) who found that the effect on enhancement of the flame increased with increasing velocity of water spray and that the key parameter related to extinction of pool fires was the imposed water flux.

Further, Mawhinney et al. (20) showed that identifying the primary mechanism involved in the extinction of a flame is a complex process and dependant on the interaction of the fuel type, enclosure environment and properties of the water spray. Regarding liquid fuel types, in order for extinction to be effective, the water mist must be sufficient to reduce the temperature of the fuel and its environment below the flashpoint of the fuel in order to prevent re-ignition. In addition, Mawhinney et al. (20) found that the interaction of mist suppression systems on charring solid fuels was further complicated as insulating char reduces the ability of the mist to act on cooling the pyrolyzing fuel, either requiring a greater volume of liquid to cool the fuel bed through the accumulation (or pooling) of droplets or early activation where “the flame height and plume velocities … are relatively low” (20).

Suh et at. (37) found that the act of applying water vapour at various concentrations, not liquid water droplets, within a counterflow diffusion flame apparatus reduced the concentration of carbon monoxide produced, while increasing the concentration of carbon dioxide. In unsuppressed forms of combustion, the oxidation of carbon monoxide is a difficult process. However, the addition of water mist produces significant amounts of the hydroxyl radical, $^{\cdot}OH$, an extremely reactive subspecies which is readily able to oxidise the carbon monoxide molecules to form carbon dioxide as shown below (38).

$$\begin{gathered} O_2 \rightarrow 2O \\ O + H_2O \rightarrow 2{\cdot}OH \\ CO + {\cdot}OH \rightarrow CO_2 + H \end{gathered} \qquad \textit{Reaction 6}$$

Suh et at. (37) propose that the hydroxyl radical present as a result of the addition of water vapour reacts with the carbon monoxide products of the intermediate chemical reaction steps to form carbon dioxide. Therefore, whilst water vapour acts to provide an inert atmosphere, inhibiting combustion and promoting the production of carbon monoxide, the hydroxyl radical acts to convert the intermediate carbon monoxide species into carbon dioxide. This behaviour is consistent with that observed within many of the analogous experimental studies within Section 2.2.3 where the measured concentration of carbon monoxide steadily reduces after a short duration spike after which the droplets have partially transitioned to vapour and the hydroxyl radical is present to interact with the intermediate species of combustion.

However, the hydroxyl radical does not act solely to reduce the level of carbon monoxide present. As noted within Section 2.2.2.1, the hydroxyl radical also acts to oxidise soot particles present to form carbon monoxide molecules (31).

2.2.3. Existing Analogous Experimental Studies

An important part of the literature review is to gain an understanding of all existing analogous experimental studies addressing the generation of products of incomplete combustion during fire and water droplet interactions. The review identified twenty different studies published within academic literature addressing this relationship to varying degrees. Approximately half of the studies identified did not explicitly explore the influence of the factors that influenced the generation of carbon monoxide and only noted the degree and duration of the readings recorded within suppression tests undertaken for other purposes, such as measuring reduction in heat release rate as a result of suppression.

The twenty analogous studies identified through the literature review have been performed utilising:

- A range of fuels,
- Significantly different scales of tests and heat release rates,
- A variety of ventilation conditions,
- A range of mist droplet size distributions, and
- A variety of heating conditions.

Despite their significant differences, from small bench-scale tests to full-scale tunnel tests utilising a diverse range of fuels, all of these studies have reported the influence that the insertion of water droplets have on the completeness of combustion. The effect of this interruption in combustion is most readily seen through the increased volume fraction of carbon monoxide present as a result of water suppression, which was recorded to be significantly influenced by the addition of water droplets.

2.2.3.1. Tunnel Fire Studies

Five of the sources identified through the literature review were studies related to tunnel fire dynamics. It is considered that the reporting of species of combustion is prevalent within tunnel fire research due to the potential extended occupant exposure durations within these environments compared to a more typical compartmented built environment.

The SP Technical Research Institute of Sweden (now known as RISE Research Institutes of Sweden) has undertaken both full-scale and reduced-scale tunnel tests of fixed firefighting systems to study the effects of suppression on the resultant heat release rate of the fire and combustion products generated (8, 39). These studies were the impetus for developing the research question forming the basis of this thesis. Ingason et al. (39) performed full-scale fire tests within the Runehamar tunnel incorporating 420 standardised wooden pallets using suppression systems with mean droplet sizes of 1-2.5 mm. The nozzles utilised within the study incorporated a horizontal spray concept developed by Brandskyddslaget AB, known as T-REX nozzles (39). It is noted that this tunnel suppression concept was taken over and commercialised by TYCO/Johnson Controls as the TN nozzle system (40). These studies found that prior to activation of the suppression system, the level of carbon monoxide at mid-tunnel height, 1000 m downstream of the test fires was undetectable. However, shortly following activation of the deluge suppression system carbon monoxide concentrations at the same location were measured as increasing to 700 ppm and 2,400 ppm, depending on the type of nozzle and operating pressure employed. It was observed that the level of carbon monoxide for each of the tests was generally proportional to the heat release rates within each of the tests.

The 1:4 scale tunnel tests undertaken by Li et al. (8) utilised a 15 m long, 2.8 m wide and 1.4 m high apparatus incorporating scaled deluge nozzles and standardised pine wood, polyethylene or polyurethane cribs as fuels. The nozzles applied within this study were 1:4 scaled T-REX nozzles producing a similar horizontal spray to what was utilised by Ingason et al. (39) within the full-scale tests, and were positioned along the roof of the scaled tunnel. It is considered that there are many advantages to scaling down commercial deluge nozzles to provide direct applicability to the scaled apparatus. However, a key disadvantage to this approach is that unknown droplet sizes are produced unless a measurement of the droplet size distribution is also undertaken as part of the study. No information is provided by Li et al. regarding how the atomisation of droplets is altered by the act of reducing the size of the nozzle and deflector plates. Li et al. (8) found that significant increases in the volume fraction of carbon monoxide were observed for all tests up to increases of approximately 450%, with less significant volume fraction increases present for plastic fuels. A key finding from this study was that fire suppression does not cause adverse effects, in terms of high carbon monoxide concentrations, if the fire size is suppressed to less than 40% of the free-burn heat release rate (8).

Similar to the results found by Ingason et al. (39), full-scale tunnel tests performed by Efectis Nederland BV (41) and Cheong et at. (9) found that when suppression systems within tunnels are activated soon after detection of the fire, the heat release rate, temperatures and volume fraction of carbon monoxide produced is significantly reduced. Further, Efectis Nederland BV (41) found that where fires consisting of liquid pools are quickly extinguished, the high temperatures and high levels of carbon monoxide concentration produced dissipate quickly. Whereas, the tests incorporating large wooden cribs took significantly longer to extinguish leading to higher temperatures and volume fractions of carbon monoxide being present for longer durations downstream (41). The type of mist nozzles utilised within this test are not specified within the report, nor are the droplet distributions listed, however it is noted that the properties of the sprays were such that only partial suppression was achieved. The Efectis study showed that the level of carbon monoxide, 50 m downstream of the fire, increased by up to 1400% for the solid fuel tests (41). The volume fraction of carbon monoxide remained elevated for lengths longer that 300 m downstream of the fire until extinguishment occurred, potentially posing a significant risk to any occupants present within this space.

The tunnel fire suppression studies undertaken by Cheong et at. (9) showed that upon activation of the suppression system, the heat release rate of the fire was approximately 4 times less than the unsuppressed heat release rate. Despite the reduced heat release rate, the carbon monoxide volume fraction increased by 500% downstream of the fire, an effective increase of 2000% given the reduced level of combustion (9).

Yang et al. (42) performed laboratory-scale tests to study how mist suppression systems are influenced by the influence of longitudinal ventilation within tunnels. This study listed nominal droplet diameters of 120 μm, 210 μm and 300 μm with no information of the distribution of these sprays. However, the results show that in a tunnel environment the act of applying a high-level water mist can result in the drag down of smoke and carbon monoxide particles downstream of the fire, with greater lower layer concentrations observed for tests involving larger droplets. The results shown within the study by Yang et al. (42) found a negligible difference between the tests of various droplet sizes and the highest volume fraction of carbon monoxide present when both the mist suppression and longitudinal ventilation were active resulting in approximately a 300% increase compared to when neither systems were active.

2.2.3.2. Plastic Fuel Studies

A key research organisation in this topic of suppression and gaseous species production is the State Key Laboratory of Fire Science at the University of Science and Technology of China which is responsible or affiliated with thirteen of the twenty identified studies (27, 28, 38, 43-52). Eleven of these studies were performed within a test chamber, having dimensions of 0.6 m x 0.6 m x 0.7 m, enabling the mist suppression system to behave as a flooding system as well as through direct application. Between 2005 and 2007, this research group published six studies investigating the resulting products of combustion when polymethyl methacrylate (PMMA) or polyvinyl chloride (PVC) fuelled fires, sustained through a conical heater, were acted upon by water mist suppression systems (27, 28, 43, 44, 49, 50). These tests incorporated a traditional ceiling nozzle configuration, discharging water droplets with mean volume diameters ranging between 70-100 µm, and imposed heat fluxes between 20-70 kW/m^2. Generally, these research studies reported that the measured concentration of carbon monoxide increased rapidly upon activation of the mist suppression system, up to 300% of the initial concentration. This period of elevated carbon monoxide concentration had a duration of less than 10 seconds before the reduced heat release rate slowed the generation of products of combustion.

Yao et al. (47) at the State Key Laboratory of Fire Science have undertaken studies of the effects of water mist suppression on PMMA fires without the use of an external heat source to maintain combustion. This study also utilised a vertical nozzle configuration, however it involved sprays with droplets having mean volume diameters in the order of 200-300 µm. Yao et al. (47) reported that upon the application of water mist the HRR reduced to 10-30% of the size of the unsuppressed fire. The effect of this reduction in combustion resulted in the absolute concentration of carbon monoxide measured being reduced to 50-80% of levels observed prior to suppression. Yao et al. state that the "local carbon monoxide production rate increased due to incomplete combustion" (47) and this is seen through examining the change in carbon monoxide yield accounting for the reduced heat release rate of combustion. The carbon monoxide yield is seen to increase by between approximately 250% for lower operating pressures tested up to approximately 700%, when the reduction of HRR is taken into account.

2.2.3.3. Liquid Fuel Studies

Two studies exploring the effects of water mist application to cooking oil fires have also been performed at the State Key Laboratory of Fire Science (38, 45). The study performed by Fang et al. (38) was concerned with the extinguishing ability of water mist on oil fires, and hence did not incorporate an external heat flux source. This study showed that droplets with mean volume diameters of approximately 100 µm resulted in the heat release rate of the oil fire more than doubling due to the droplets having sufficient velocity (approximately 5 m/s in the tests performed) to reach the surface of the fuel and cause flare-up. Qin et al. (45) found that when cooking oil fires were externally heated with 40 kW/m^2 and subject to water droplets with mean volume diameters of approximately 60-100 µm, the concentration of carbon monoxide increased by 500-600%, up to an absolute concentration of 3,000 ppm within the exhaust gas mixture. Similar to Fang et al. (38), Qin et al. found that, depending on water pressure, the heat release rate of the fire increases by 150-250% before the water flux reaches a critical level and extinguishment occurs.

Two recent studies (51, 52) have been undertaken jointly between the State Key Laboratory of Fire Science and Central South University in China concerning the use of water mist fire suppression on gasoline and diesel fuels, featuring no external heat flux source. These studies report the application of average droplet diameters in the order of 100 μm within a 3 m x 3 m x 3 m enclosure, with a door opening, subject to differing levels of exhaust flow. The results show that prior to the application of water mist the concentration of carbon monoxide measured was negligible. Following the application of water mist, the volume fraction of carbon monoxide measured increased to between 30 ppm and 60 ppm, with the higher concentrations being present within the lower ventilated cases. It is noted that these measured volume fractions remained relatively stable at these higher concentrations even while the HRR reduced significantly, to the point of extinguishment for most cases.

Gupta et al. (32) studied the effects of water mist on a heptane fire, subject to no external heat source and placed within a 1 m x 1 m x 1 m enclosure as a total flooding suppression design. A gaseous energy atomiser type nozzle was employed generating a spray consisting of very fine droplets having a median droplet diameter (D_{v50}) of 20-30 μm. Gupta et al. found that upon activation of the mist suppression system, the volume fraction of carbon monoxide increased rapidly to a level approximately 400% of levels observed prior to suppression. It was found that tests utilising higher operating pressures, with corresponding higher water flux rates, droplet velocities and distributions of smaller droplets, generally resulted in higher concentrations of carbon monoxide being present. Due to the largely sealed compartment, once gases were generated, they remained present until the experiment was terminated and the hot gases flushed out.

2.2.3.4. Other Studies

Downie et al. (53) performed a laboratory-scale test considering the effects of mist suppression on a natural gas fire within a 2 m x 2 m x 2 m enclosure, utilising a nozzle producing a hollow cone spray with droplet distributions having a Sauter mean diameter of 250-270 μm. This study employed a traditional ceiling discharge of droplets, however it was noted that the "the plume-to-spray ratio was large, resulting in a strong deflection of the spray away from the fire" (53). The momentum of the plume was sufficient to overcome the momentum of droplets. Despite the plume imposing a momentum thrust 5-10 times that of the spray, the enclose effect of the experimental set-up resulted in droplets being entrained into the region of combustion. The application of mist showed a negligible change in measured centreline plume temperatures. Carbon monoxide readings, sampled directly from the combustion region, showed a significant increase (between 50-150%) as a result of the addition of water mist.

Yao et al. (48) studied the effects of water mist suppression on samples of pine and ethanol. The experiments were performed within a 0.6 m x 0.6 m x 0.7 m enclosure utilising a mean droplet diameter (D_{v50}) of approximately 80 μm, and a 20 kW/m^2 radiant heat source. Yao et al. report that the key variable regarding suppression, and eventual extinguishment, is the volume flux of water within the region of combustion. Where the volume flux of water was not large enough to cause extinguishment, the volume fraction of carbon monoxide was seen to increase by approximately 300% and the degree of interruption to the process of combustion was seen to be significantly greater when the applied spray consisted of a distribution of finer droplets. Yao et al. also note that the volumetric effects of pyrolysis within a solid fuel are less influenced by the cooling effects associated with the water spray (48), and hence mist suppression systems are less effective at extinguishing charring solid fuels.

Qin et al. (46) studied the effect of water mist suppression on ghee flames, a material commonly used within eternal lamps featured in historical and spiritual buildings throughout Asia. The experiments were performed within the State Key Laboratory of Fire Science's 0.6 m x 0.6 m x 0.7 m enclosure utilising mean droplet diameters between 40 μm and 120 μm. An external heat flux of 50 kW/m^2 and 70 kW/m^2 were imposed to provide stable burning conditions. Qin et al. found that upon activation of the mist suppression system, the level of carbon monoxide increased to a maximum of 3000 ppm, an increase of 300-600% compared to the pre-suppressed concentration. It was reported that the higher operating pressures, and associated smaller droplet distributions and larger water flow rates, resulted in higher peak heat release rates and carbon monoxide level occurring.

2.2.3.5. Summary of Key Findings

The vast majority of existing analogous studies identified in literature are predominantly concerned with the effects of mist suppression on the heat release rate of fires and temperature development. As a result, the reporting of all key experimental parameters associated with the generation of carbon monoxide have not been listed within this previous research. Therefore, drawing comparisons between results of different papers in literature and this study is challenging based on the information published.

For the majority of experiments, utilising a range of fuels, the activation of mist suppression systems corresponds with a short duration peak in carbon monoxide concentration detected. After which, the trend in carbon monoxide concentration over time is consistent with the change in heat release rate over time. In other words, if the properties of suppression are such that the heat release rate of the fire is reduced, the level of carbon monoxide measured is seen to reduce in a similar manner.

A key consideration within the studies identified is the influence of different water droplet sizes on the extent of heat release rate reduction. As such, the vast majority of studies show that sprays consisting of smaller water droplets correspond with higher increases in carbon monoxide concentrations. This is considered to be due to the greater efficiency of heat and mass transfer associated with the increased aggregate droplet surface area.

However, many of the studies listed have not been explicit in the distribution of droplet sizes within the water sprays considered within the tests, with the majority simply reporting a single characteristic diameter. Given the importance of small changes in droplet diameters on the efficiency of heat and mass transfer through suppression, having a more robust understanding of all droplet sizes interacting with the flame, not just the mean or median size, is crucial for understanding the results.

3. Experimental Set-up

The experimental set-up was designed to focus on the effect of water droplet interaction on the gas phase chemistry of the fire. The intent of this study is centred on fire suppression, not extinguishment. Key findings from the literature review used to inform the experimental design are discussed in detail in this section. Components of the testing regime are described in detail for transparency.

3.1. Apparatus

The experimental apparatus was designed to determine how the products of combustion vary when fires are partially suppressed under differing conditions including:

- Water droplet size within a water spray,
- Rate of water applied through a spray,
- Fuel type (gaseous, liquid, or solid), and
- Heat release rate of the fire.

Figure 8 provides a schematic of the experimental apparatus utilised within the liquid pool fire and solid fuel tests. The apparatus for the gaseous fuel experiments were identical with the exception that the fuel and spill pans were replaced by a sandbox burner.

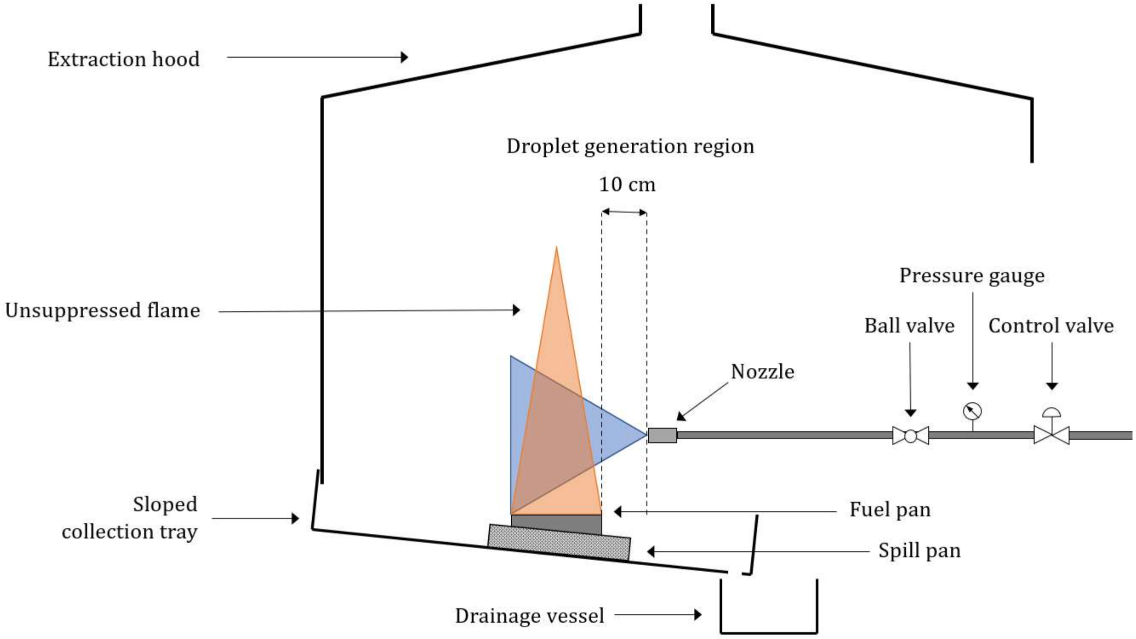

Figure 8 – Experimental apparatus

The entire set-up was positioned beneath an oxygen consumption calorimetry extraction hood to capture and analyse the products of combustion. The fuel bed was positioned so as to remain level on a sloped water collection tray. This tray was utilised in order to quantify the volume of water which did not vaporise within the flame.

The fuel pan was placed within a larger spill pan. In the event that water was discharged into the fuel pan causing it to overflow, this spill pan would capture the fuel keeping the fire to a manageable size until the flow of water could be ceased and allow time for the fire extinguisher to be applied as necessary.

The nozzle was orientated perpendicular to the flame and positioned such that there was the greatest interaction with the flame as possible whilst ensuring that no water was discharged within the fuel pan and maintaining a droplet generation region of at least 10 cm. This droplet generation region is considered appropriate to prevent the undue build-up of soot particulate on the nozzle orifice, prior to activation, which would potentially lead to impaired nozzle performance. Further, studies undertaken by Santangelo (21) show that an axial distance of 10 cm is appropriate to balance the competing processes of coalescence and secondary atomisation as a function of Weber number.

A control valve was used to adjust the water pressure from the mains water supply to the pre-defined levels and a ball valve was used to initiate the discharge of mist within the set suppression periods.

3.2. Factors Influencing Experimental Design

In this section, it is described how concepts from the literature informed the decision making in the development of the experimental set-up detailed within Section 3.1.

3.2.1. Perpendicular Discharge of Water

For the most common fires present within the built environment, being those involving solid materials, the dominant mechanism resulting in extinguishment is fuel cooling (12). Conversely, the application of water to liquid pool fires can result in flare-up as the vaporising water increases the surface area of the liquid fuel potentially significantly increasing the heat release rate of the fire (24). Studies undertaken by Rasbash et al. (26) showed that perpendicular water sprays acting on pool fires resulted in no extinction or significant changes in heat release rate. For the purposes of this study, a perpendicular discharge/spray is one in which the spray momentum flows act perpendicularly (horizontally) on the predominant momentum flows of the flame (which are vertical). Further, the collection of water within the gaseous fuel sandbox burner significantly increases the likelihood of flame extinguishment and the potential explosive risk.

For the reasons listed above, it was decided to minimise the potential for water to interact directly with the fuel bed, through the use of a perpendicular application of water mist with the nozzle positioned in such a way to avoid direct water impingement on the fuel surface.

3.2.2. External Heat Source

A common feature in the analogous experimental studies involving solid fuels, detailed in Section 2.2.3, is the use of an external heat source, typically in the form of a conical heater, to ensure that the fuel is provided with sufficient energy to undergo pyrolysis and reduce the ease to which a fire will be extinguished. Given this study will predominantly focus on gaseous and liquid fuels, as well as the intent to avoid direct water impingement on the fuel surface through perpendicular application, it was considered that the use of an external heat source was not necessary to ensure that the test fires were suppressed and not extinguished.

A solid fuel test was performed for comparison to the liquid and gaseous fuel tests undertaken. An external heat source, in the form of a pool of heptane, was utilised as an ignition source and to ensure stable combustion of the chosen plastic polymer.

3.2.3. Decoupling of Droplet Sizes and Water Flow Rate

A feature of pressure energy atomisers (the types of nozzles utilised within this study) is that the generation of droplets and rate of water dispersed are both functions of the incoming pressure of the water supply. Therefore, to decouple the effects of droplet size and water flow rate on the results, two different nozzles were utilised within the study: one producing a solid cone of water droplets; and one producing a hollow cone of water droplets.

3.2.4. Free-burning Fire Arrangement

The nature of real-world fires subject to mist suppression systems is that they occur within the built environment and therefore within some sort of enclosure, whether within a building compartment, tunnel, or smaller enclosure such as an engine compartment.

A key consideration in developing the experimental apparatus was whether the study should consider a well-ventilated and free-burning fire, or a fire positioned within a scaled compartment. Performing tests within an enclosure was considered to more accurately represent a real-world application of mist suppression systems and promote the entrainment of droplets into the region of combustion. However, in order to isolate the effects of partial suppression on carbon monoxide production from incomplete combustion occurring as a result of the ventilation conditions imposed, a free-burning fire arrangement was adopted within this study.

3.3. Testing Regime

A total of 74 experiments were undertaken as part of this study, varying fuel type, nozzle type, water pressure and conducting three trials of each test to ensure repeatability. The testing regime is detailed within the following sections.

3.3.1. Fuel Types

The majority of this study involved tests utilising either heptane (liquid) or propane (gaseous) fuels. These fuels were chosen based on their inherent sootiness and carbon monoxide yields within well-ventilated free-burn conditions (54) to promote the adverse results of the potential imposed incomplete combustion as a result of suppression. Another factor in the selection of these fuels was their familiarity and ready availability within the laboratory.

A single solid fuel test set involving acrylonitrile butadiene styrene (ABS), a thermoset polymer with a relatively high smoke yield and propensity for incomplete combustion (55) was also undertaken to provide a starting point for future studies incorporating other fuels. The ABS plastic was placed above a pool of heptane which acted as an ignition source and ensured that the solid fuel was not extinguished as a result of mist activation. Further details are listed within Section 3.3.6.

3.3.2. Fire Size

The influence of heat release rate on the generated products of combustion was explored through the use of two different fire sizes for each fuel. The heptane fuel tests were undertaken utilising pans of 20 cm and 25 cm in diameter, respectively representing the low and high heat release rates. Due to the potential for partial heat transfer enclosure effects as a result of the steel plates installed to assist with water collection and drainage, heat release rates were measured through oxygen consumption calorimetry rather than calculated theoretically. The gas analysis undertaken showed that the unsuppressed heat release rate of these heptane fires was approximately 77 kW for the larger fire and 48 kW for the smaller fire. For tests involving propane, the flow rate of this fuel was controlled in order to achieve a heat release rate consistent with that measured through the heptane fuel pans.

Table 2 – Heat release rates applied

Test ID Range	Fuel	HRR Identification	Initial HRR. (kW)	Suppressed HRR. (kW)
T1-T6	Liquid	High	77.6 ± 4.9	69.4 ± 6.1
T7-T12	Liquid	Low	48.5 ± 4.3	45.4 ± 4.4
T13-T18	Gas	High	77.3 ± 1.6	76.3 ± 2.4
T19-T24	Gas	Low	43.2 ± 1.1	41.7 ± 1.6

It is noted that the first low HRR liquid fuel fires tested, which were used to determine the appropriate comparative propane flow rate, were on the lower end of the resultant range of heat release rates (approximately 44 kW). Hence, this accounts for the slight difference in averages between the smaller HRRs measured for the gas and liquid fuels.

3.3.3. Nozzle Types

The act of generating water droplets and the knowledge of the spray created are key aspects of the analysis undertaken as part of this work. Two different mist generation nozzles were utilised within this study to enable the effects of droplet size to be considered independently from the quantity of water applied, whilst still employing pressure energy atomiser nozzles. By using a nozzle discharging a solid cone of water droplets and another discharging a hollow cone of droplets, the volume flow rate of water applied can be compared independently of the droplets produced via each nozzle. The two nozzles selected are the GW Sprinkler AS, GW M2 nozzle (a solid cone nozzle) and the Lechler Series 216.496 (a hollow cone nozzle). The technical specifications of each nozzle are provided within Appendix C.

Table 3 – Mist nozzle properties

Property	**GW M2** (56)	**Lechler 216** (57)
Spray profile	Solid cone	Hollow cone
Spray angle	60°	90°
Intended applications	Enclosed space fire suppression, i.e. within ductwork or engine compartments	Cooling and cleaning of gas, spray drying and desuperheating

Figure 9 – Mist nozzles utilised
GW Sprinkler AS, GW M2 (left) and Lechler Series 216.496 (right)

A simplified concept of the cross-sectional interaction between the sprays generated by each of the nozzles and a theoretical 25 cm diameter heptane pool fire is shown within Figure 10. It is noted that these figures are conceptual in nature and intended to provide a simple visualisation of the effects of how the properties of the nozzles influence the spray pattern generated. The complex interaction between the momentum flows of the spray and flame have been omitted from these conceptualisations. The comparatively high momentum of the water spray, even at low pressures, compared to the momentum of gaseous flows of the flame would result in a strong deflection of the flame around the cone of water spray. Therefore, the resulting interaction volume of the water spray and flame is more complex than simply considering the overlapping regions shown within Figure 10.

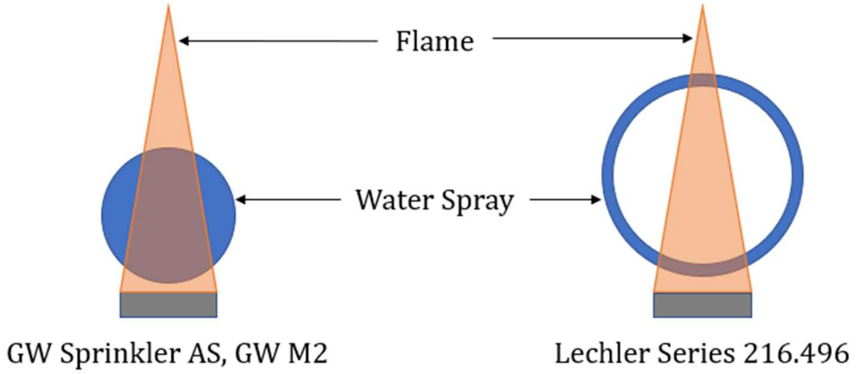

Figure 10 – Interaction area of the nozzle sprays with a theoretical fire

Both GW Sprinkler A/S and Lechler have undertaken measurement studies of the droplet size distribution produced within these polydisperse sprays over a range of operating pressures, which have been included within the technical specification documentation in Appendix C. As discussed within Section 2.2.1, it is common to define droplet size distributions as three volume diameters, typically D_{v10}, D_{v50} and D_{v90}, representing the 10th, 50th and 90th volume percentile. The results of the manufacturer's droplet size distribution studies have been extracted within Table 4.

Table 4 – Droplet size distribution

Operating pressure (bar)	**Droplet size (µm)**					
	GW M2 (56)			**Lechler 216** (58)		
	D_{v10}	D_{v50}	D_{v90}	D_{v10}	D_{v50}	D_{v90}
1.5	-	-	-	114	287	472
3	66	163	268	94	253	476
5	-	-	-	91	221	398
7	43	116	211	-	-	-
12	37	103	117	-	-	-

3.3.4. Testing Pressures

When developing the experimental apparatus, it was initially desired to conduct tests over the greatest range of operating pressures as possible, ideally up to approximately 10 bar. However, it quickly became evident that it would not be possible to store the required amount of water at pressure to provide the desired duration of mist application within a set-up that could readily be developed within the laboratory for pressure energy atomiser nozzles. Initial trials showed that, whilst containers were able to hold water pressurised to approximately 8 bar, after more than a few seconds of activation the pressure had reduced to less than 3 bar. It was considered that such a range of water pressures over the period of activation was not appropriate to analyse the influence of water droplet sizes, nor water application rates.

The mains water pressure available within the laboratory was measured to achieve up to 3.5 bar with slight fluctuations over time of ±0.1 bar. Whilst this pressure is listed as the lower limit of the operating pressure for the GW Sprinkler AS, GW M2 nozzle, water droplet size distributions are provided for pressures down to 3 bar (56). On the other hand, the Lechler Series 216.496 has an operating pressure of between 1 and 20 bar with water droplet size distributions provided for pressures down to 1.5 bar (57, 58).

It is considered that uncertainties associated with the adoption of lower than ideal testing pressures are more than outweighed by the increased confidence in the results from having a longer mist application period through the use of unlimited water volume from the water mains. Given the droplet size distribution studies undertaken by the manufacturers, it was considered that testing pressures of 1.5, 2 and 3 bar would allow for testing of sprays consisting of a cross section of droplet distributions and water discharge rates within the bounds of what was readily achievable within the laboratory.

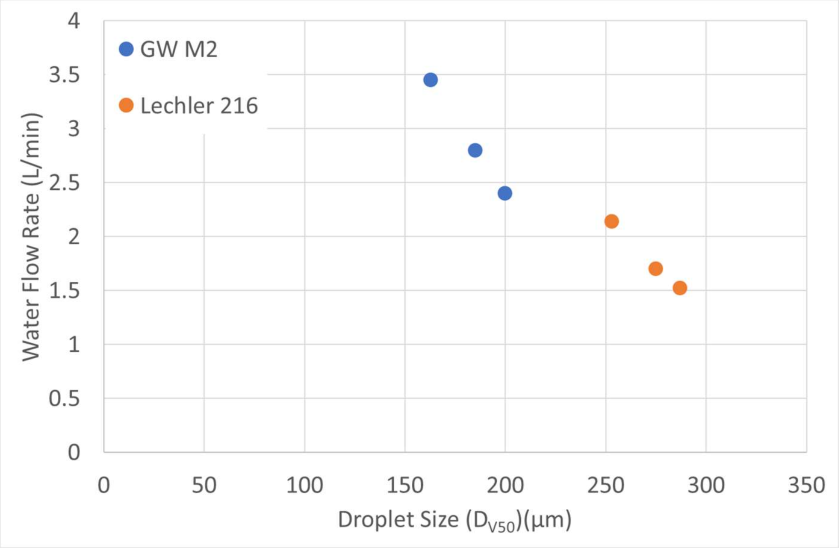

Figure 11 – Water flow rate and volume median diameter at testing pressures

The testing pressures adopted result in the GW M2 nozzle producing Class 2 sprays and the Lechler 216 producing Class 3 sprays in accordance with the classification system and chart shown within Figure 5.

3.3.5. Accuracy and Calibration

In order to ensure the accuracy of the measurements taken, strict gas analysis equipment calibrations were performed frequently throughout the testing process. The calibration process adopted was similar to that utilised within the gas analyser calibration detailed for cone calorimeters as per ISO 5660-1:2015 (59).

A key feature of oxygen consumption calorimetry and gas analysers is that the analysis is required to be undertaken on a dry basis to determine a species mole fraction (60). As a result of the experimental set-up utilised within this study, it is likely that a proportion of the applied water droplets would be drawn through the hood exhaust system and to the point of gas sampling. Therefore, a source of error is the potential drift in readings as the result of moisture influencing the calculated species mole fraction.

To maintain the accuracy of readings throughout the process of testing, and across the range of gas concentrations anticipated to be sampled, frequent low and high calibrations of O_2, CO_2 and CO were performed within the gas analyser. Low calibration readings were performed utilising a pure sample of nitrogen to calibrate the readings of O_2, CO_2 and CO to zero. The high calibration of CO_2 and CO was performed through the use of a standardised span gas having a certified concentration of 5% carbon dioxide and 0.5% carbon monoxide. The high calibration of O_2 was performed through the use of ambient air.

This calibration was performed a minimum of twice daily. The ambient conditions within the fire laboratory proved to be relatively stable. Therefore, prior to the initiation of each test, the relative concentrations of the ambient air being sampled were checked and the gas analyser was recalibrated if any drift in ambient readings was observed.

Further, the filtration system, including the drying agent, moisture traps and balston filter, were changed or emptied daily. In addition, the balston filter was also changed when the sampling gas flow rate dropped as a result of particulate build up through the gas sampling tube.

3.3.6. Solid Fuel Tests

A set of tests were performed utilising a sample of acrylonitrile butadiene styrene (ABS). Combustion tests performed with solid fuels are inherently more complex and variable than those performed with comparatively simpler gaseous or liquid fuels.

For tests involving solid fuels it is not possible to establish a quasi-steady state heat release rate in order to undertake a comparison of baseline exhaust gas analysis followed immediately by a period of suppression, and associated gas analysis. Therefore, two identical samples of ABS were prepared: one utilised within a test in which no suppression was applied; and the other in which the mist suppression system was activated for 180 seconds during the central period of burning. A 10 cm x 10 cm sample of ABS weighing 77.5±0.1 g was wrapped in metallic foil to keep the plastic contained as it melted. An 8 cm x 8 cm piece of foil was removed to expose a face of the plastic and the sample was placed upon a 10 cm x 10 cm piece of insulating board elevated within the fuel pan as shown within Figure 12. Heptane was added to the fuel pan until it reached the underside of the insulating board.

Figure 12 – Solid fuel experimental set-up

3.3.7. Test Protocol

Table 5 lists the testing regime that was undertaken as part of this work. With the exception of the solid fuel tests, each of the test ID numbers were performed three times to ensure that an appropriate level of precision of the results was obtained. The order of tests undertaken was randomised in order to minimise the influence of a drift in parameters or systematic user error.

For each of the tests involving heptane and propane:

- Quasi-steady state burning conditions were established.
- Exhaust gases were sampled for a duration of 120 s during a period in which no mist suppression was applied, in order to establish a baseline exhaust gas profile.
- The baseline period was immediately followed by period of 120 s of mist suppression acting on the fire, and a comparison made of the influence of the applied water mist on the exhaust gas profile.

Table 5 – Testing regime

Test ID	Fuel	HRR	Nozzle	Pressure (bar)	Dv10 (µm)	Dv50 (µm)	Dv90 (µm)	Flow Rate (L/min)
T1	Liquid	High	GW M2	1.5	85[1]	200[1]	330[1]	2.4
T2	Liquid	High	GW M2	2	75[1]	185[1]	305[1]	2.8
T3	Liquid	High	GW M2	3	66[2]	163[2]	268[2]	3.5
T4	Liquid	High	Lechler 216	1.5	114[2]	287[2]	472[2]	1.5
T5	Liquid	High	Lechler 216	2	105[3]	275[3]	473[3]	1.7
T6	Liquid	High	Lechler 216	3	94[2]	253[2]	476[2]	2.1
T7	Liquid	Low	GW M2	1.5	85[1]	200[1]	330[1]	2.4
T8	Liquid	Low	GW M2	2	75[1]	185[1]	305[1]	2.8
T9	Liquid	Low	GW M2	3	66[2]	163[2]	268[2]	3.5
T10	Liquid	Low	Lechler 216	1.5	114[2]	287[2]	472[2]	1.5
T11	Liquid	Low	Lechler 216	2	105[3]	275[3]	473[3]	1.7
T12	Liquid	Low	Lechler 216	3	94[2]	253[2]	476[2]	2.1
T13	Gas	High	GW M2	1.5	85[1]	200[1]	330[1]	2.4
T14	Gas	High	GW M2	2	75[1]	185[1]	305[1]	2.8
T15	Gas	High	GW M2	3	66[2]	163[2]	268[2]	3.5
T16	Gas	High	Lechler 216	1.5	114[2]	287[2]	472[2]	1.5
T17	Gas	High	Lechler 216	2	105[3]	275[3]	473[3]	1.7
T18	Gas	High	Lechler 216	3	94[2]	253[2]	476[2]	2.1
T19	Gas	Low	GW M2	1.5	85[1]	200[1]	330[1]	2.4
T20	Gas	Low	GW M2	2	75[1]	185[1]	305[1]	2.8
T21	Gas	Low	GW M2	3	66[2]	163[2]	268[2]	3.5
T22	Gas	Low	Lechler 216	1.5	114[2]	287[2]	472[2]	1.5
T23	Gas	Low	Lechler 216	2	105[3]	275[3]	473[3]	1.7
T24	Gas	Low	Lechler 216	3	94[2]	253[2]	476[2]	2.1
S1	Solid + Liquid	-	N/A	N/A	N/A	N/A	N/A	N/A
S2	Solid + Liquid	-	GW M2	3	66[2]	163[2]	268[2]	3.5

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[1] Extrapolation from manufacturers technical specifications
[2] Listed within manufacturers technical specifications
[3] Interpolation from manufacturers technical specifications

4. Theoretical Species Concentration

A theoretical calculation of the carbon monoxide yields has been undertaken in order to gain an insight into how consistent hand calculations are with the experimentally measured concentrations prior to mist suppression. It is noted that there is a degree of simplification incorporated within these calculations, firstly due to the assumption of a single, stable heat release rate which was not the case for the liquid fuel fires and secondly due to the inherent uncertainty of species production during fire. Further, Karlsson and Quintiere note that "Although the generality of the experimentally derived yield data are not well established, they offer the best way to estimate species concentrations" (5).

The following information is considered necessary in order to theoretically predict the concentration of chemical species in fires:

- Chemical composition of the fuel,
- Equivalence ratio of the combustion,
- Mass flow rate of the fuel,
- Mass flow rate of oxygen into the plume, and
- Experimentally determined species yield appropriate to the points listed above.

4.1. Example Calculation Procedure and Results

The example theoretical species concentration calculation below has been undertaken for the larger heptane fires tested, which were determined to have an average heat release rate of 77.6 kW. Table 8 at the rear of this section, contains the results of all of the theoretical calculations undertaken for the fires considered within this study.

<u>Calculate Mass Flow Rate of Fuel</u>

The free burn fuel mass flow rate of a pool of liquid fuel is typically calculated theoretically through Equation 5.

$$\dot{\mathrm{m}}_{\mathrm{f}} = \mathrm{A}_{\mathrm{f}} \cdot \dot{\mathrm{m}}''_{\infty}\left(1 - e^{-k\beta \mathrm{D}}\right) \qquad \textit{Equation 5}$$

As discussed in Section 3.3.2, the steel plates utilised for water collection and drainage result in partial enclosure heat transfer effects and enhanced levels of radiative feedback to the fire. The effect of this is that the free burn considerations within Equation 5 are not valid for the liquid fuel fire. Therefore, the fuel mass flow rate has been calculated through dividing the experimentally measured heat release rate by the effective heat of combustion of the fuel, to enable effective comparison with the species concentrations seen during the tests. The average heat release rate of the large heptane fires tested was determined to be 77.6 kW. The effective heat of combustion of heptane is reported within the SFPE Handbook (61) as 44.6 MJ/kg.

$$\dot{\mathrm{m}}_{\mathrm{f}} = \frac{77.6}{44600}$$

$$\dot{\mathrm{m}}_{\mathrm{f}} = 0.00174\ \mathrm{kg/s}$$

Calculate Mass Flow Rate of Oxygen

Figure 13 shows the steady-state mass flows within the pre-suppression condition. Due to the conservation of mass flows, the incoming flow of air is equal to the difference between the flow of exhaust products and rate of vaporisation of the fuel. The exhaust mass flow rate is determined based on the exhaust fan parameters utilised within the experimental tests.

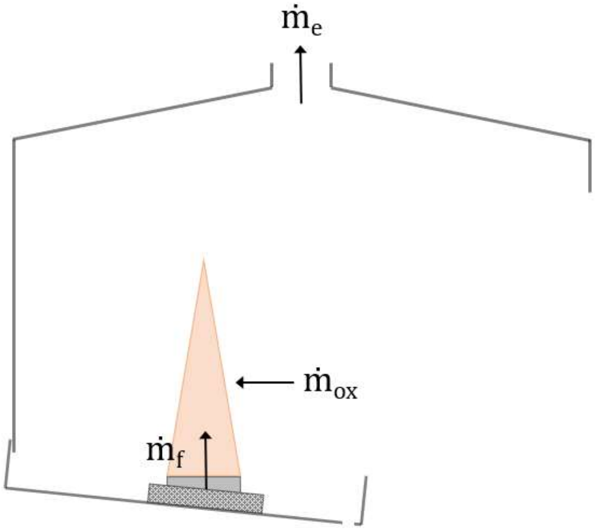

Figure 13 – Mass flows within test scenario

The mass flow rate of oxygen is calculated through Equation 6.

$$\dot{\mathrm{m}}_{\mathrm{ox}} = w_{ox}(\dot{\mathrm{m}}_{\mathrm{e}} - \dot{\mathrm{m}}_{\mathrm{f}}) \qquad \textit{Equation 6}$$

Table 6 provides a list of input parameters used to calculate the mass flow rate of fuel.

Table 6 – Oxygen mass flow rate – Input parameters

Parameter	Value
w_{ox}	0.23
$\dot{m}_e$ (kg/s)	1.33
$\dot{m}_f$ (kg/s)	0.00174

$$\dot{m}_{ox} = 0.23(1.33 - 0.00174)$$

$$\dot{m}_{ox} = 0.305 \text{ kg/s}$$

Calculate Yield of Carbon Monoxide

The ventilation conditions of combustion are considered to have the largest influence on the product yields, and are represented by the equivalence ratio, ϕ. The equivalence ratio is an expression of the fuel mixture fraction compared to the ideal stoichiometric mixture.

The stoichiometric combustion of heptane results in a ratio of 0.284 kg of fuel to 1 kg of oxygen based on the following balanced chemical reaction and the molecular weights of the molecules.

$$C_7H_{16} + 11O_2 \rightarrow 7CO_2 + 8H_2O \qquad \textit{Reaction 7}$$

Table 7 – Molecular weights

Molecule	Molecular Weight (g/mol)
C_7H_{16}	100.2
O_2	32.0

The stoichiometric ratio, r, of fuel and oxygen for the combustion of heptane is shown to be 0.284.

$$r = \frac{M_{C_7H_{16}}}{11 \cdot M_{O_2}}$$

$$r = 0.284$$

Now that the mass flow rates of fuel and oxygen are known for our test set-up, the equivalence ratio can be equated as shown within Equation 7.

$$\phi = \frac{\dot{m}_f/\dot{m}_{ox}}{r} \qquad \textit{Equation 7}$$

$$\phi = \frac{0.00174/0.305}{0.284}$$

$$\phi = 0.0201$$

Well-ventilated fires are defined as those with equivalence ratios less than 1. Therefore, the combustion conditions within this experimental set-up are very much well-ventilated.

Studies undertaken by Tewarson, utilising the ASTM E2058 fire propagation apparatus, have shown that well-ventilated heptane fires have a carbon monoxide yield, y_{co}, of 0.01 g/g (55).

The theoretical mass fraction of carbon monoxide, Y_{CO}, present within the exhaust products is calculated in accordance with Equation 8.

$$Y_{CO} = y_{CO} \cdot f \qquad \textit{Equation 8}$$

Where f is the fuel mass fraction:

$$f = \frac{\dot{m}_f}{\dot{m}_e} \qquad \textit{Equation 9}$$

$$f = \frac{0.00174}{1.33}$$

$$f = 0.0013$$

$$Y_{CO} = 0.01 \cdot 0.0013$$

$$Y_{CO} = 0.0013\% \text{ or } 13 \text{ ppm}$$

As will be shown within Section 5, the volume fraction readings within the exhaust gases, utilising a 25 cm diameter heptane fire and prior to the application of water mist, show values of carbon monoxide of 20.4±0.6 ppm. The results for the other theoretical species yields are provided within Table 8. However, these experimentally measured concentrations include a degree of background level carbon monoxide not considered within the theoretical calculations. Ambient gas concentrations were measured within the laboratory prior to ignition of the test fires. Due to the large amounts of makeup air entering the laboratory as a result of operating the exhaust hood, the ambient readings of carbon monoxide remained relatively constant around 8 ppm. This ambient level of carbon monoxide has been taken into account when drawing comparisons between the theoretically calculated values and those measured experimentally.

It is seen that the theoretically calculated species concentrations vary from the experimentally observed concentrations. As Hull notes "the evolution of carbon monoxide is highly dependent on the conditions, the most significant of which are difficult to create on a small scale" (62). It is important to recognise that chemical species yields do not consist of unique values and are highly variable as a function of temperature, presence of oxygen in the region of combustion and the enclosure environment. Therefore, Hull suggests that "uncertainty or confidence limits should be used with toxic hazard data, because they are often relatively large" (62). As a result, the analysis undertaken within this study will focus on the percentage change in carbon monoxide concentration as a result of suppression, and not on absolute numbers which would vary with the uncertainty in species yield.

The difference between the theoretical yields and experimentally measured yields of carbon monoxide within the propane fuel fires was greater than that observed for the heptane fuel fires. Whereas the heat release rate of a liquid heptane fire is proportional to the area of the fuel, the heat release rate of the propane fires is proportional to the flow rate of gas independent of the size of the burner. Therefore, the availability of an oxidiser to reach the fuel molecules emanating from the gas burner is seen to vary in accordance with the fuel flow rate. It is hypothesised that by not maintaining an equivalent fuel area to heat release rate ratio as utilised within the heptane fuel fires, the yield of carbon monoxide would increase as a result of reduced oxygen availability.

Table 8 – Theoretical species concentration calculation summary

Parameter	**Value**			
Fuel	Heptane	Heptane	Propane	Propane
HRR (kW)	77.6	48.5	77.3	43.2
ΔH_c (MJ/kg)	44.6 (61)	44.6 (61)	46.5 (63)	46.5 (63)
$\dot{m}_f$ (kg/s)	0.00174	0.00109	0.00166	0.0093
$\dot{m}_e$ (kg/s)	1.33	1.33	1.33	1.33
$\dot{m}_{ox}$ (kg/s)	0.305	0.306	0.306	0.306
r	0.284	0.284	0.276	0.276
ϕ	0.0201 Well-ventilated	0.0125 Well-ventilated	0.0197 Well-ventilated	0.0110 Well-ventilated
y_{co} (g/g)	0.01 (55)	0.01 (55)	0.005 (55)	0.005 (55)
f	0.00131	0.00082	0.00125	0.00070
Y_{co} (%)	0.00131	0.00082	0.00063	0.00035
Y_{co} (ppm)	13.1	8.2	6.3	3.5
Difference in experimental measurements from theory (%)	-2.9±3.1	+1.1±3.6	+11.7±5.0	+17.6±3.9

5. Results

In this chapter, the experimental results from the tests outlined within Section 3.3.7 are presented and examined. The results have been separated into two sections; Section 5.1 which documents the results of the 72 tests conducted on the liquid and gaseous fuels, and Section 5.2 documenting the results of the two solid fuel tests. This has been done as the tests on the solid fuels consisted of a single set of dependent variables and no repetitions.

The effects of partial mist suppression of fire on the independent variables, and the high-level influences of the dependent variables considered, are examined within this section. Further detail on the trends and implications of the obtained results are included within the discussion of the results in Section 6.

5.1. Liquid and Gaseous Fuels

The concentration of carbon monoxide under the initial baseline conditions; the concentrations when the fires are suppressed; and the respective percentage increase are shown within Table 9. As noted in Section 4, the absolute yield of carbon monoxide is highly variable, being a function of many combustion variables. Therefore, the results presented and the analysis undertaken have been centred around the percentage changes in carbon monoxide concentration as a result of suppression.

The data presented within Table 9 are the average concentrations recorded over the three repeat measurements for each Test ID, with the plus-minus value representing the range of values recorded over the repeat measurements. As a result of how the experimental set-up within this study was designed, the short duration spike in carbon monoxide readings observed within many of the analogous experimental studies within Section 2.2.3 was not exhibited. The concentration readings reported within Table 9 have been taken as the average over 90 seconds for each condition with the measurements taken within the transition period of the mist suppression being initialised being omitted (30 seconds either side).

Table 9 – Change in carbon monoxide concentration as a result of suppression

Test ID	Fuel	HRR	Nozzle	Pressure (bar)	Initial CO Conc. (ppm)	Suppressed CO Conc. (ppm)	Change (%)
T1	Liquid	High	GW M2	1.5	20.2±1.0	47.5±0.9	+135±17
T2	Liquid	High	GW M2	2	20.8±1.0	62.7±0.9	+200±20
T3	Liquid	High	GW M2	3	19.7±1.1	72.0±1.06	+264±28
T4	Liquid	High	Lechler 216	1.5	19.9±1.6	37.0±1.4	+86±23
T5	Liquid	High	Lechler 216	2	21.5±1.1	43.3±1.0	+101±16
T6	Liquid	High	Lechler 216	3	20.6±1.2	47.5±1.1	+131±20
T7	Liquid	Low	GW M2	1.5	16.0±0.6	33.9±0.5	+112±12
T8	Liquid	Low	GW M2	2	15.7±0.8	35.1±0.7	+123±18
T9	Liquid	Low	GW M2	3	16.8±0.8	44.4±0.7	+164±17
T10	Liquid	Low	Lechler 216	1.5	15.8±1.2	34.6±1.1	+119±25
T11	Liquid	Low	Lechler 216	2	17.2±0.7	33.4±0.6	+95±12
T12	Liquid	Low	Lechler 216	3	16.6±0.6	35.6±0.5	+114±11
T13	Gas	High	GW M2	1.5	16.5±0.2	22.8±0.2	+38±3
T14	Gas	High	GW M2	2	15.6±0.5	31.9±0.4	+105±9
T15	Gas	High	GW M2	3	15.0±0.3	48.8±0.3	+226±10
T16	Gas	High	Lechler 216	1.5	15.7±0.2	18.0±0.2	+14±2
T17	Gas	High	Lechler 216	2	15.7±0.1	23.0±0.2	+46±2
T18	Gas	High	Lechler 216	3	17.0±0.3	27.0±0.3	+59±5
T19	Gas	Low	GW M2	1.5	13.1±0.3	21.0±0.3	+60±6
T20	Gas	Low	GW M2	2	14.2±0.4	26.4±0.4	+85±8
T21	Gas	Low	GW M2	3	13.3±0.2	31.2±0.2	+134±4
T22	Gas	Low	Lechler 216	1.5	13.2±0.3	21.1±0.3	+60±7
T23	Gas	Low	Lechler 216	2	13.4±0.2	20.7±0.2	+54±4
T24	Gas	Low	Lechler 216	3	13.9±0.3	21.5±0.3	+54±6

Figure 14 illustrates the change in carbon monoxide concentrations, averaged over the three repetitions, as a result of mist suppression for each Test ID.

Figure 15 shows an example of the variation in measured carbon monoxide levels recorded for each of the three test repetitions for both a heptane fire and propane fire. It can be seen that the level of fluctuation in carbon monoxide concentration, around the mean, is comparatively small during the baseline period compared to when the mist system is active.

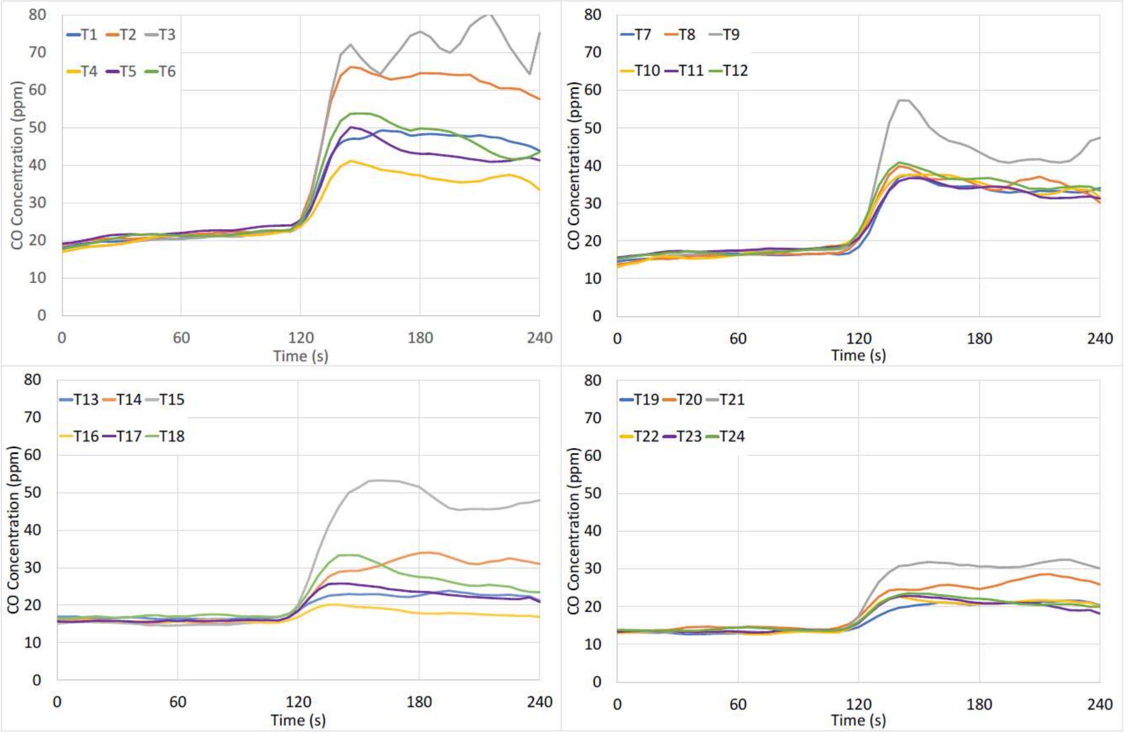

Figure 14 – CO concentration change due to mist suppression
Top left: High HRR Heptane; Top right: Low HRR Heptane; Bottom left: High HRR Propane;
Bottom right: Low HRR Propane

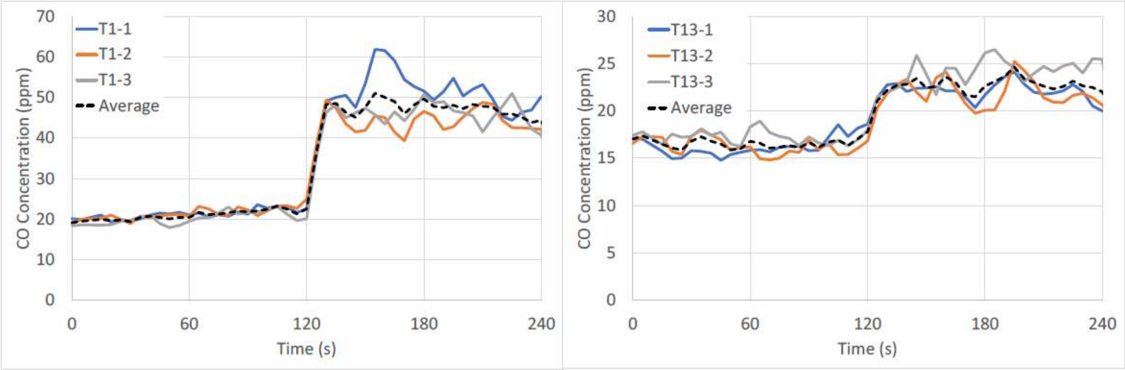

Figure 15 – Example of variation in CO across the three test repetitions

Table 10 details how the heat release rate of the fire was influenced by the act of mist suppression on the fire. Similar to the approach for carbon monoxide concentrations, the heat release rate measurements reported within Table 10 are the averages over a

90 second period for each condition with the measurements taken within the transition period of the mist suppression being initialised being omitted (30 seconds either side). These results are visualised within Figure 16.

Table 10 – Change in HRR as a result of suppression

Test ID	Fuel	HRR	Nozzle	Pressure (bar)	Initial HRR. (kW)	Suppressed HRR. (kW)	Change (%)
T1	Liquid	High	GW M2	1.5	78.8±5.0	61.2±2.1	-22±8
T2	Liquid	High	GW M2	2	78.0±5.6	63.3±2.2	-19±9
T3	Liquid	High	GW M2	3	77.7±4.5	69.9±2.1	-10±8
T4	Liquid	High	Lechler 216	1.5	75.7±4.8	73.3±2.6	-3±10
T5	Liquid	High	Lechler 216	2	79.2±4.5	76.6±2.3	-3±9
T6	Liquid	High	Lechler 216	3	76.0±4.5	71.6±3.8	-6±11
T7	Liquid	Low	GW M2	1.5	48.8±3.6	39.9±0.7	-18±8
T8	Liquid	Low	GW M2	2	47.4±3.8	40.3±1.9	-15±12
T9	Liquid	Low	GW M2	3	53.1±4.5	49.7±2.1	-7±13
T10	Liquid	Low	Lechler 216	1.5	46.4±4.1	45.5±1.8	-2±14
T11	Liquid	Low	Lechler 216	2	48.4±3.9	48.2±1.8	-0±13
T12	Liquid	Low	Lechler 216	3	46.7±2.3	48.6±2.2	-4±10
T13	Gas	High	GW M2	1.5	77.1±0.9	77.2±0.8	-0±2
T14	Gas	High	GW M2	2	77.3±0.7	76.7±2.2	-3±4
T15	Gas	High	GW M2	3	77.6±0.7	74.6±3.3	-4±5
T16	Gas	High	Lechler 216	1.5	77.0±0.6	77.5±0.7	+1±2
T17	Gas	High	Lechler 216	2	78.1±0.8	79.1±1.1	+1±3
T18	Gas	High	Lechler 216	3	74.5±0.4	73.7±1.0	-1±2
T19	Gas	Low	GW M2	1.5	42.6±0.7	41.8±1.0	-2±4
T20	Gas	Low	GW M2	2	42.5±0.9	40.4±1.9	-5±7
T21	Gas	Low	GW M2	3	44.6±0.3	41.8±2.2	-6±6
T22	Gas	Low	Lechler 216	1.5	44.4±0.7	43.7±0.5	-2±3
T23	Gas	Low	Lechler 216	2	42.9±0.6	42.0±0.9	-2±4
T24	Gas	Low	Lechler 216	3	42.5±0.7	41.5±0.9	-2±4

It can be seen that, prior to application of water mist, the heat release rate of the heptane fires was not steady with time. Rather, it increased as the level of radiative feedback to the fuel rose due to the increasing temperature of the steel plates utilised within the experimental set-up. In other words, the test fire radiates heat to the steel water collection plates which, as they get hot, radiate heat back to the liquid fuel increasing the rate of fuel evaporation and generation of gaseous fuel, and hence heat release rate of the fire.

Figure 16 shows that the measured heat release rate of the heptane fires decreased upon activation of the mist suppression, and then remained relatively stable. On the other hand, the heat release rates of the propane fires were much less influenced by the water mist. Following activation of the mist suppression system, the heat release rates of the heptane fires are seen to stabilise with minor fluctuations over time. It is considered that the behaviour of the measured heat release rates of the suppressed heptane fires is a result of a proportion of the water spray acting directly on the steel water collection plates. The water spray acts to maintain a relatively constant temperature of the steel plates, reducing the amount of radiative feedback to the fuel pan and providing a constant mass flow rate of vaporising fuel.

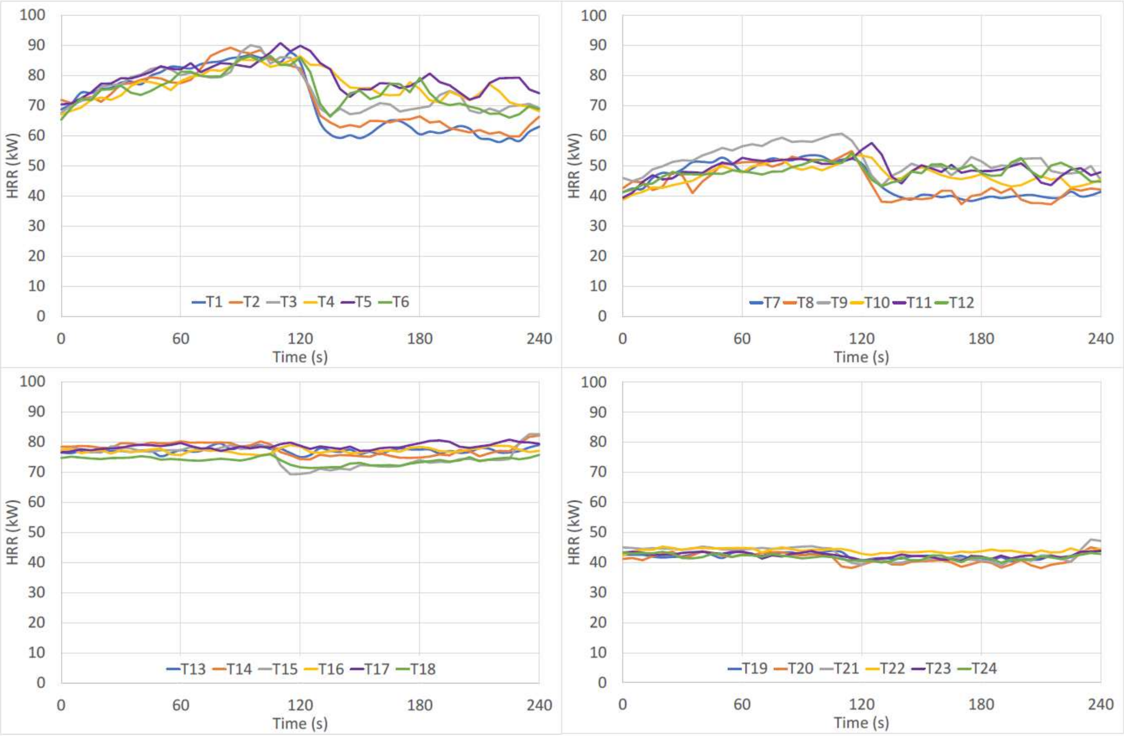

Figure 16 – Heat release rate change due to mist suppression
Top left: High HRR Heptane; Top right: Low HRR Heptane; Bottom left: High HRR Propane; Bottom right: Low HRR Propane

When the mist spray is applied to the fire, not all of the droplets will interact with the flame. As seen within the simplified conceptualisation of the flame and spray interactions (Figure 10, Section 3.3.3), a significant amount of the droplets are likely to travel past the flame with relatively little interaction. Further, in all combinations of the test parameters, the momentum flow of the water mist spray was observed to be significantly greater than the gaseous momentum flow of the flame, resulting in the deflection of the flame around the cone of water spray applied. The result of this was that the interaction of droplets within the region of combustion occurred over a fluctuating and complex three-dimensional volume, which was unable to be expressly determined within this study. However, the level of water flux within this droplet-flame interaction volume is considered to be proportional to the amount of water which was vaporised within the flame. Therefore, a comparison was made between the quantity of water applied and the quantity that was collected within the drainage vessel. The volume of water evaporated within each Test ID is shown within Table 11.

Table 11 – Quantity of water evaporated over the period of suppression

Test ID	Fuel	HRR	Nozzle	Pressure (bar)	Volume Evaporated (L)
T1	Liquid	High	GW M2	1.5	1.19±0.05
T2	Liquid	High	GW M2	2	1.52±0.07
T3	Liquid	High	GW M2	3	2.02±0.22
T4	Liquid	High	Lechler 216	1.5	1.12±0.06
T5	Liquid	High	Lechler 216	2	1.25±0.07
T6	Liquid	High	Lechler 216	3	1.53±0.04
T7	Liquid	Low	GW M2	1.5	0.97±0.01
T8	Liquid	Low	GW M2	2	1.24±0.08
T9	Liquid	Low	GW M2	3	1.73±0.19
T10	Liquid	Low	Lechler 216	1.5	0.81±0.08
T11	Liquid	Low	Lechler 216	2	0.87±0.10
T12	Liquid	Low	Lechler 216	3	0.83±0.55
T13	Gas	High	GW M2	1.5	1.31±0.08
T14	Gas	High	GW M2	2	1.67±0.06
T15	Gas	High	GW M2	3	2.16±0.26
T16	Gas	High	Lechler 216	1.5	1.07±0.04
T17	Gas	High	Lechler 216	2	1.19±0.10

Test ID	Fuel	HRR	Nozzle	Pressure (bar)	Volume Evaporated (L)
T18	Gas	High	Lechler 216	3	1.47±0.08
T19	Gas	Low	GW M2	1.5	1.01±0.05
T20	Gas	Low	GW M2	2	1.23±0.11
T21	Gas	Low	GW M2	3	2.04±0.71
T22	Gas	Low	Lechler 216	1.5	0.85±0.07
T23	Gas	Low	Lechler 216	2	0.74±0.09
T24	Gas	Low	Lechler 216	3	1.01±0.04

5.2. Solid Fuels

As discussed within Section 3.3.6, the tests undertaken for the solid fuels utilised two identical samples of acrylonitrile butadiene styrene (ABS). The weight of each sample, before and after each test, is shown within Table 12. These results indicate that each ABS sample burnt in a similar manner, which is consistent with the visual observations, and that it is appropriate to compare the heat release rate and chemical species production data of each test.

Table 12 – ABS sample mass

Test ID	ABS Sample Mass (g)	ABS Sample Mass with Foil Wrap (g)	Combustion Residue Mass (g)	Loss during Combustion (g)
S1	77.6	86.5	21.9	64.6
S2	77.5	86.0	21.6	64.4

The results of the carbon monoxide concentrations and heat release rates of the solid fuel tests, both subject to mist suppression and no suppression, are shown within Figure 17. The water mist was activated between 300 s and 480 s, evidenced by the increased volume fraction of carbon monoxide during this period. During suppression, the volume fraction of carbon monoxide increased by 91±12% compared to the test where no mist was applied. Over the same period, the heat release rate of the suppressed solid fuel test reduced by 14±5%.

The duration of the mist suppression period during the solid fuel tests was 180 s compared to 120 s duration applied during the liquid and gaseous fuel tests. During the

180 s of spray activation, 10.35 L of droplets were generated by the nozzle, 1.70 L of which were evaporated by the solid fuel test.

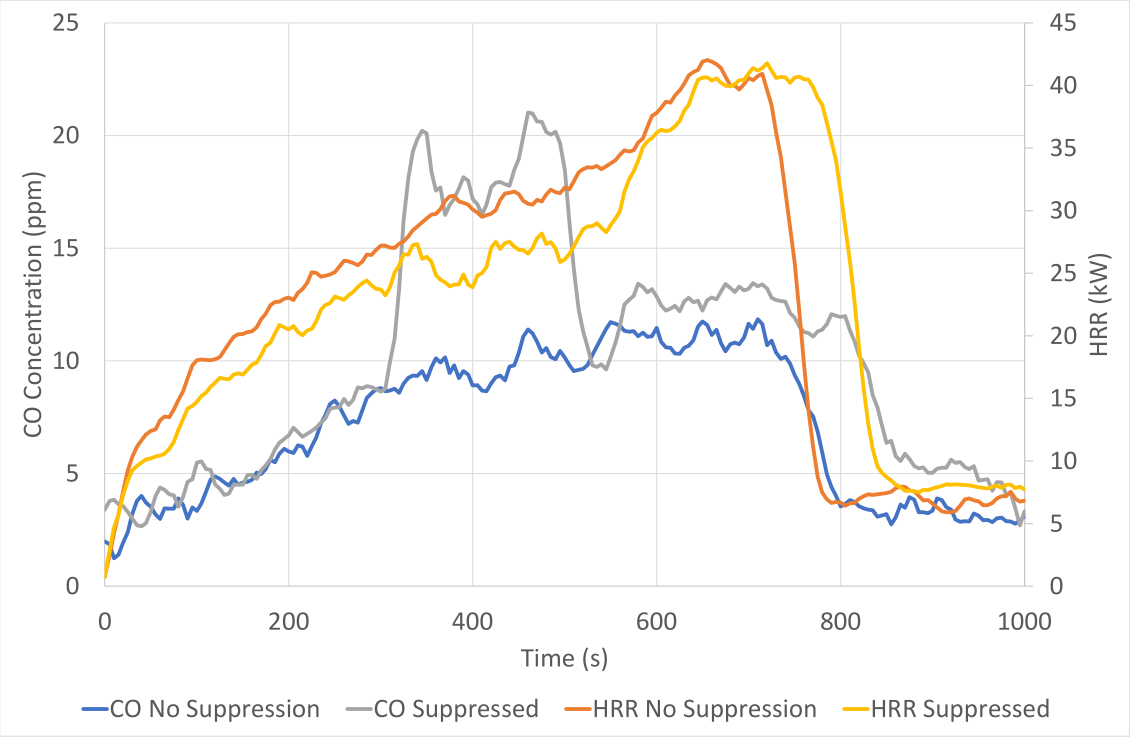

Figure 17 – CO concentration and HRR change due to mist suppression

6. Discussion

The results obtained in this research project support the phenomena observed within existing literature, in that the volume fraction of carbon monoxide present within the fire environment can significantly increase upon the application of water mist. The results indicate that the most influential factor in promoting the generation of carbon monoxide is the three-dimensional droplet-flame interaction volume. Due to the complexities in quantifying and controlling this droplet-flame interaction volume, it is proposed to consider the proportion of water vaporised as a correlated and more readily quantified variable. The enhanced heat transfer qualities that come from the application of smaller water droplets was also seen to be an important factor in inhibiting combustion and the formation of carbon monoxide during suppression. The results suggest that fuels with an inherent tendency to produce carbon monoxide exhibit a greater degree of carbon monoxide species increase as a result of partial suppression. The overarching implication of this study is that commonly applied species product yields, such as Tewarson's (55), may not be appropriate when fires are subject to partial mist suppression with limited reduction in heat release rate.

The following sections explore the trends and implications of the experimental results in further detail.

6.1. Analysis of Variables

A graphical analysis of the factors considered within this study influencing the generation of carbon monoxide within partially suppressed fires has been undertaken to determine their relationship. A scatter plot of all possible bivariate relationships that exist within the multivariate data set is shown within Figure 18. This plot provides a visualisation of the relationship between each variable controlled within this study and the experimental outputs to determine variables that demonstrate correlation for the liquid and gaseous fuel tests. Whilst the grayscale nature of the data points within Figure 18 does not allow specific information as to the trends within each test triplet (i.e. Test ID 1-3) to be discerned, general trends and correlations can be observed. The results of the solid fuel tests are omitted from the scatterplot matrix since only one data point was obtained and hence response trends as a function of variables are unable to be obtained.

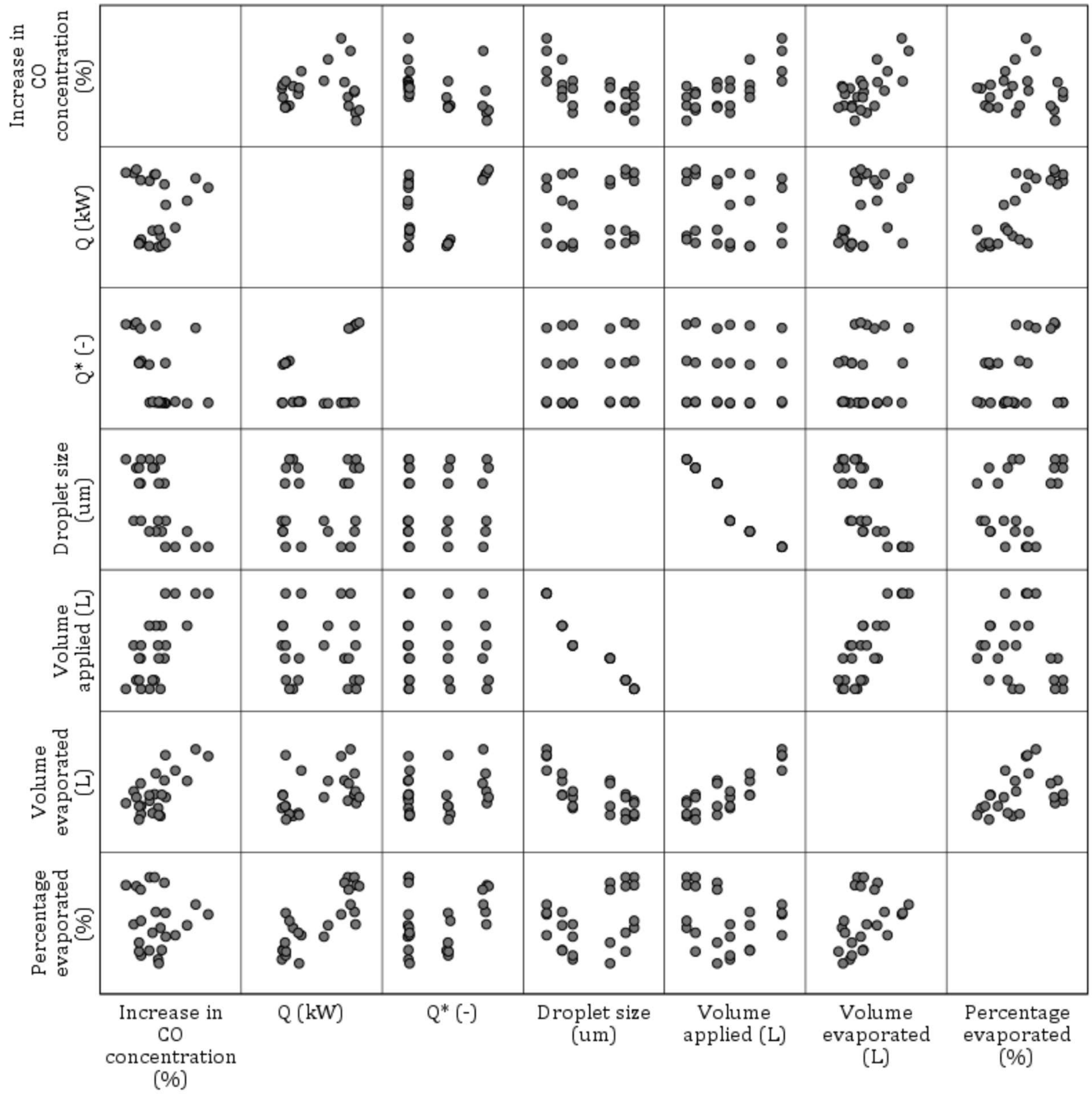

Figure 18 – Scatterplot matrix of experimental variables

It can be seen within Figure 18 that the amount of water interacting/evaporated within the flame and the D_{v50} droplet size of the imposed spray are inversely proportional. This data has been reproduced within Figure 19 to clarify the Test ID corresponding to each data point. Viewing this trend in context with the physical and chemical mechanisms of water spray suppression detailed within Section 2.2.2, it is clear that as droplet sizes decrease, the degree of heat and mass transfer increases as a result of the increased total surface area leading to a greater evaporative efficiency of smaller droplets (22).

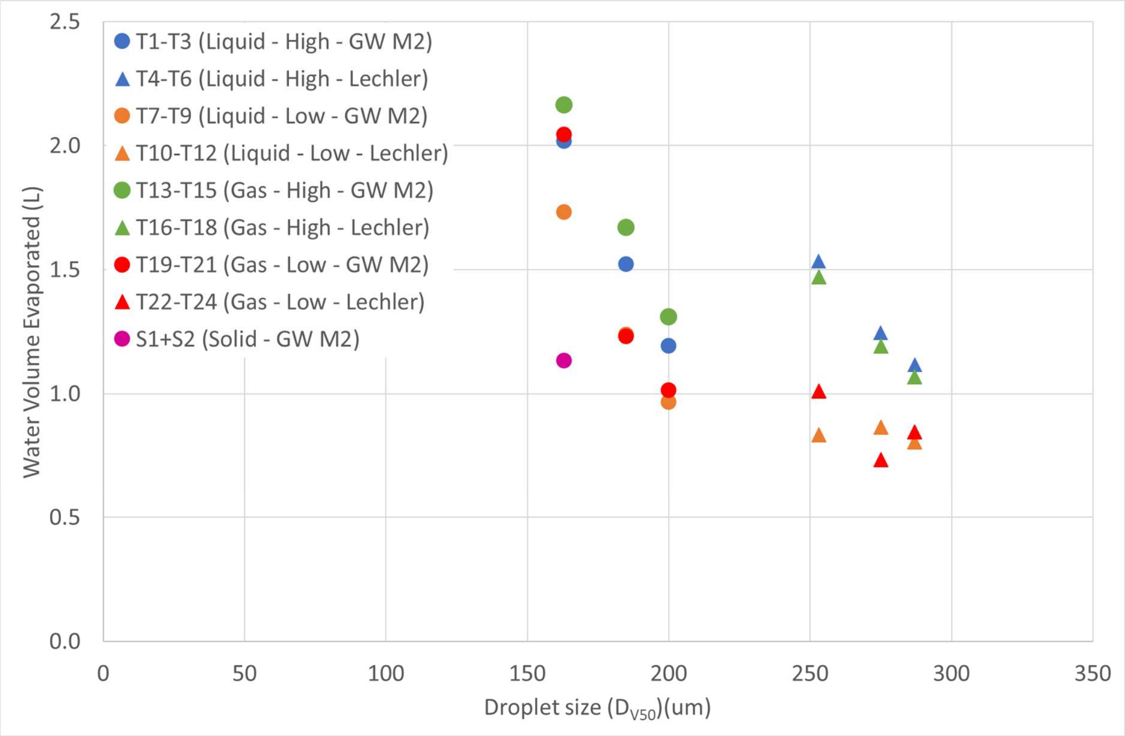

Figure 19 – Water volume evaporated as a function of droplet size

As discussed within Section 3.2.3, pressure energy atomisers vary both the rate of water dispersed and distribution of droplet sizes generated as a function of operating pressure. Figure 20 shows that the volume of water interacting/evaporated within the flame is generally proportional to the rate of water dispersed from the nozzle. It is noted that the correlation is weaker, or not present, within the smaller heat release rate tests that have utilised the Lechler 216 hollow cone nozzle (Test IDs T10-T12 and T22-T24).

In other words, the greater the level of water flux being applied to the region of combustion, the more droplets that are present to absorb heat and evaporate. This is logical. Nevertheless, it becomes critical when considering the flame cooling and chemical inerting mechanisms as discussed in Section 6.2.

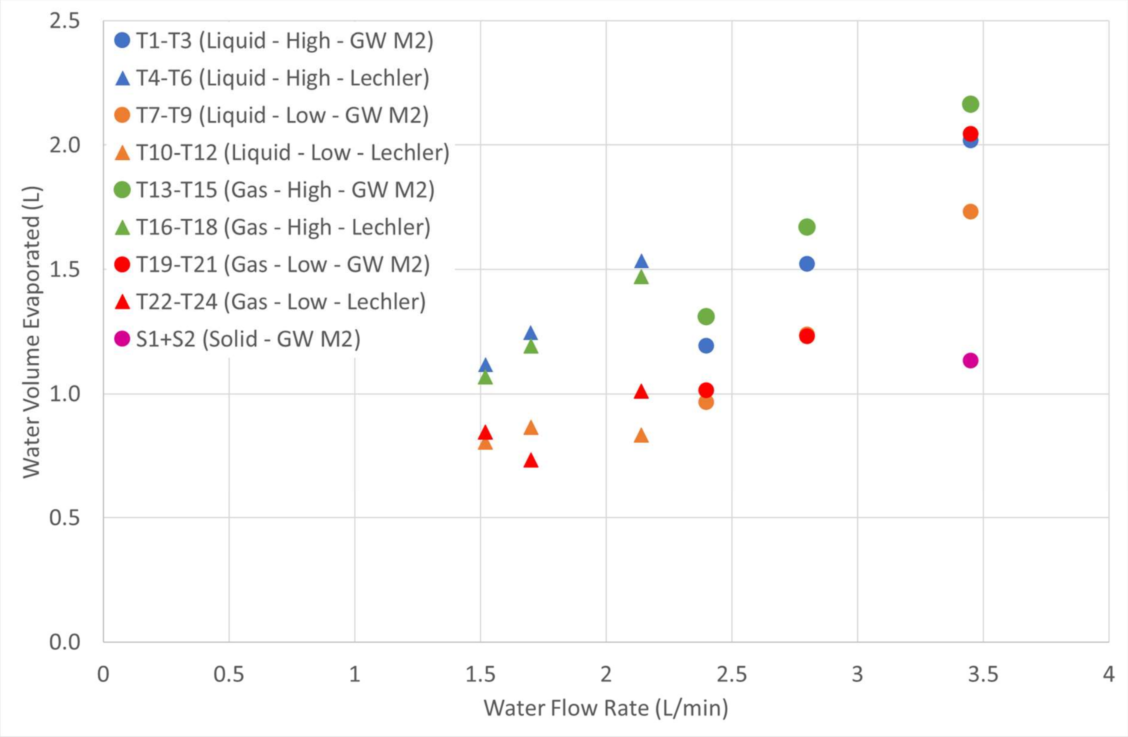

Figure 20 – Water volume evaporated as a function of water flow rate applied

The scatter plot matrix of Figure 18 illustrates that, for the experiments undertaken, there is no clear trend in heat release rate, or dimensionless heat release rate ($\dot{Q}$*), in terms of increase of carbon monoxide concentration. These individual factors are considered to contribute to form the droplet-flame interaction volume as discussed below.

6.2. Water Flux and Droplet-Flame Interaction Volume

Within the pool fire water mist extinction limit study undertaken by Kim et al. (36), it was found that imposed water flux was the key extinction parameter. Extinction can be viewed as the complete suppression of a fire and hence imposed water flux can be considered as an important parameter concerning mist suppression studies. However, imposed water flux is only relevant where it directly interacts with the process of combustion. The tests undertaken within this study have demonstrated the difficulty in quantifying and controlling the droplet-flame interaction volume, as a result of the unsteady nature of the interaction of the momentum flows of the flame and water spray. When observing data trends within Figure 18, it is important to recognise how the unsteady interaction volume influences the results obtained when drawing comparisons indicated to be due to the variation of individual parameters.

Through consideration of Figure 14, it could be postulated that the degree of increase of carbon monoxide concentration as a result of mist suppression is greater for heptane/liquid fuels than propane/gaseous fuels. However, without considering the respective droplet-flame interaction volumes, it is unknown whether these findings are a result of a fuel property or a difference in how the water sprays have acted on the flame geometry.

The proportion of water vaporised within each test, being the difference between that discharged through the nozzle and collected within the drainage vessel, is considered to be proportional to the size of the droplet-flame interaction volume of each test. Whilst it is acknowledged that discharged water may evaporate due to radiation to regions remote from the area of combustion, it is assumed that the degree of water evaporated within each test would be largely proportional to the size of the droplet-flame interaction volume.

Table 13 is a reproduction of the results recorded within Table 9 and Table 11 which have been rearranged to show the independence of the volume of water evaporated from the fuel type and respective flame geometries, as well as the degree of difference between the increase in carbon monoxide concentrations between these two fuel types. This data is also visually expressed within Figure 21.

It can be seen within Table 13 that, for a given heat release rate, there is comparatively little difference between the volume of water spray vaporised within each of the heptane and propane tests. However, with the exception of T9 (Liquid fuel, low HRR, GW M2 nozzle, 3 bar testing pressure) and T21 (Gaseous fuel, low HRR, Lechler 216 nozzle, 3 bar testing pressure), a significant difference in the degree of carbon monoxide concentration increase as a result of mist suppression was observed. This indicates that there may be substance to the postulation that the degree of increase of carbon monoxide concentration as a result of mist suppression is greater for heptane/liquid fuels than propane/gaseous fuels.

Table 13 – Independence of water volume evaporated to fuel type/flame geometry

Test ID	Volume Evaporated (L)	Volume Evaporated Difference	CO Conc. Increase (%)	CO Conc. Increase Difference
T1	1.19±0.05	10%	135±17	+255%
T13	1.31±0.08		38±3	
T2	1.52±0.07	10%	200±20	+90%
T14	1.67±0.06		105±9	
T3	2.02±0.22	7%	264±28	+17%
T15	2.16±0.26		226±10	
T4	1.12±0.06	4%	86±23	+514%
T16	1.07±0.04		14±2	
T5	1.25±0.07	5%	101±16	+120%
T17	1.19±0.10		46±2	
T6	1.53±0.04	4%	131±20	+122%
T18	1.47±0.08		59±5	
T7	0.97±0.01	4%	112±12	+87%
T19	1.01±0.05		60±6	
T8	1.24±0.08	1%	123±18	+45%
T20	1.23±0.11		85±8	
T9	1.73±0.19	18%	164±17	+22%
T21	2.04±0.71		134±4	
T10	0.81±0.08	5%	119±25	+98%
T22	0.85±0.07		60±7	
T11	0.87±0.10	15%	95±12	+76%
T23	0.74±0.09		54±4	
T12	0.83±0.55	22%	114±11	+111%
T24	1.01±0.04		54±6	

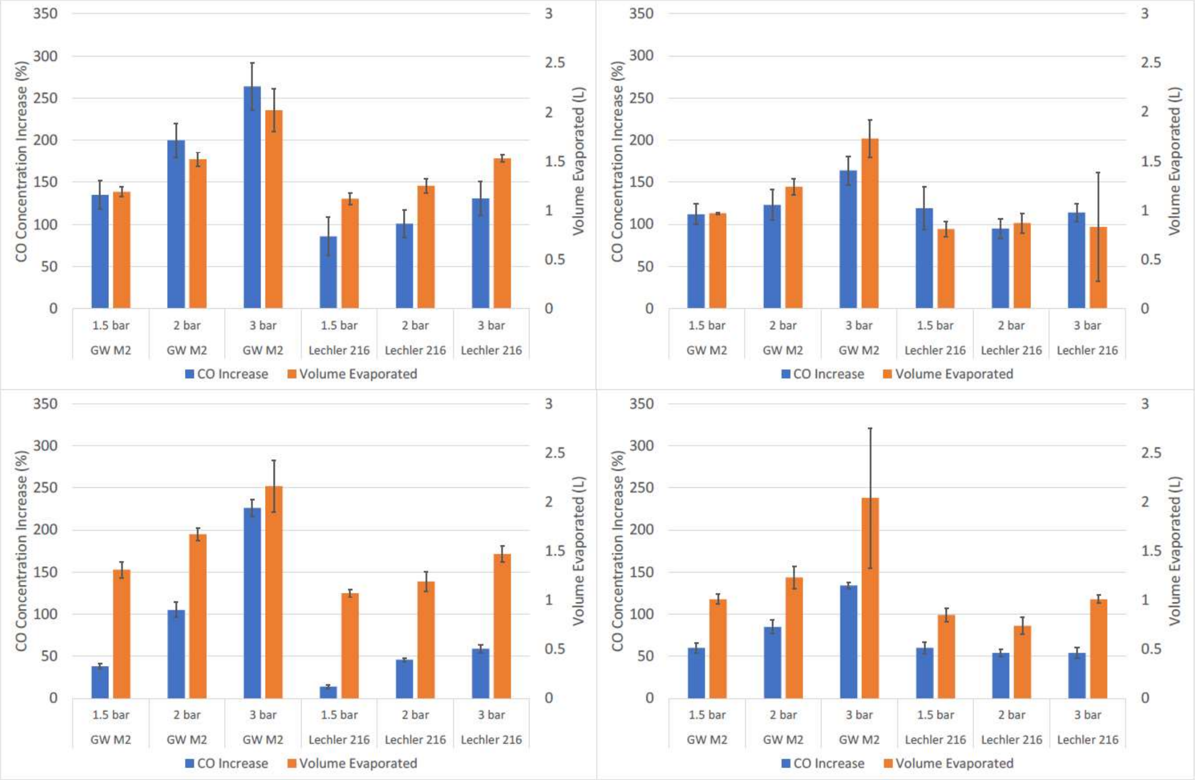

Figure 21 – Comparison of CO concentration change and volume of water evaporated
Top left: High HRR Heptane; Top right: Low HRR Heptane; Bottom left: High HRR Propane; Bottom right: Low HRR Propane

Due to experimental time restrictions within this study, tests were limited to a single fuel of each state so it cannot be confirmed whether the degree of carbon monoxide increase is a result of a fuel property or the state of the fuel. As discussed within Section 2.2.2.1, the main elementary reactions which result in the formation of carbon monoxide are the oxidation of soot by oxygen, the reduction of carbon dioxide molecules by soot particles (15) and the oxidation of soot by the hydroxyl radical (31), reproduced below.

$$\mathrm{C} + \tfrac{1}{2}\mathrm{O}_2 \rightarrow 2\mathrm{CO} \qquad \textit{Reaction 3}$$

$$\mathrm{CO}_2 + \mathrm{C} \rightarrow 2\mathrm{CO} \qquad \textit{Reaction 4}$$

$$\mathrm{C}_i + \cdot\mathrm{OH} \rightarrow \mathrm{C}_{i-1} + \mathrm{CO} + \tfrac{1}{2}\mathrm{H}_2 \qquad \textit{Reaction 5}$$

Through all of these processes, it is clear that the number of carbon atoms within a fuel molecule will influence the presence of carbon within the reaction zone and therefore the potential for carbon monoxide to be formed through these elementary reactions. Further supporting this are the studies undertaken by Tewarson showing that well-ventilated heptane fires have a carbon monoxide yield (y_{co}) of 0.01 g/g, and that well-ventilated propane fires have a carbon monoxide yield of 0.005 g/g (55).

It is proposed that fuels with an inherent tendency to produce greater levels of carbon monoxide within free burning conditions may experience a greater degree of combustion process interruption as a result of the applied water mist, and consequently produce even greater amounts of carbon monoxide when partially suppressed. Further experiments consisting of a number of different liquid and gaseous fuels are required to be undertaken to verify this hypothesis.

6.2.1. Carbon Monoxide Concentration as a Function of Water Evaporated

Through observation of Figure 18, it can be seen that the most closely correlated variable to the percentage increase in carbon monoxide is the volume of water spray evaporated within the combustion region. This relation suggests that the most significant factor in the generation of carbon monoxide within partially suppressed fires is the degree of the water flux and size of the flame interaction volume.

The generation of carbon monoxide can be viewed as a metric of the completeness of combustion reaction chemistry processes. Therefore, the increase in volume fraction of carbon monoxide as a result of water mist suppression can be seen to be influenced by the same parameter as Kim et al. (36) found as being most responsible for extinction due a water spray, the imposed water flux.

The data showing the relationship between carbon monoxide increase and volume of water spray evaporated is shown within Figure 22. There are many trends evident within this data. It can be seen that, with the exception of the smaller heat release rate tests that have utilised the Lechler 216 hollow cone nozzle (Test IDs T10-T12 and T22-T24), a positive linear relationship is present between the volume of water mist spray evaporated and the degree of increase in carbon monoxide. It is noted that Test IDs T10-T12 and T22-T24 are the same tests noted within Section 6.1 as having less correlation between the amount of water applied and that evaporated.

Further, it is observed that despite having a significantly lower heat release rate, the degree of increase in carbon monoxide concentration for the low HRR, liquid fuel fires subject to the GW M2 nozzle is larger than that for the large HRR liquid fuel fires subject to the Lechler 216 nozzle. This is considered to emphasise the importance of the properties of the water spray on forming the droplet-flame interaction volume.

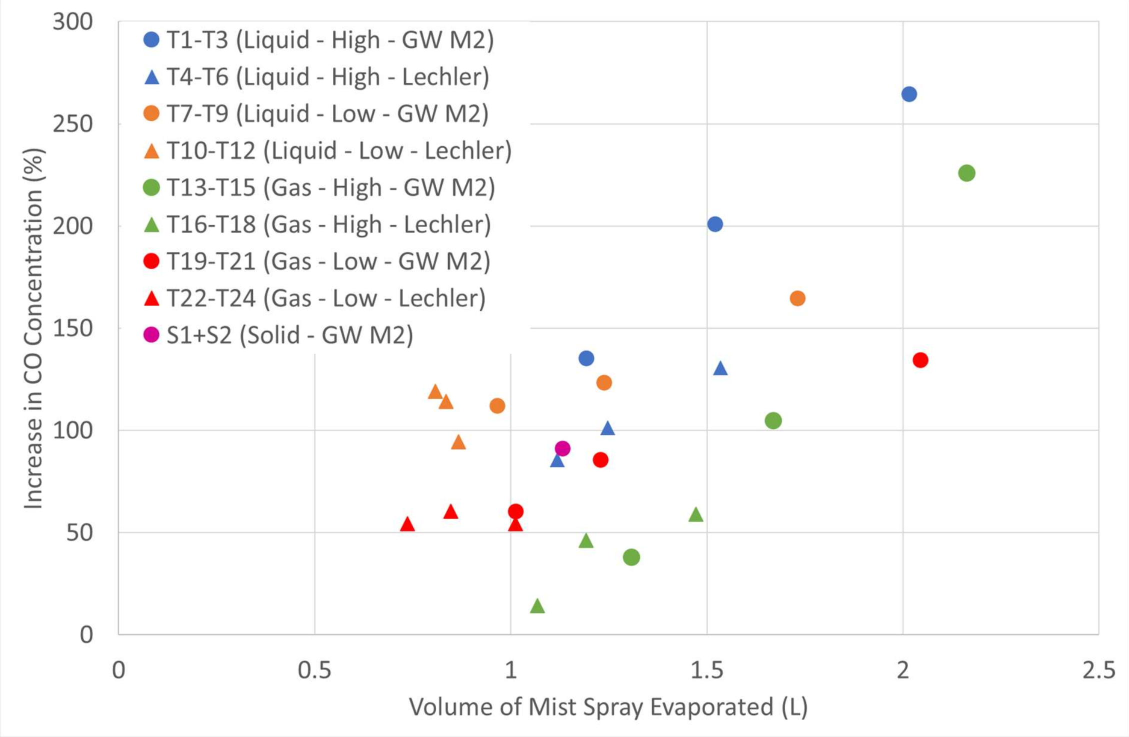

Figure 22 – CO concentration increase as a function of water volume evaporated

6.2.2. Carbon Monoxide Concentration as a Function of Droplet Size

As detailed within the literature review in Section 2.2 and preliminarily discussed within Section 6.1, the size of droplet dictates how well it absorbs heat from the gas phase of the fire and evaporates, and therefore how each droplet inhibits the combustion process through both flame cooling and chemical inerting (22). Figure 23 illustrates how the degree of increase in carbon monoxide production is influenced as a result of the applied droplet size. Figure 24 takes this data one step further and illustrates how the total surface area of droplets considered interacting within the flame influences the degree of carbon monoxide increase.

In general, smaller water droplets, having a larger total surface area, were observed to result in a more significant increase in carbon monoxide volume fractions recorded, which is consistent with the trends observed within the existing analogous experimental studies identified within Section 2.2.3.

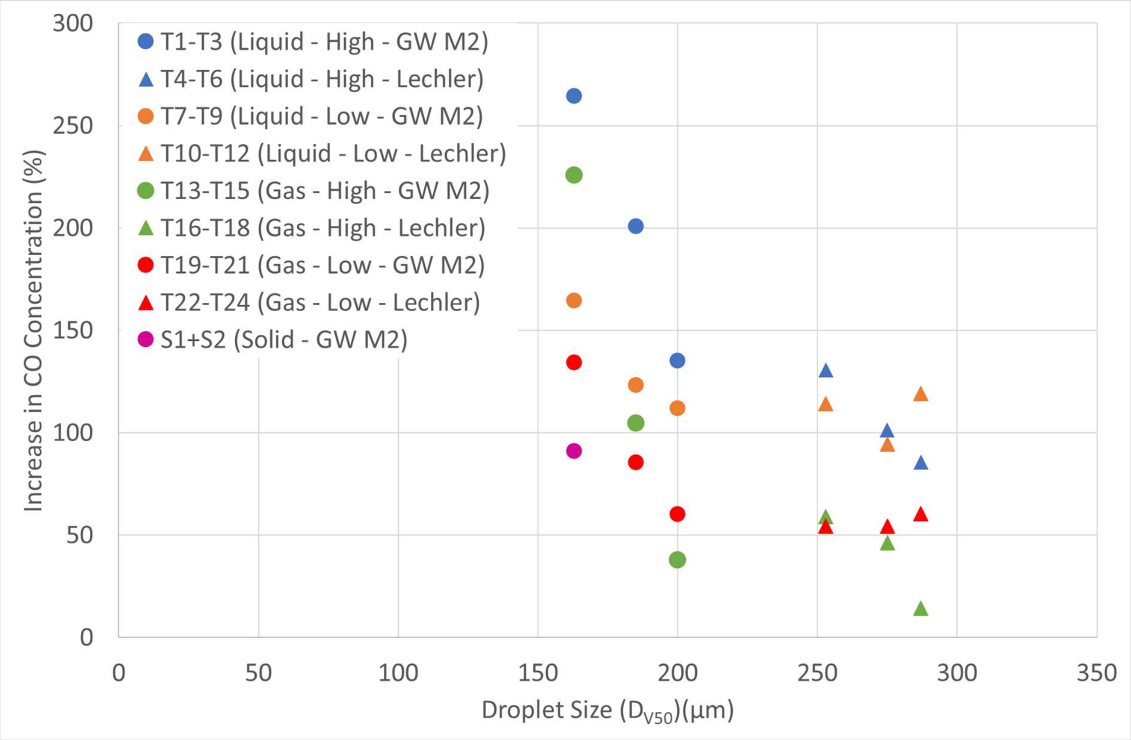

Figure 23 – Percentage increase in CO concentration as a function of droplet size

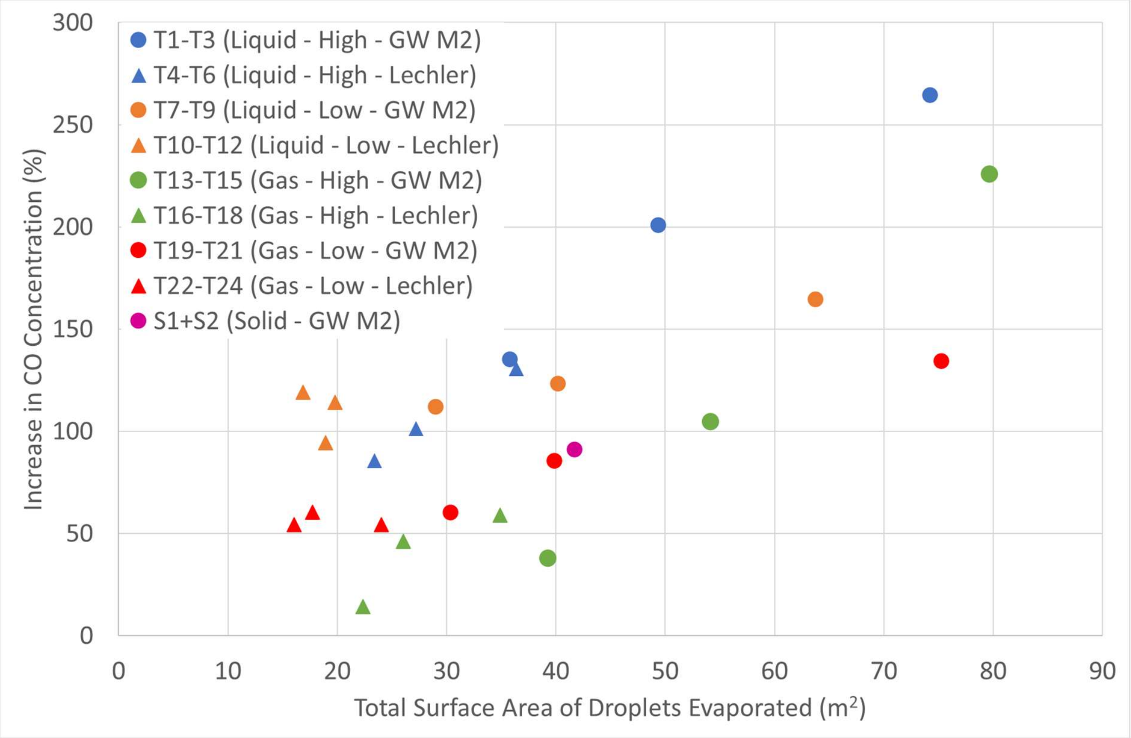

Figure 24 – Increase in CO concentration as a function of total surface area of droplets evaporated

As shown by Mawhinney et al. (20), identifying the primary mechanism involved in extinction, or suppression, is complex. Since both flame cooling and chemical inerting processes are controlled by the size of water droplets applied to the region of combustion, it is beyond the scope of these results to determine the relative importance of these mechanisms in producing carbon monoxide.

6.3. Uncertainty in Mist Spray

Key aspects of this study are the knowledge and characterisation of the mist sprays produced by each nozzle at the various test pressures. As discussed within Section 2.2.1, sprays produce a distribution of droplet sizes. For simplicity, the analysis undertaken has considered a single droplet size, the volume median diameter (D_{v50}), to represent the characteristics of a water spray consisting of a range of different droplet sizes, all of which would have a slightly differing degree of interaction with the combustion process.

If it is accepted that there are limitations that come with considering the spray distribution as a single characteristic diameter, there remains the uncertainty that the distribution of droplets produced by the experimental set-up are actually consistent with the characteristic diameter. The testing pressures necessitated by the experimental set-up did not line up with the sample of operating pressures at which the nozzle manufacturers had undertaken their droplet size distribution studies. Therefore, a degree of interpolation and extrapolation was required in order to estimate the spray characteristics at these intermediate operating pressures, resulting in some uncertainty in the characteristic diameters of the spray applied to each of the tests. The interpolation and extrapolation were undertaken on the basis of applying the closest fitting, technically feasible trendline to determine a best possible approximation of the actual distribution of droplets produced at the relevant testing pressures. It is acknowledged that there is a significant potential for error in applying these droplet sizes, and the characteristic droplet sizes have hence been rounded to the nearest 5 μm.

Further, as reported by Santangelo (21), the size of droplets measured can vary as function of axial distance from the nozzle. Neither of the technical specifications provided by the nozzle manufacturer's (Appendix C) detail the axial distance at which the droplet size distributions were undertaken. Hence, there is uncertainty in the suitability of the reported droplet sizes at the axial discharge distance applicable to this experimental set-up.

Over the course of tests undertaken the operating pressure delivered by the mains water supply was observed to fluctuate or pulse slightly over time by ±0.1 bar. Whilst relatively minor, this fluctuation would slightly alter the distribution of droplet diameters, as well as the flow rate of water, being discharged from the nozzle.

6.4. Comparison to Analogous Experimental Studies

As previously discussed within Section 2.2.3.5, the analogous studies identified in literature have largely focused on the influence of droplet size on heat release rate reduction and changes in gaseous species concentration. The results of this study have demonstrated that the size of water droplets applied does have a significant impact on how the concentration of carbon monoxide changes as a result of suppression by water mist. However, the key factor was found to be the quantity of water actually interacting within the region of combustion, a parameter which has not been expressly identified within the existing studies. Therefore, drawing absolute comparisons between this study and the results of previous studies is not possible, and only trends within data can be compared.

The first clear trend seen in the data recorded during the existing analogous experiments is that smaller water droplets correspond with a greater increase in carbon monoxide concentration being measured, indicating a greater degree of interruption of the combustion process. As shown within Figure 23, the results of this study are consistent with these findings, with the water sprays consisting of smaller characteristic diameter droplets resulting in the greatest increases of carbon monoxide concentrations measured.

Another trend apparent in the literature is that the behaviour of carbon monoxide concentration measured over time is consistent with how the heat release rate varies as a result of suppression. The results of this study similarly show that quasi-steady state heat release rates were established under mist suppression conditions and that the concentration of carbon monoxide measured also generally maintained quasi-steady state values.

6.5. Evaluation of Experimental Set-up

Given that the experimental apparatus and testing procedure was developed specifically to assess this research question, it is important to evaluate the appropriateness of experimental decisions made in the context of the results obtained. Overall, it is considered that the experimental apparatus and testing procedure adopted within this study were appropriate to focus on the interaction of fine water mist droplets on fire gas phase chemistry.

It is acknowledged that the perpendicular application of water, compared to the predominant momentum flows within the flame, is not a configuration commonly adopted within larger-scale built environment applications in which occupants may be egressing through these fire gas environments for extended durations. However, this experimental arrangement allowed the study to focus solely on gas phase suppression without the application of water influencing the cooling of fuel or flare-up of liquid fuels, both of which would potentially influence the heat release rate of the fire and consequently the generation of carbon monoxide (12, 24). It is considered that any experimental set-up developed to test this phenomenon would be highly influenced by the position and direction of discharge of a nozzle, in that these properties are key factors in developing the droplet-flame interaction volume.

As discussed within Section 3.3.4, testing pressures of 1.5, 2 and 3 bar were adopted as a result of the water pressures and flows which were readily obtainable within the laboratory. The impact of this was a less than initially desired range of sizes of droplets produced and water application rates as illustrated within Figure 11, resulting in a current narrow range of direct practical applicability. In order to incorporate higher testing pressures through the use of typical laboratory equipment, it is considered that the use of gaseous energy atomisers, which use the rapid movement of a typically inert gas through a nozzle to atomise water, would be required (12). However, the addition of an inert medium to atomise the water droplets, such as nitrogen gas, is considered to 'artificially' increase the number of inert molecules within the region of combustion. The use of a gaseous energy atomiser approach to obtain higher testing pressures requires careful consideration to quantify the degree to which carbon monoxide is generated due to the act of mist suppression, compared to other inerting factors. It is considered that the testing pressures adopted within this study were appropriate to develop this proof of concept for future studies.

As mentioned within Sections 3.3.4 and 6.3, the experimental set-up adopted required that the tests within this study be undertaken at system pressures which did not all directly align with the pressures at which the nozzle manufacturers had undertaken their droplet distribution studies. Further, uncertainties were present concerning the potential for droplet distributions to vary as a function of axial distance from the nozzle. Therefore, a significant question is whether the distribution of droplet sizes considered to be applied to the region of combustion is in fact what was applied experimentally. It is considered that the approach taken within this study is satisfactory to establish this proof of concept. However, it is suggested that droplet distribution studies be undertaken in future works at the testing pressures and axial distances adopted.

Studies undertaken on well-ventilated, plastic fuelled fires have shown that the carbon monoxide yield significantly increases with decreasing temperature of the combustion environment, as shown within Figure 25 (64). A key limitation of the experimental set-up adopted is that the temperature change within the region of combustion has not been measured nor quantified. The primary reason for this was the difficulty in reliably measuring flame temperature with the deflection of flame around the cone of water spray. Further, the coalescence of water droplets on thermocouples placed to measure flame temperatures adds additional considerations to determining how flame cooling could be quantified within this testing arrangement.

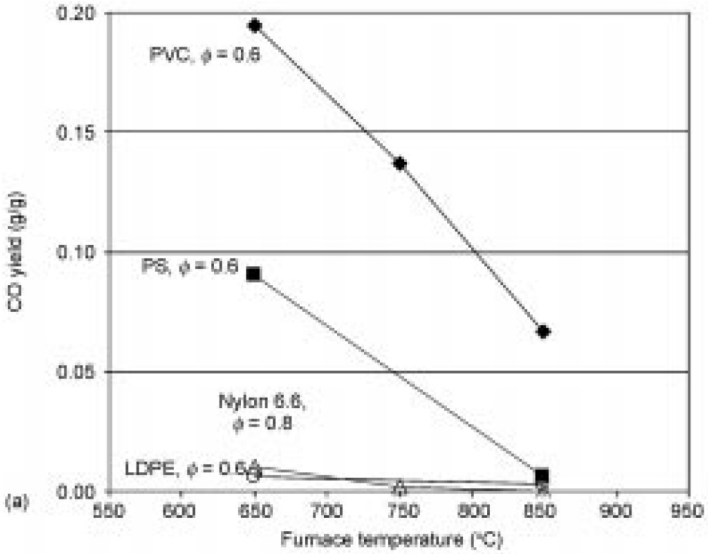

Figure 25 – Influence of temperature on yields of carbon monoxide within well-ventilated, plastic fuelled fires
Extracted from (64)

6.6. Implications for Fire Safety Engineering Designs

Whilst these experiments consist of a number of simplifications due to the scope of work, it is considered that this study establishes a proof of concept that typical product yields that are frequently adopted fire safety engineering designs, may not be appropriate when fires are subject to partial mist suppression, without a significant reduction to heat release rate.

The results have shown that upon activation of the mist suppression, the volume fraction of carbon monoxide within the fire environment significantly increases. Fire safety engineering designs developed on the basis of predicted toxicity dose taken up by egressing occupants, in which mist suppression systems are installed, are potentially significantly underestimating the levels of toxic exposure.

It is acknowledged that properly designed mist suppression systems are likely to significantly reduce the fire heat release rate, and in, turn limit the volume fraction of carbon monoxide within the fire environment. This is consistent with many of the existing analogous studies covered in the literature review utilising a vertical discharge of droplets and water fluxes sufficient to significantly suppress or extinguish the test fires. However, this study has shown that under certain configurations, it is possible for the activation of mist suppression systems to have a negligible influence over the heat release of a fire (Table 10) whilst the concentration of carbon monoxide produced increases significantly (Table 9).

It is important for fire safety engineers to understand how fire suppression sprays influence the combustion process and gaseous species produced.

The scope of this research is not broad enough to draw conclusions regarding an appropriate adjustment factor to apply to typical species product yields, such as Tewarson's (55), applicable within fire safety engineering designs where partial suppression scenarios could be expected. Such scenarios include:

- A shielded vehicular fire within a tunnel featuring a fixed firefighting system, or
- A fire within a rack storage structure with ceiling mounted sprinkler heads.

The results indicate a need for closer examination of how water sprays influence toxic species production, and raise uncertainly on the applicability of typical applied species yields when fires are partially suppressed through water droplets.

It is noted that, whilst a tunnel deluge suppression system or conventional sprinkler system would incorporate a distribution of droplets significantly larger than that considered within this study, only the smallest droplets within these sprays would be able to be entrained and interact with the flames of these shielded fires.

The results of this study have demonstrated that the commonly applied free burning carbon monoxide yields have the potential to be significantly lower than the yields present in scenarios in which fires are partially suppressed. Therefore, until more expansive studies are undertaken and knowledge of this phenomenon is developed, it is recommended that fire safety engineers consider whether it is appropriate to adopt a more conservative safety factor in relevant scenarios.

6.7. Future Work

The scope of this work was impacted significantly by time limitations of the experimental measurements and by the inherent trial and error process involved in designing the experimental set-up. Therefore, this study can be seen as the initial step in a more expansive piece of research studying the precise mechanics of how fine water droplets influence the production of chemical species through combustion. Relevant future directions of study include:

- Undertake tests utilising different sized gaseous burners to alter flame geometry as a means to control the region of flame and droplet interaction, whilst varying other parameters of combustion and suppression.
- Undertake additional experiments with multiple gaseous and liquid fuels of different molecular weights and carbon atom amounts to confirm that the results observed are due to the chemical makeup of the particular fuel and its tendency to produce carbon monoxide in well-ventilated conditions.
- Undertake additional experiments utilising nozzle systems that can operate over higher testing pressures to confirm the applicability of the findings of this study over a greater range of droplet size distributions.

- Undertake combustion tests within a controlled environment of various water vapour concentrations to determine the respective influence of water droplets acting through a cooling mechanism and water vapour acting as an inert substance interfering with the process of combustion.

7. Conclusions

The interaction of water droplets on the gas phase chemistry of fire and their potential to interrupt the chemical combustion process is complex with many competing factors affecting the pathway of oxidation. The act of partially suppressing combustion through the use of water mist has been shown within literature to increase the volume fraction of carbon monoxide produced if fires are not extinguished. The objective of this thesis, detailed within Section 1.2, was to assess the factors which influence the rate, and significance, of carbon monoxide generation within partially suppressed fires.

To assess this, a series of laboratory-scale experiments were designed and undertaken. It was found, through the experimental apparatus developed, that mist suppression systems acting solely on the gas phase of a fire result in relatively minor reductions to the heat release rate. At the same time, the concentration of carbon monoxide present within the gaseous products of the fire was observed to increase by up to 250%.

Fine water mists were observed to interrupt the combustion reaction process and restrict the pathway to oxidation. The most significant factors relevant to the production of carbon monoxide as a result of partial fire suppression were found to be:

- The size of the droplet-flame interaction volume,
- The size of the water droplets applied, and
- The degree of water flux applied.

The results suggest that fuels with an inherent tendency to produce carbon monoxide exhibit a greater degree of carbon monoxide species increase as a result of partial suppression.

This study represents a proof of concept to a currently largely under explored phenomenon. Additional research is required to confirm the applicability of the results across a range of fuels and scenarios. However, the significant increases of up to 250% in carbon monoxide concentrations observed as a result of mist suppression raise uncertainly on the applicability of typical applied species yields when fires are partially suppressed through fine water sprays. The results obtained suggest that additional safety factors should be adopted by fire safety engineers within fire and life safety assessments where it could be anticipated that the suppression systems would not result in extinguishment.

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Appendix A. Data Extraction Table

Author	Title	Source Type	Category	Reference	Nature of Source	Key Points	Summary of Findings
Atreya et al. (2000)	A study of the chemical and physical mechanisms of fire suppression by water	Conference paper	Mechanism focused study	(35)	Bench-scale tests of PMMA subject to fire suppression.	• Increased water concentration, increased flame temperature and completeness of combustion.	Chemical enhancement of combustion due to fire suppression.
Cheong et al. (2014)	Heat release rate of heavy goods vehicle fire in tunnels with fixed water based fire-fighting system	Journal article	Analogous experimental study	(9)	Full-scale tunnel fire tests measuring HRR of HGV fires with and without fire suppression.	• Influence of suppression on CO production is significant. • HRR is substantially reduced with early activation of suppression.	The suppressed fire size was approximately 4 times less than the unsuppressed HRR. Despite that, the results for CO concentration are approximately 5 times higher downstream of the fire. Therefore, accounting for the reduction in HRR, an increase in CO yield of 2000% is observed.
Chow et al. (2005)	Bench scale test on controlling plastic fires with water mists	Journal article	Analogous experimental study	(43)	Bench-scale tests on mist suppression of PMMA and PVC fires.	• CO and smoke quantity increased with application of mist. • Discharging mist did not initially significantly influence HRR. Critical level of suppression achieved reducing HRR.	The tests were conducted with a constant external heat flux. • PMMA at 20 kW/m^2 – 3 times increase in CO before reducing with HRR. • PMMA at 30 kW/m^2 – Minor increase in CO before reducing with HRR. • PMMA at 40 kW/m^2 – 2 times increase in CO before reducing with HRR. • PVC at 50 and 70 kW/m^2 – Negligible change to CO concentration.

Author	Title	Source Type	Category	Reference	Nature of Source	Key Points	Summary of Findings
Downie et al. (1995)	Interaction of a water mist with a buoyant methane diffusion flame	Journal article	Analogous experimental study	(53)	Lab-scale fire tests on mist suppression, via a hollow cone nozzle, of natural gas fires.	• Not concerned with extinguishment, only partial suppression. • "The plume-to-spray ratio was large, resulting in a large, strong deflection of the spray away from the fire".	• Upon activation of mist, negligible change in measured centreline plume temperatures and CO concentrations increased.
Efectis Nederland BV (2008)	Effects of water mist on real large tunnel fires; Experimental determination of BLEVE-risk and tenability during growth and suppression	Report	Analogous experimental study	(41)	Full-scale tunnel fire tests. Solid and liquid fuels tested with HRR up to 200 MW.	• Report focuses on risk of high temperatures and untenable conditions being present downstream of fire.	• Where fires are quickly extinguished, high temperatures and high levels of CO concentration quickly dissipate. • Fires taking much longer to extinguish resulted in untenable conditions being present downstream until the fire was eventually extinguished.
Fang et al. (2006)	Experimental studies on interaction of water mist with class K fires	Journal article	Analogous experimental study	(38)	Full-scale cooking oil tests subject to water mist suppression.	• Provides discussion of competing chemical processes relating to CO production. • Important factors for extinguishment; spray coverage, water flow rate and spray momentum.	• Mist both suppresses and enhances the physical and chemical mechanisms of combustion, dependent on how and how much water is applied. • Size of the fire more than doubled for a short time upon activation of water mist, before reducing.

Author	Title	Source Type	Category	Reference	Nature of Source	Key Points	Summary of Findings
Grant et al. (2000)	Fire suppression by water sprays	Journal article	Mechanism focused study	(14)	Review of theory underpinning fire suppression by water sprays.	• Paper addresses fire suppression with the intent to extinguish. No discussion of toxic species. • Detailed discussion of water/fire mechanisms. • Discussion of optimum droplet sizes.	• Paper addresses fire suppression with the intent to extinguish. No discussion of toxic species. • Detailed discussion of water/fire mechanisms.
Grant et al. (1997)	The suppression and extinction of Class A fires using water sprays	Research report	Mechanism focused study	(12)	Detailed literature review of suppression and extinction of solid fuels.	• Means of generating droplets. • Classification of suppression systems.	• Dominant mechanism in extinguishment of solid fuels is fuel cooling.
Grant et al. (1996)	A review of the extinction mechanisms of diffusion flame fires	Research report	Mechanism focused study	(22)	Detailed literature review to identify gaps in knowledge of fire suppression and extinction.	• Physical and chemical extinguishment mechanisms detailed.	• Smaller droplets of mist suppression systems evaporate more readily and absorb heat more effectively
Gupta et al. (2012)	An experimental study of the effects of water mist characteristics on pool fire suppression	Journal article	Analogous experimental study	(32)	Lab-scale test on mist suppression of pool fires.	• Atomiser nozzle utilised. Very small droplets produced. D_{V50} 20-30 μm.	• Rapid increase in CO concentration upon activation of mist. 4 x increase. • CO concentrations higher for higher mist suppression pressures.

Author	Title	Source Type	Category	Reference	Nature of Source	Key Points	Summary of Findings
Ingason et at. (2016)	Large scale fire tests with different types of fixed fire fighting system in the Runehamar tunnel	Report	Analogous experimental study	(39)	Full-scale tunnel tests with a FFFS.	• Side throw deluge nozzles. • Mean droplet size 1-2.5 mm.	• The concentration of CO increases significantly upon activation of water suppression.
Kim et al. (1997)	Extinction limit of a pool fire with a water mist	Journal article	Mechanism focused study	(36)	Lab-scale test of extinction of pool fire with water mist.	• Water mist and pool fire interaction have fire enhanced and fire extinction region.	• Effective water flux is key parameter for extinction of pool fires.
Li et al. (2015)	Influence of fire suppression on combustion products in tunnel fires	Report	Analogous experimental study	(8)	Scaled tunnel tests with and without suppression.	• Fire suppression does not cause adverse effects (high CO concentrations) if the fire size is suppressed to less than 40% of the free-burn HRR.	• Significant increases in CO concentration are observed for all tests involving wooden cribs, approximately 3.5-4.5 times the yields seen in free-burn scenarios. • CO concentration increases are less significant for plastic fuels.
Liu et al. (2000)	A review of water mist fire suppression systems - Fundamental Studies	Journal article	Mechanism focused study	(33)	Review of theory and research of water mist fire suppression.	• Significant discussion on factors that affect water mist performance. • Water vapour enhances chemical reactions within flames, up to about 30% water vapour in the fuel-air mixture.	• Detailed discussion of extinguishing mechanisms: ○ Heat extraction ○ Oxygen displacement ○ Radiant heat attenuation ○ Kinetic effects

Author	Title	Source Type	Category	Reference	Nature of Source	Key Points	Summary of Findings
Liu et al. (2007)	Experimental study on suppressing PVC fire with water mist in a confined space	Journal article	Analogous experimental study	(44)	Bench-scale tests on mist suppression of PVC fires.	• Discharging mist significantly reduced HRR. • CO levels initially increased before decreasing with HRR.	• Upon application of mist, CO concentration increased quickly for approximately 6 s before decreasingly rapidly with HRR. • Negligible difference in CO concentration between tests of different water pressures (i.e. droplet sizes and droplet velocities).
Mawhinney et al. (1994)	A closer look at the fire extinguishing properties of water mist	Conference paper	Mechanism focused study	(20)	Review of theory and research of water mist fire suppression.	• Discussion on the definitions and classifications of mist systems.	• HRRs of fuels with lower flash points are less impacted by water mist and more likely to experience re-ignition following extinction. • Detailed discussion of extinguishing mechanisms: ○ Heat extraction ○ Oxygen displacement ○ Radiant heat attenuation ○ Kinetic effects
Novozhilov (2007)	Fire suppression studies	Journal article	Mechanism focused study	(34)	Review of the current (2007) state of water-based suppression research.	• Discussion of the history, definitions and mechanisms of automatic fire suppression. • Significant discussion on computational modelling of water sprays.	• Mist systems are more flexible in that they can act as a total flooding agent more similar to a gaseous agent. • Primary modes of suppression: - Surface - Gaseous

Author	Title	Source Type	Category	Reference	Nature of Source	Key Points	Summary of Findings
Qin et al. (2005)	Bench-scale tests on PMMA fires with water mist	Journal article	Analogous experimental study	(27)	Bench-scale tests on mist suppression of PMMA fires.	• Fire suppressed through O_2 displacement, evaporative cooling and radiant heat attenuation. • Combustion enhanced through expansion of mixture and chain reaction.	• Upon application of mist, CO concentration doubled for a short duration before decreasingly rapidly with HRR. • More toxic gases may be produced during or after discharging water mist than those scenarios under normal conditions. • Water vapour inhibits soot formation and reduces radiant heat loss, promoting complete combustion. • Water mist cools the flame, displaces O_2 and attenuates radiant heat, inhibiting complete combustion.
Qin et al. (2004)	Experimental study of suppressing cooking oil fire with water mist using a cone calorimeter	Journal article	Analogous experimental study	(45)	Lab-scale tests on mist suppression of cooking oil fires.	• Combustion process initially enhanced by application of mist. • Mist systems with sufficient momentum can reach fuel surface. Low pressure systems producing small droplets do not reach fuel.	• CO concentration increases by a factor of 5-6 upon discharge of mist, up to 3000 ppm. • Depending on mist pressure, HRR increases by a factor of 1.5-2.5 before reducing to extinguishment.

Author	Title	Source Type	Category	Reference	Nature of Source	Key Points	Summary of Findings
Qin et al. (2006)	Preliminary study of water mist suppressing ghee flame in historical building in the northwest China	Journal article	Analogous experimental study	(46)	Lab-scale tests on mist suppression of ghee fires.	• Operation of mist system enhances mixing of fuel and air • The higher the operating pressure, the higher peak HRR and CO concentration produced.	The tests were conducted with a constant external heat flux. • 50 kW/m^2 – Temporary increase to 1500 ppm CO (300% increase) at 0.4 MPa. Temporary increase to 3000 ppm CO (600% increase) at 0.7 MPa. • 70 kW/m^2 – Temporary increase to 3000 ppm CO (300% increase) at 0.4 MPa and 0.7 MPa. • All measured concentrations of carbon monoxide quickly dissipated reducing with HRR.
Rasbash (1986)	The extinction of fire with plain water: A review	Conference paper	Mechanism focused study	(7)	Review of solid and liquid fuel fire extinction with water.	• Heat absorption properties of water is key to its ability to extinguish fires. • Care should be taken in defining a single droplet diameter to represent the distribution within a spray.	• Diluents, like water vapour, can reduce the adiabatic flame temperature to the lower flammability limit.
Rasbash et al. (1955)	The extinction of open fires with water spray; The effect of drop size of spray on the extinction	Report	Mechanism focused study	(25)	Experimental study on the effects of droplet size on the extinction of liquid fires.	• Detailed discussion on the mechanisms involved in extinguishment of a liquid pool fire.	• The key mechanisms involved in the extinction of liquid fires are dilution through steam production and fuel cooling below the fire point. • The effect of droplet size on extinction is highly dependent on the fire point of the fuel.

Author	Title	Source Type	Category	Reference	Nature of Source	Key Points	Summary of Findings
	of different liquid fires						• Fine droplets interacting with the fuel surface can temporarily increase the heat release rate of the fire due to the increased surface area of the fuel.
Rasbash et al. (1960)	Mechanisms of extinction of liquid fires with water sprays	Journal article	Mechanism focused study	(26)	Experimental study on the mechanisms involved in the extinction of liquid fires with water	• Two key types of extinction: - Gradual reduction in flames - Temporary significant increase in flame volume then disappearance of the flames.	• Rasbash et al. were unable to extinguish pool fires through the act of applying a horizontal water spray.
Santangelo et al. (2010)	Fire control and suppression by water-mist systems	Journal article	Mechanism focused study	(13)	Review of theory and research of water mist fire suppression.	• Details suppression mechanisms, spray characteristics and research approaches.	• Fire and water mist interactions are very complex and still not very well understood. • Much more experimental and numerical research is needed to improve understanding of these systems.

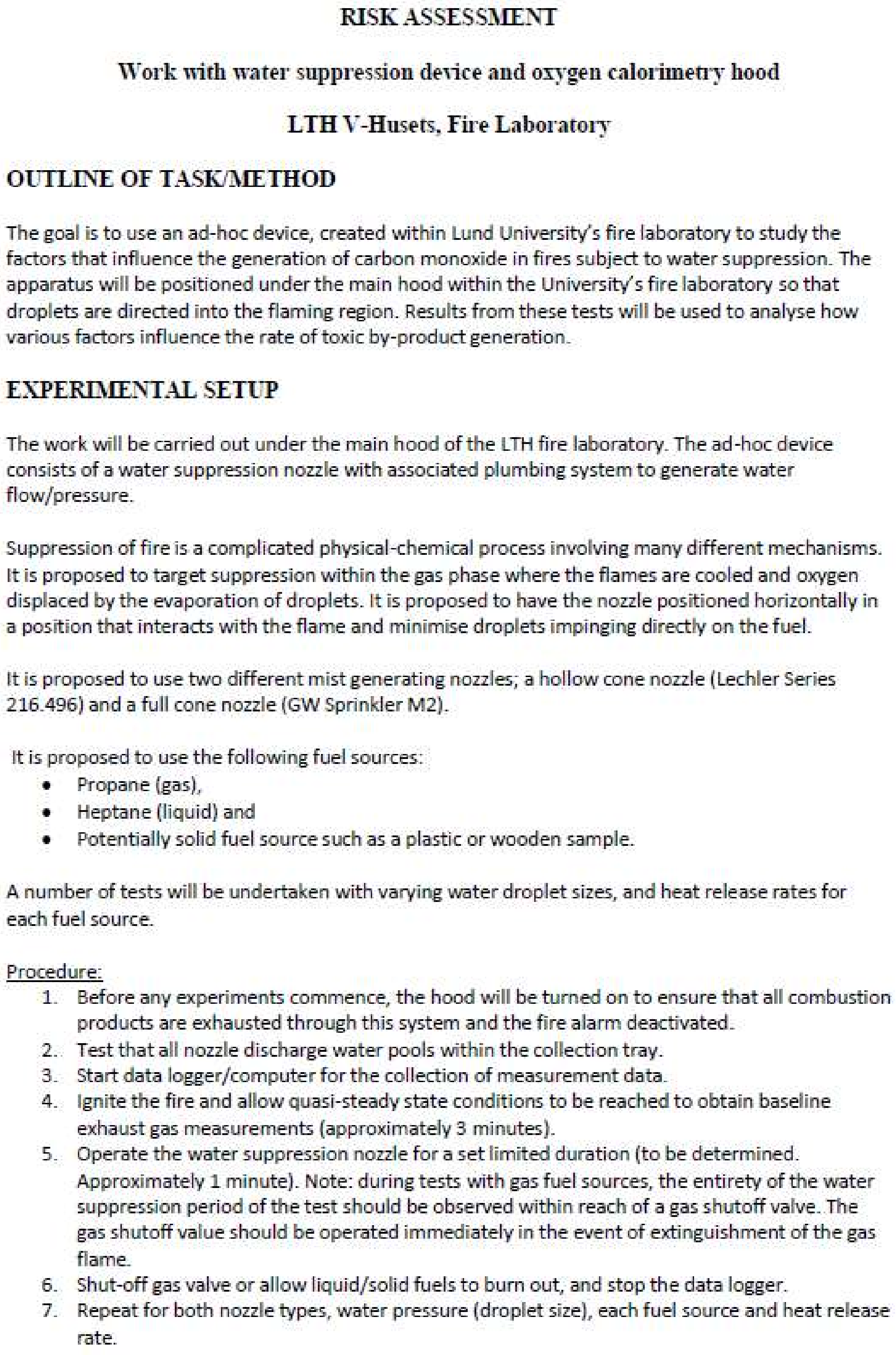
Author	Title	Source Type	Category	Reference	Nature of Source	Key Points	Summary of Findings
Santangelo (2012)	Experiments and modelling of discharge characteristics in water-mist sprays generated by pressure-swirl atomizers	Journal article	Mechanism focused study	(21)	Experimental study to characterise the dispersion and atomisation of a mist spray nozzle.	• Secondary atomisation controls droplet size near to the point of discharge up to a turning point. • Coalescence controls droplet size as axial distance increases.	• Coalescence as a result of droplet collision is observed in the near-field region to the nozzle. • Due to secondary atomisation (Weber number) the minimum droplet diameters are seen around 100 mm from the nozzle. • However, as the distance from the nozzle increases the Weber number significantly decreases due to decreasing droplet velocity and coalescence increases the size of the characteristic droplet diameters.
Suh et al. (1995)	The effect of water vapor on counterflow diffusion flames	Conference paper	Mechanism focused study	(37)	Bench-scale tests and computational studies.	• Exact suppression mechanisms are not well understood.	• Upon application of water: ○ CO_2 production increases, ○ CO concentration decreased. • This is proposed to be due to reaction of CO with the OH radical within water vapour.
Weng et al. (2006)	Study on the suppression mechanism of water mist on poly(methyl methacrylate) and poly(vinyl chloride) flames	Journal article	Analogous experimental study	(28)	Lab-scale tests on mist suppression of PMMA and PVC fires.	• Difference between PMMA and PVC is that within the PVC flame the aromatics are unable to be burned.	The tests were conducted with a constant external heat flux. • PMMA at 20 kW/m^2 – 3 times increase in CO before reducing with HRR. • PVC at 50 and 70 kW/m^2 – Immediate and rapid decrease in CO concentration.

Author	Title	Source Type	Category	Reference	Nature of Source	Key Points	Summary of Findings
Wighus (1995)	Engineering relations for water mist fire suppression systems	Conference paper	Mechanism focused study	(23)	Case study of the application of a water mist suppression system application and key considerations.	• Two approaches to mist suppression systems: - Local application with a mist flow rate per unit volume of flame. - Total flooding with a water fraction achieved within an enclosure volume.	• Three main mechanisms: - Cooling, - Inerting, and - Thermal radiation attenuation • Three different classes of fire under suppression - Open unconfined fire. - Enclosed open fire. - Enclosed shielded fire.
Yang et al. (2018)	The study on influence of water mist particle size on the fire smoke migration with longitudinal ventilation in road tunnel	Journal article	Analogous experimental study	(42)	Lab-scale tunnel test on influence of longitudinal ventilation on water mist.	• Dragdown of smoke/CO greatest with largest mist particle size.	• No Mist/No Vent – CO only in smoke layer. • Mist/No Vent – CO mixed and diluted. More even across height. • No Mist/Vent – Two layers. CO concentration in smoke 2 x without ventilation. • Mist/Vent – CO mixed and diluted. CO concentration 3 x without ventilation.

Author	Title	Source Type	Category	Reference	Nature of Source	Key Points	Summary of Findings
Yao et al. (2012)	Experimental study of suppressing Poly(methyl methacrylate) fires using water mists	Journal article	Analogous experimental study	(47)	Full-scale tests on mist suppression of PMMA fires.	• Surface cooling found to be key extinguishing mechanism.	• HRR reduced rapidly with mist application, with higher water pressures resulting in lower a HRR. • HRR 10-30% that of unsuppressed fire. • CO production rate reduced to 50-80% of unsuppressed fire on mist application. • Increase of local production rate increased with mist application.
Yao et al. (1999)	Interaction of water mists with a diffusion flame in a confined space	Journal article	Analogous experimental study	(48)	Lab-scale tests on mist suppression of ethanol and pine fires.	• Water mist influence more complex on solid fuel than liquid fuels. • Volume flux of water is key factor.	• CO concentration rapidly increases by a factor of 3 for fires that are partial suppressed and not extinguished.
Yimin et al. (2005)	Preliminary burning tests on PVC fires with water mist	Journal article	Analogous experimental study	(49)	Bench-scale tests on mist suppression of PVC fires.	• Discharging mist significantly reduced HRR. • CO levels initially increased before decreasing with HRR.	• Upon application of mist, CO concentration increased quickly for approximately 6 s before decreasingly rapidly with HRR. • Higher operating pressures resulted in a more rapid reduction in CO concentration.

Author	Title	Source Type	Category	Reference	Nature of Source	Key Points	Summary of Findings
Zhang et al. (2007)	Experimental study of the interaction between the water mists and PVC fire	Journal article	Analogous experimental study	(50)	Bench-scale tests on mist suppression of PVC fires.	• Discharging mist significantly reduced HRR. • CO levels initially increased before decreasing with HRR.	• Upon application of mist, CO concentration increased quickly for approximately 8 s before decreasingly rapidly with HRR. • Higher operating pressures resulted in a more rapid reduction in CO concentration.
Zhou et al. (2018)	Assessment of a clean and efficient fire-extinguishing technique; Continuous and cycling discharge water mist system	Journal article	Analogous experimental study	(51)	Room test on mist suppression of gasoline and diesel pool fires under various exhaust conditions. High levels of instrumentation.	• Combustion restrained by mist. Burns more incompletely. • Peak and sustained levels of CO lower with cycling discharge of mist.	• Upon application of mist, HRR and CO concentration increased rapidly. • HRR dropped to below lower heat release rate than prior to mist application, but did not extinguish until fuel burnout. • CO concentration stayed at an elevated level steadily reducing as fuel was consumed.
Zhou et al. (2019)	Performance evaluation of water mist fire suppression; A clean and sustainable fire-fighting technique in mechanically-ventilated place	Journal article	Analogous experimental study	(52)	Room test on mist suppression of gasoline and diesel pool fires under various exhaust conditions. High levels of instrumentation.	• Mist activation suppresses combustion and promotes incomplete reactions.	• Volume fraction of CO negligible prior to mist activation. Quickly increases with mist. • Levels of CO are lower for higher exhaust levels.

Appendix B. Risk Assessment Documentation



RISK ASSESSMENT

Work with water suppression device and oxygen calorimetry hood

LTH V-Husets, Fire Laboratory

OUTLINE OF TASK/METHOD

The goal is to use an ad-hoc device, created within Lund University's fire laboratory to study the factors that influence the generation of carbon monoxide in fires subject to water suppression. The apparatus will be positioned under the main hood within the University's fire laboratory so that droplets are directed into the flaming region. Results from these tests will be used to analyse how various factors influence the rate of toxic by-product generation.

EXPERIMENTAL SETUP

The work will be carried out under the main hood of the LTH fire laboratory. The ad-hoc device consists of a water suppression nozzle with associated plumbing system to generate water flow/pressure.

Suppression of fire is a complicated physical-chemical process involving many different mechanisms. It is proposed to target suppression within the gas phase where the flames are cooled and oxygen displaced by the evaporation of droplets. It is proposed to have the nozzle positioned horizontally in a position that interacts with the flame and minimise droplets impinging directly on the fuel.

It is proposed to use two different mist generating nozzles; a hollow cone nozzle (Lechler Series 216.496) and a full cone nozzle (GW Sprinkler M2).

It is proposed to use the following fuel sources:

- Propane (gas),
- Heptane (liquid) and
- Potentially solid fuel source such as a plastic or wooden sample.

A number of tests will be undertaken with varying water droplet sizes, and heat release rates for each fuel source.

<u>Procedure:</u>

1. Before any experiments commence, the hood will be turned on to ensure that all combustion products are exhausted through this system and the fire alarm deactivated.
2. Test that all nozzle discharge water pools within the collection tray.
3. Start data logger/computer for the collection of measurement data.
4. Ignite the fire and allow quasi-steady state conditions to be reached to obtain baseline exhaust gas measurements (approximately 3 minutes).
5. Operate the water suppression nozzle for a set limited duration (to be determined. Approximately 1 minute). Note: during tests with gas fuel sources, the entirety of the water suppression period of the test should be observed within reach of a gas shutoff valve. The gas shutoff value should be operated immediately in the event of extinguishment of the gas flame.
6. Shut-off gas valve or allow liquid/solid fuels to burn out, and stop the data logger.
7. Repeat for both nozzle types, water pressure (droplet size), each fuel source and heat release rate.

Test Variables:

- Liquid fuel pans:
    - 20 cm – Approx. 25kW (unsuppressed).
    - 25 cm – Approx. 50 kW (unsuppressed).
- Gas fuel:
    - Gas flows controlled to reproduce the HRRs obtained in the liquid fuel tests.
- Solid fuel:
    - To be determined.
- Each nozzle is to be tested under pressures of 1.5, 2 and 3 bar.
- Each test is to be repeated three times.

FIRE LABORATORY LAYOUT

The layout of the Fire Laboratory is shown in the following figure.

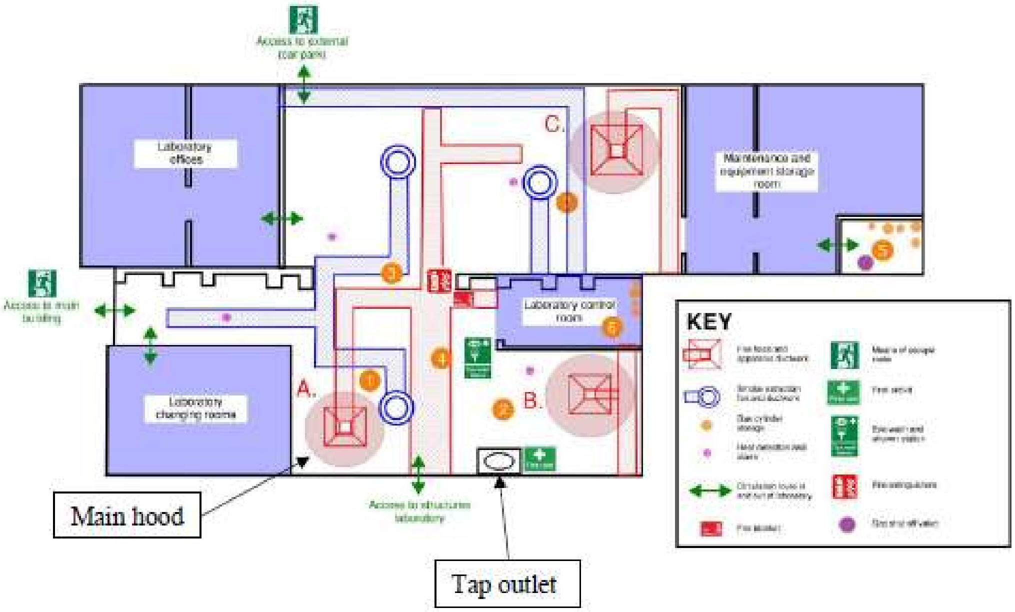


Figure 1. Room geometry of Fire Laboratory.

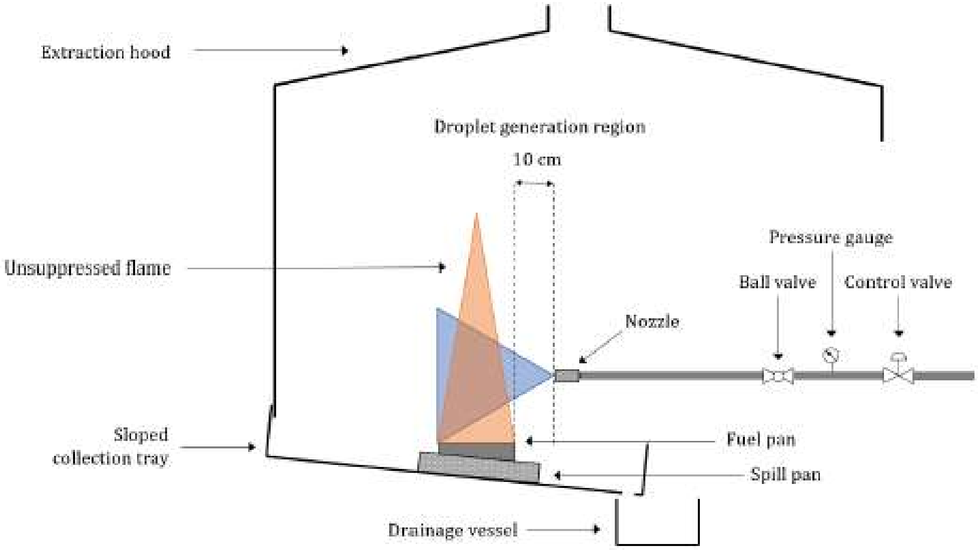
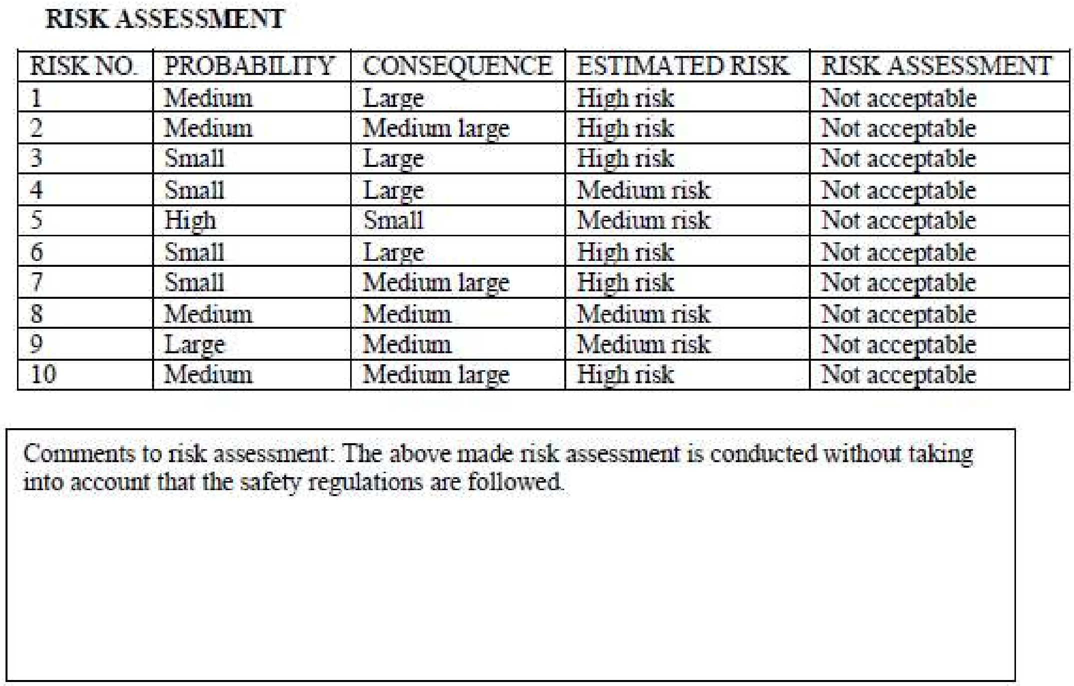


Figure 2. Experimental Schematic.

Figure 3. Experimental Apparatus – General Arrangement (Note: this image does not show the outer spill pan or the clamps used to secure the steel plates to the extraction hood)

RISK IDENTICATION

RISK NO.	TYPE	MOMENT / ACTIVITY	PROPERTY/ RISK	PLACE	AREA in Figure 1
1	Extinguishment of gas flame during suppression.	During gas fuel source suppression experiments.	Explosion.	Whole lab.	Whole lab.
2	Overflow of fuel pan during suppression.	During liquid fuel source suppression experiments.	Uncontrolled fire growth.	In vicinity of test apparatus.	Near the location of the fire in the test apparatus.
3	Spread of flammable gases.	During, between and after experiments.	Leakage/explosion.	Whole lab.	Whole lab.
4	Spread of asphyxiant gases.	During, between and after experiments.	Suffocation.	Whole lab.	Whole lab.
5	Spread of smoke.	During, between and after experiments.	Affecting respiratory system.	Whole lab.	Whole lab.
6	Experiment with flammable liquids.	During, between and after experiments.	Leakage/ignition.	Whole lab.	Whole lab.
7	Heat flux.	During and after experiments.	Material and products near the hot object/fire is affected, melts or is damaged.	In vicinity (1 m) from the hot object/fire.	1 m from the test apparatus.
8	Tripping over cables and hoses.	All the time.	Damage to person and equipment.	In vicinity of apparatus and tap outlet.	Between apparatus and tap outlet.
9	Hot surfaces.	During, between and after experiments.	Burns/ignition of combustibles.	In vicinity of test apparatus.	Near the location of the fire in the test apparatus.
10	Deflection of hot surfaces.	During experiments.	Uncontrolled fire growth as a result of deflection causing collapse of apparatus.	In vicinity of test apparatus.	Near the location of the fire in the test apparatus.



RISK ASSESSMENT

RISK NO.	PROBABILITY	CONSEQUENCE	ESTIMATED RISK	RISK ASSESSMENT
1	Medium	Large	High risk	Not acceptable
2	Medium	Medium large	High risk	Not acceptable
3	Small	Large	High risk	Not acceptable
4	Small	Large	Medium risk	Not acceptable
5	High	Small	Medium risk	Not acceptable
6	Small	Large	High risk	Not acceptable
7	Small	Medium large	High risk	Not acceptable
8	Medium	Medium	Medium risk	Not acceptable
9	Large	Medium	Medium risk	Not acceptable
10	Medium	Medium large	High risk	Not acceptable

Comments to risk assessment: The above made risk assessment is conducted without taking into account that the safety regulations are followed.

RISK REDUCING MEASURES

RISK NO.	MEASURES	PROBA BILITY	CONSE QUENCE	ESTIMATED RISK	RISK ASSESSMENT
1	Ventilation system in operation. The test apparatus is not to be left unattended during experiments. Attention should be paid to the burner at all times during combustion. Gas shutoff value to be within reach at all times water is being applied.	Small	Small	Low risk	Acceptable
2	The fuel pan is surrounded by an outer spill pan. In the event of water discharge into the pan, causing an overflow of the fuel, the spill will be contained. Extinguishing equipment in readiness.	Small	Small	Low risk	Acceptable
3	Ventilation system in operation. Entire apparatus located beneath hood. Close gas bottles between experiments.	Small	Small	Low risk	Acceptable
4	Ventilation system in operation. Entire apparatus located beneath hood. Close gas bottles between experiments.	Small	Small	Low risk	Acceptable
5	Operate exhaust hood at all times during experiments.	Small	Small	Low risk	Acceptable
6	No storage of flammable liquids in the vicinity of the test apparatus. Extinguishing equipment in readiness.	Small	Small	Low risk	Acceptable
7	Keep distance to hot parts/fire (1 m).	Small	Small	Low risk	Acceptable
8	Minimise lab access via the southern/structural lab door where the crossing of hydraulic lines is unavoidable. Place signage in this area.	Small	Small	Low risk	Acceptable
9	If you are not wearing safety gloves or equipment to carry hot parts, keep distance from hot surfaces.	Small	Small	Low risk	Acceptable

10	Each steel piece of water collection apparatus is fixed securely to each other. The apparatus is checked multiple times a day for movement or instability. Extinguishing equipment in readiness.	Small	Small	Low risk	Acceptable

RISK ASSESSMENT

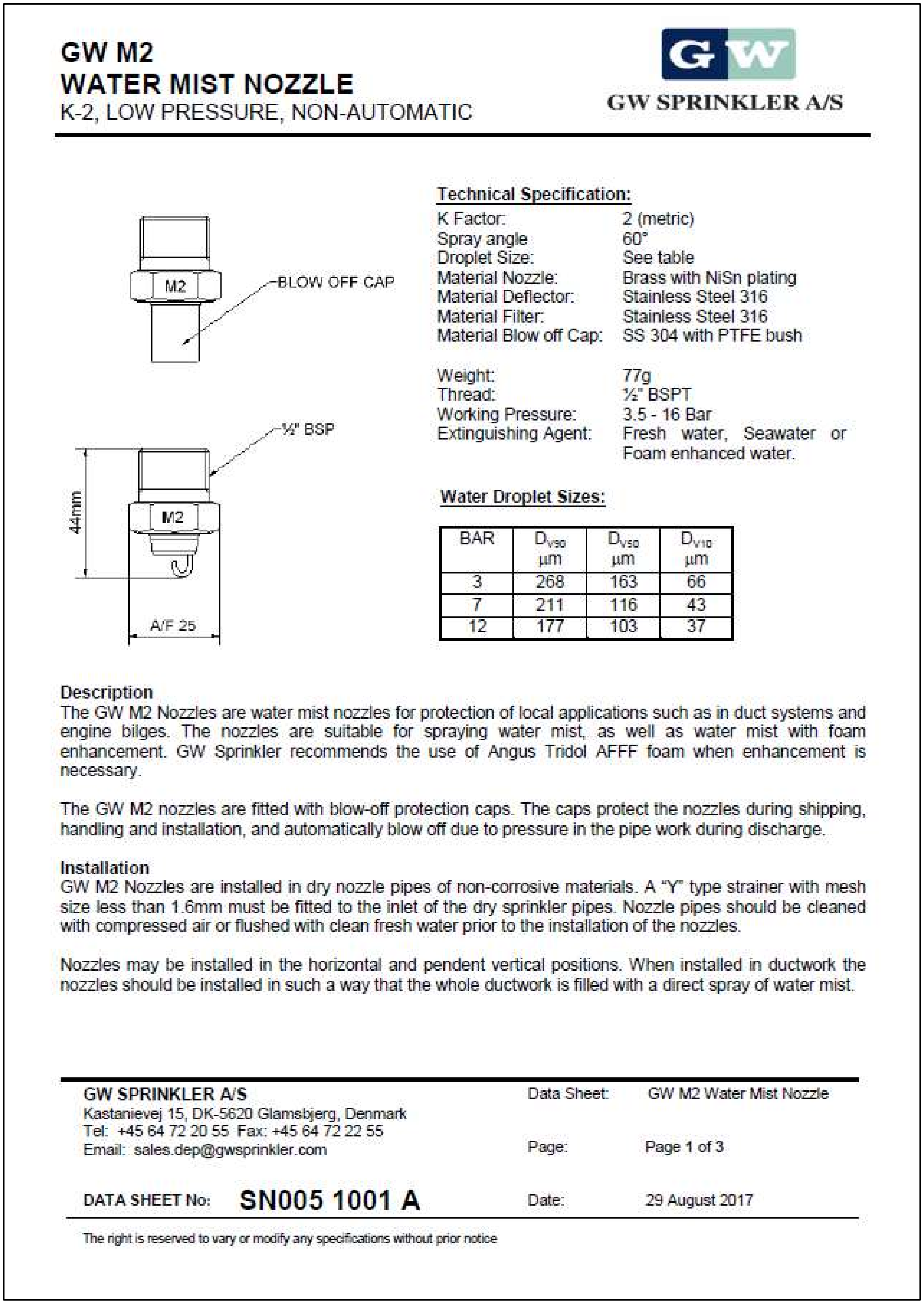
Comments to Risk reducing measures:
There are some risks left but these are assessed as acceptable.

Safety procedures of the fire lab are to be followed. No lone work, at least two students should be in the lab for all tests. Supervisor or lab responsible shall attend the initial tests to approve the practical handling of tests.

Conducted by	**Approved by:**
Haydn Lewis	Lab responsible Dan Madsen
Supervisor Nils Johansson	

Appendix C. Nozzle Technical Specifications

GW Sprinkler A/S – GW M2



GW M2
WATER MIST NOZZLE
K-2, LOW PRESSURE, NON-AUTOMATIC

GW SPRINKLER A/S

Technical Specification:

K Factor:	2 (metric)
Spray angle	60°
Droplet Size:	See table
Material Nozzle:	Brass with NiSn plating
Material Deflector:	Stainless Steel 316
Material Filter:	Stainless Steel 316
Material Blow off Cap:	SS 304 with PTFE bush
Weight:	77g
Thread:	½" BSPT
Working Pressure:	3.5 - 16 Bar
Extinguishing Agent:	Fresh water, Seawater or Foam enhanced water.

Water Droplet Sizes:

BAR	D_{V90} µm	D_{V50} µm	D_{V10} µm
3	268	163	66
7	211	116	43
12	177	103	37

Description

The GW M2 Nozzles are water mist nozzles for protection of local applications such as in duct systems and engine bilges. The nozzles are suitable for spraying water mist, as well as water mist with foam enhancement. GW Sprinkler recommends the use of Angus Tridol AFFF foam when enhancement is necessary.

The GW M2 nozzles are fitted with blow-off protection caps. The caps protect the nozzles during shipping, handling and installation, and automatically blow off due to pressure in the pipe work during discharge.

Installation

GW M2 Nozzles are installed in dry nozzle pipes of non-corrosive materials. A "Y" type strainer with mesh size less than 1.6mm must be fitted to the inlet of the dry sprinkler pipes. Nozzle pipes should be cleaned with compressed air or flushed with clean fresh water prior to the installation of the nozzles.

Nozzles may be installed in the horizontal and pendent vertical positions. When installed in ductwork the nozzles should be installed in such a way that the whole ductwork is filled with a direct spray of water mist.

GW SPRINKLER A/S
Kastanievej 15, DK-5620 Glamsbjerg, Denmark
Tel: +45 64 72 20 55 Fax: +45 64 72 22 55
Email: sales.dep@gwsprinkler.com

Data Sheet: GW M2 Water Mist Nozzle
Page: Page 1 of 3

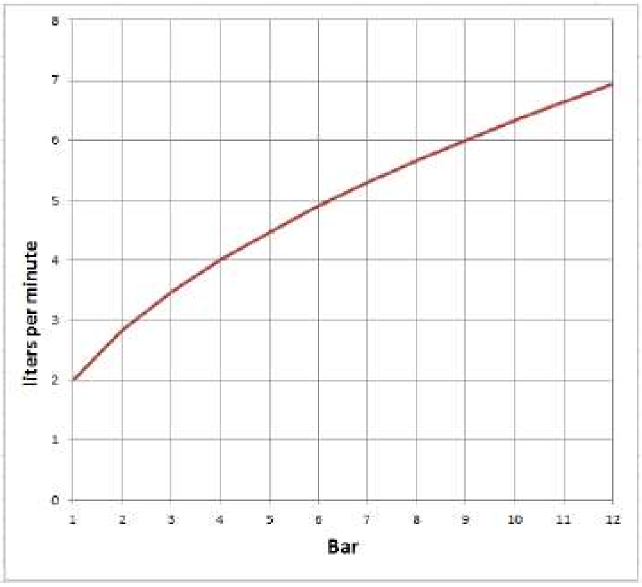
DATA SHEET No: **SN005 1001 A**
Date: 29 August 2017

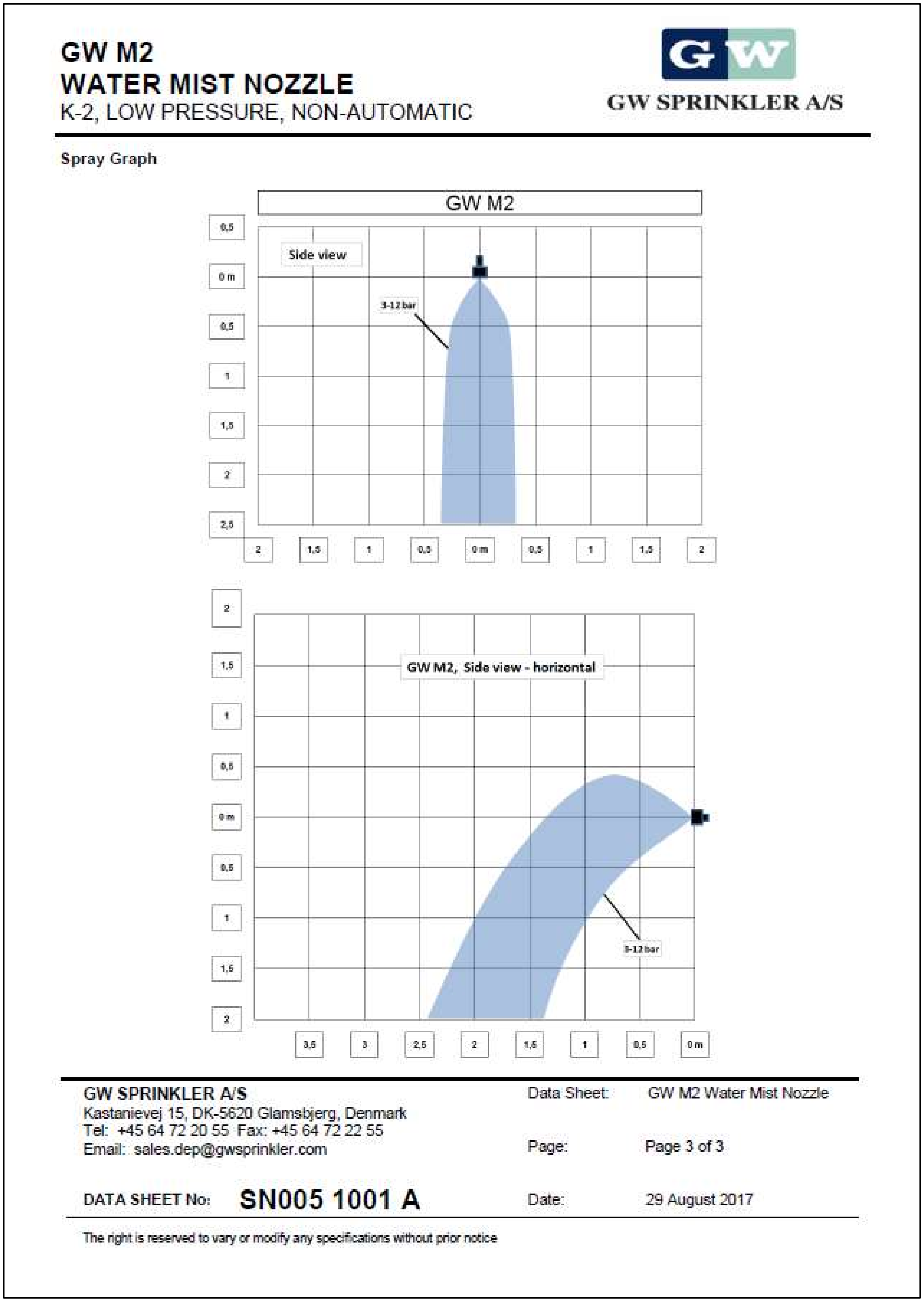
The right is reserved to vary or modify any specifications without prior notice

GW M2
WATER MIST NOZZLE
K-2, LOW PRESSURE, NON-AUTOMATIC

GW SPRINKLER A/S

Pressure / Flow





GW M2
WATER MIST NOZZLE
K-2, LOW PRESSURE, NON-AUTOMATIC

GW SPRINKLER A/S

Spray Graph

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Data Sheet: GW M2 Water Mist Nozzle

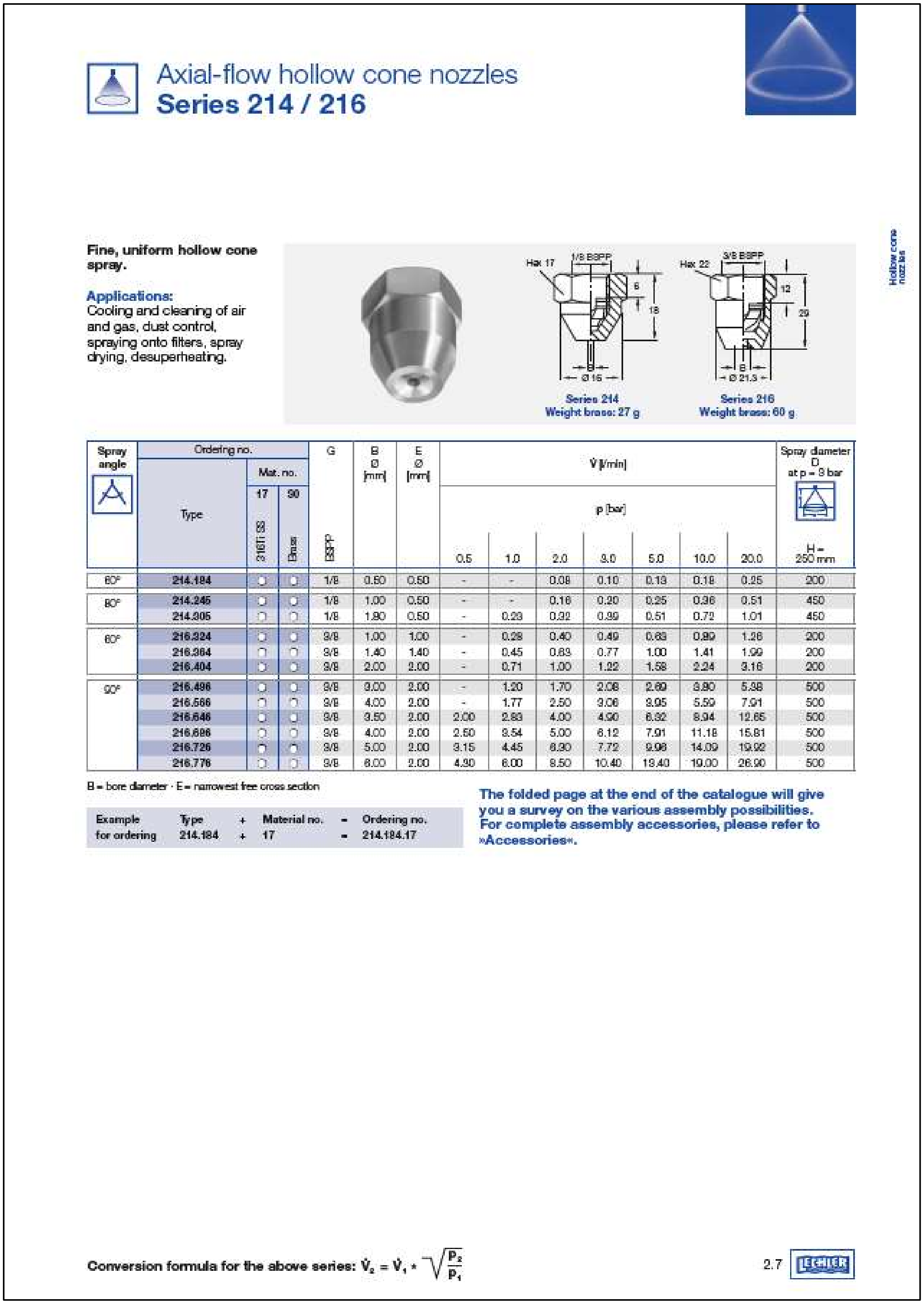
Page: Page 3 of 3

DATA SHEET No: **SN005 1001 A**

Date: 29 August 2017

The right is reserved to vary or modify any specifications without prior notice

Lechler – Series 216.496



Axial-flow hollow cone nozzles
Series 214 / 216

Fine, uniform hollow cone spray.

Applications:
Cooling and cleaning of air and gas, dust control, spraying onto filters, spray drying, desuperheating.

Series 214
Weight brass: 27 g

Series 216
Weight brass: 60 g

Spray angle	Ordering no. Type	Mat. no. 17 316Ti SS	Mat. no. 30 Brass	G BSPP	B Ø [mm]	E Ø [mm]	V̇ [l/min] p [bar] 0.5	1.0	2.0	3.0	5.0	10.0	20.0	Spray diameter D at p = 3 bar H = 250 mm
60°	214.184	○	○	1/8	0.50	0.50	-	-	0.08	0.10	0.13	0.18	0.25	200
80°	214.245	○	○	1/8	1.00	0.50	-	-	0.16	0.20	0.25	0.36	0.51	450
	214.305	○	○	1/8	1.80	0.50	-	0.23	0.32	0.39	0.51	0.72	1.01	450
60°	216.324	○	○	3/8	1.00	1.00	-	0.28	0.40	0.49	0.63	0.89	1.26	200
	216.364	○	○	3/8	1.40	1.40	-	0.45	0.63	0.77	1.00	1.41	1.99	200
	216.404	○	○	3/8	2.00	2.00	-	0.71	1.00	1.22	1.58	2.24	3.16	200
90°	216.496	○	○	3/8	3.00	2.00	-	1.20	1.70	2.08	2.69	3.80	5.38	500
	216.566	○	○	3/8	4.00	2.00	-	1.77	2.50	3.06	3.95	5.59	7.91	500
	216.646	○	○	3/8	3.50	2.00	2.00	2.83	4.00	4.90	6.32	8.94	12.65	500
	216.686	○	○	3/8	4.00	2.00	2.50	3.54	5.00	6.12	7.91	11.18	15.81	500
	216.726	○	○	3/8	5.00	2.00	3.15	4.45	6.30	7.72	9.96	14.09	19.92	500
	216.776	○	○	3/8	6.00	2.00	4.30	6.00	8.50	10.40	13.40	19.00	26.90	500

B = bore diameter · E = narrowest free cross section

Example for ordering	Type	+	Material no.	=	Ordering no.
	214.184	+	17	=	214.184.17

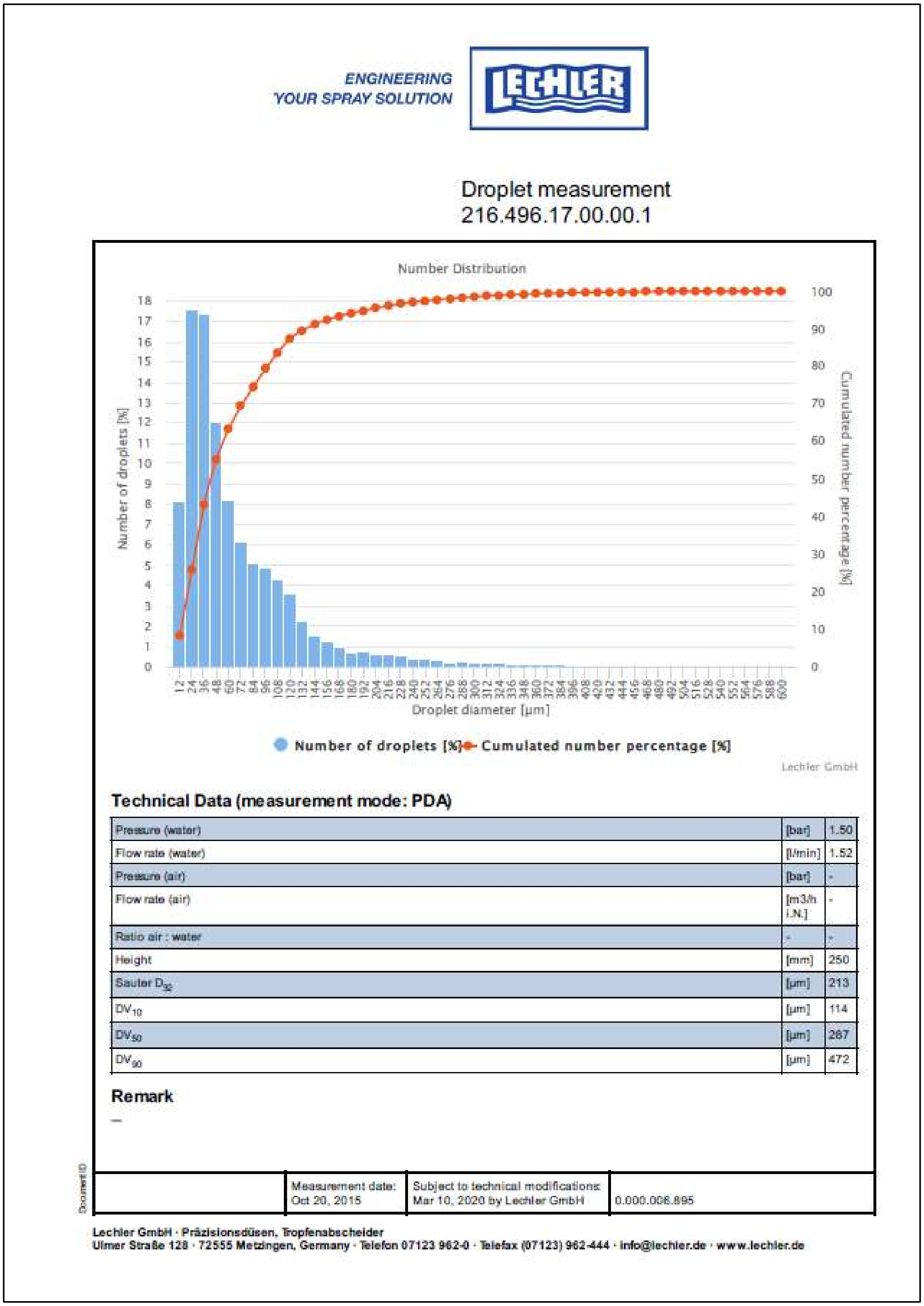
The folded page at the end of the catalogue will give you a survey on the various assembly possibilities. For complete assembly accessories, please refer to »Accessories«.

Conversion formula for the above series: $\dot{V}_2 = \dot{V}_1 \cdot \sqrt{\frac{P_2}{P_1}}$

2.7

Lechler – Series 216.496 – Phase Doppler Anemometry

Operating pressure – 1.5 bar



ENGINEERING
YOUR SPRAY SOLUTION

LECHLER

Droplet measurement
216.496.17.00.00.1

Technical Data (measurement mode: PDA)

Pressure (water)	[bar]	1.50
Flow rate (water)	[l/min]	1.52
Pressure (air)	[bar]	-
Flow rate (air)	[m3/h i.N.]	-
Ratio air : water	-	-
Height	[mm]	250
Sauter D_{32}	[µm]	213
DV_{10}	[µm]	114
DV_{50}	[µm]	267
DV_{90}	[µm]	472

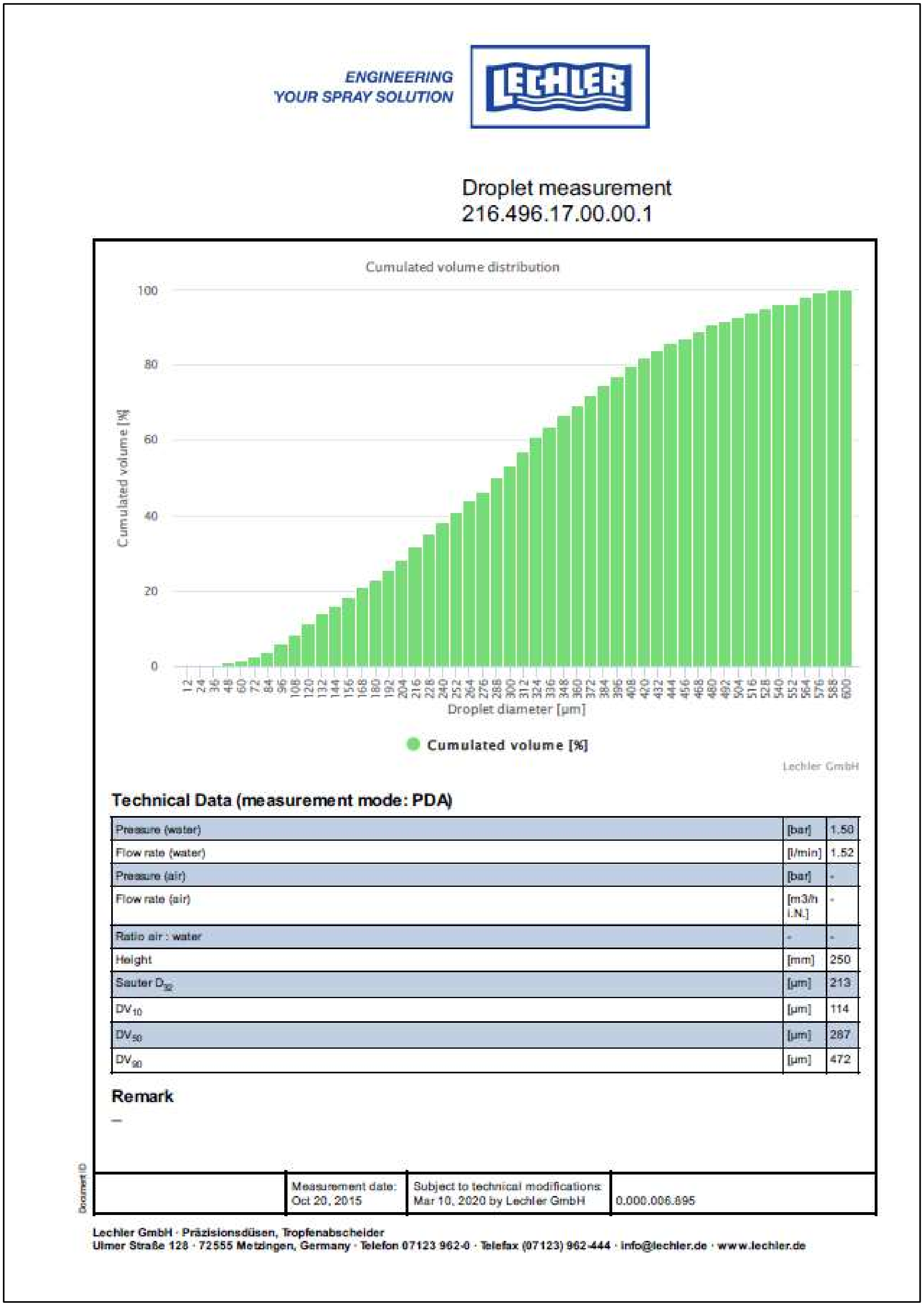
Remark

–

Document ID

	Measurement date: Oct 20, 2015	Subject to technical modifications: Mar 10, 2020 by Lechler GmbH	0.000.006.895

Lechler GmbH · Präzisionsdüsen, Tropfenabscheider
Ulmer Straße 128 · 72555 Metzingen, Germany · Telefon 07123 962-0 · Telefax (07123) 962-444 · info@lechler.de · www.lechler.de



ENGINEERING
YOUR SPRAY SOLUTION

LECHLER

Droplet measurement
216.496.17.00.00.1

Technical Data (measurement mode: PDA)

Pressure (water)	[bar]	1.50
Flow rate (water)	[l/min]	1.52
Pressure (air)	[bar]	-
Flow rate (air)	[m3/h i.N.]	-
Ratio air : water	-	-
Height	[mm]	250
Sauter D_{32}	[µm]	213
DV_{10}	[µm]	114
DV_{50}	[µm]	287
DV_{90}	[µm]	472

Remark

–

	Measurement date: Oct 20, 2015	Subject to technical modifications: Mar 10, 2020 by Lechler GmbH	0.000.006.895

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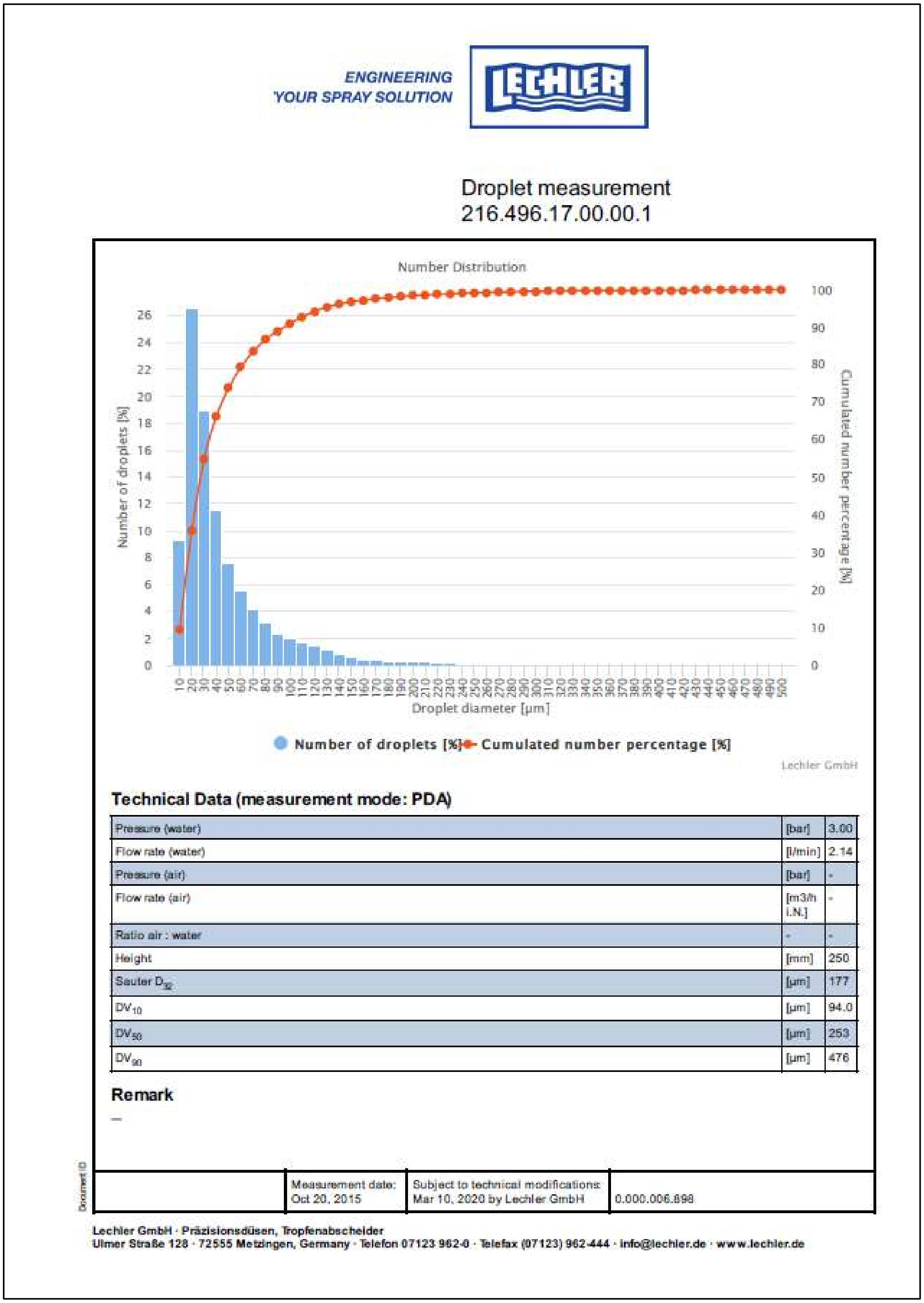
Ulmer Straße 128 · 72555 Metzingen, Germany · Telefon 07123 962-0 · Telefax (07123) 962-444 · info@lechler.de · www.lechler.de

Operating pressure – 3 bar



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Droplet measurement
216.496.17.00.00.1

Technical Data (measurement mode: PDA)

Pressure (water)	[bar]	3.00
Flow rate (water)	[l/min]	2.14
Pressure (air)	[bar]	-
Flow rate (air)	[m3/h i.N.]	-
Ratio air : water	-	-
Height	[mm]	250
Sauter D_{32}	[µm]	177
DV_{10}	[µm]	94.0
DV_{50}	[µm]	253
DV_{90}	[µm]	476

Remark

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Document ID

	Measurement date: Oct 20, 2015	Subject to technical modifications: Mar 10, 2020 by Lechler GmbH	0.000.006.898

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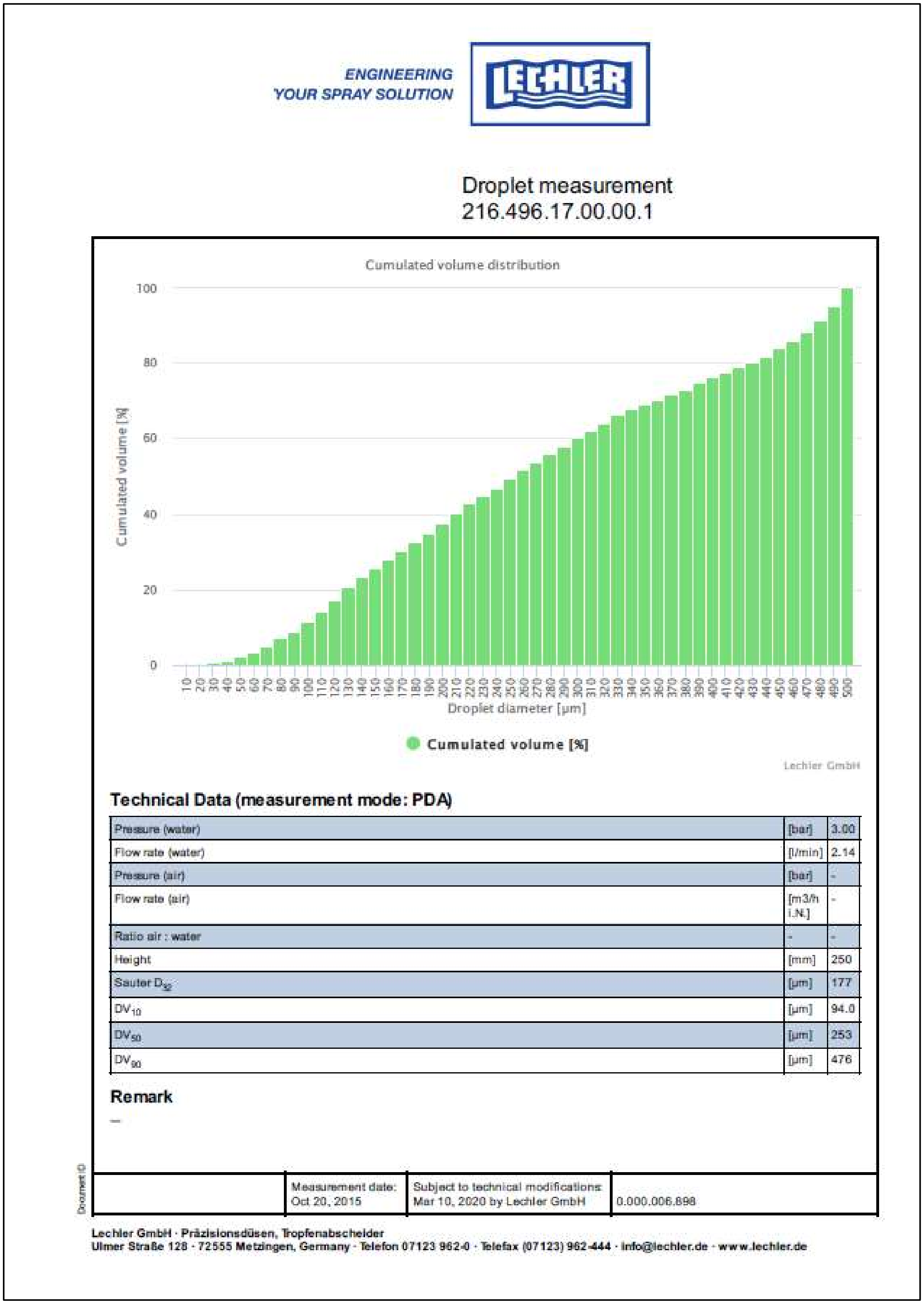

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Droplet measurement
216.496.17.00.00.1

Technical Data (measurement mode: PDA)

Pressure (water)	[bar]	3.00
Flow rate (water)	[l/min]	2.14
Pressure (air)	[bar]	-
Flow rate (air)	[m3/h i.N.]	-
Ratio air : water	-	-
Height	[mm]	250
Sauter D_{32}	[µm]	177
DV_{10}	[µm]	94.0
DV_{50}	[µm]	253
DV_{90}	[µm]	476

Remark

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	Measurement date: Oct 20, 2015	Subject to technical modifications: Mar 10, 2020 by Lechler GmbH	0.000.006.898

Document ID

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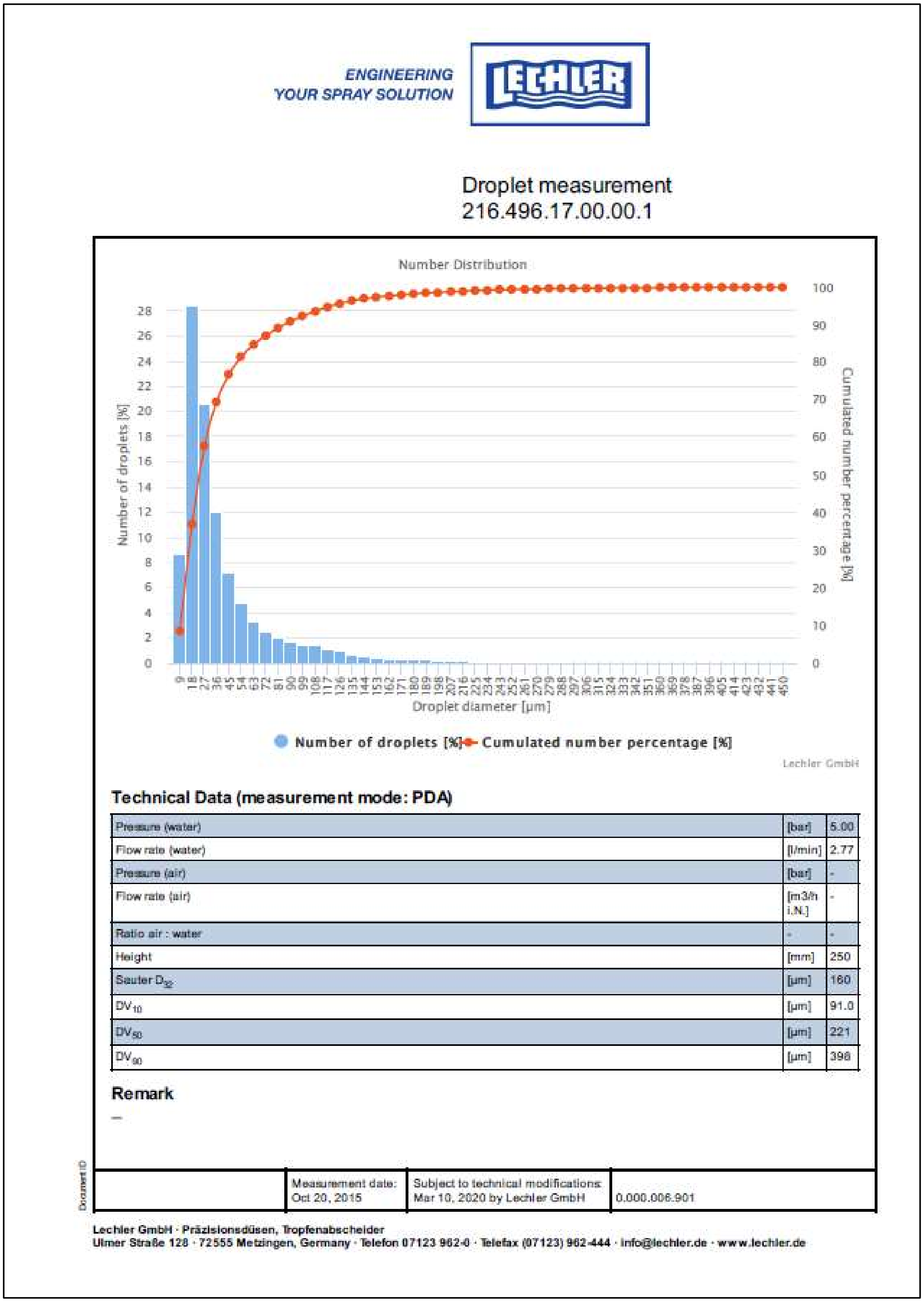
<u>Operating pressure – 5 bar</u>



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Droplet measurement
216.496.17.00.00.1

Technical Data (measurement mode: PDA)

Pressure (water)	[bar]	5.00
Flow rate (water)	[l/min]	2.77
Pressure (air)	[bar]	-
Flow rate (air)	[m3/h i.N.]	-
Ratio air : water	-	-
Height	[mm]	250
Sauter D_{32}	[µm]	160
DV_{10}	[µm]	91.0
DV_{50}	[µm]	221
DV_{90}	[µm]	398

Remark

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Document ID

	Measurement date: Oct 20, 2015	Subject to technical modifications Mar 10, 2020 by Lechler GmbH	0.000.006.901

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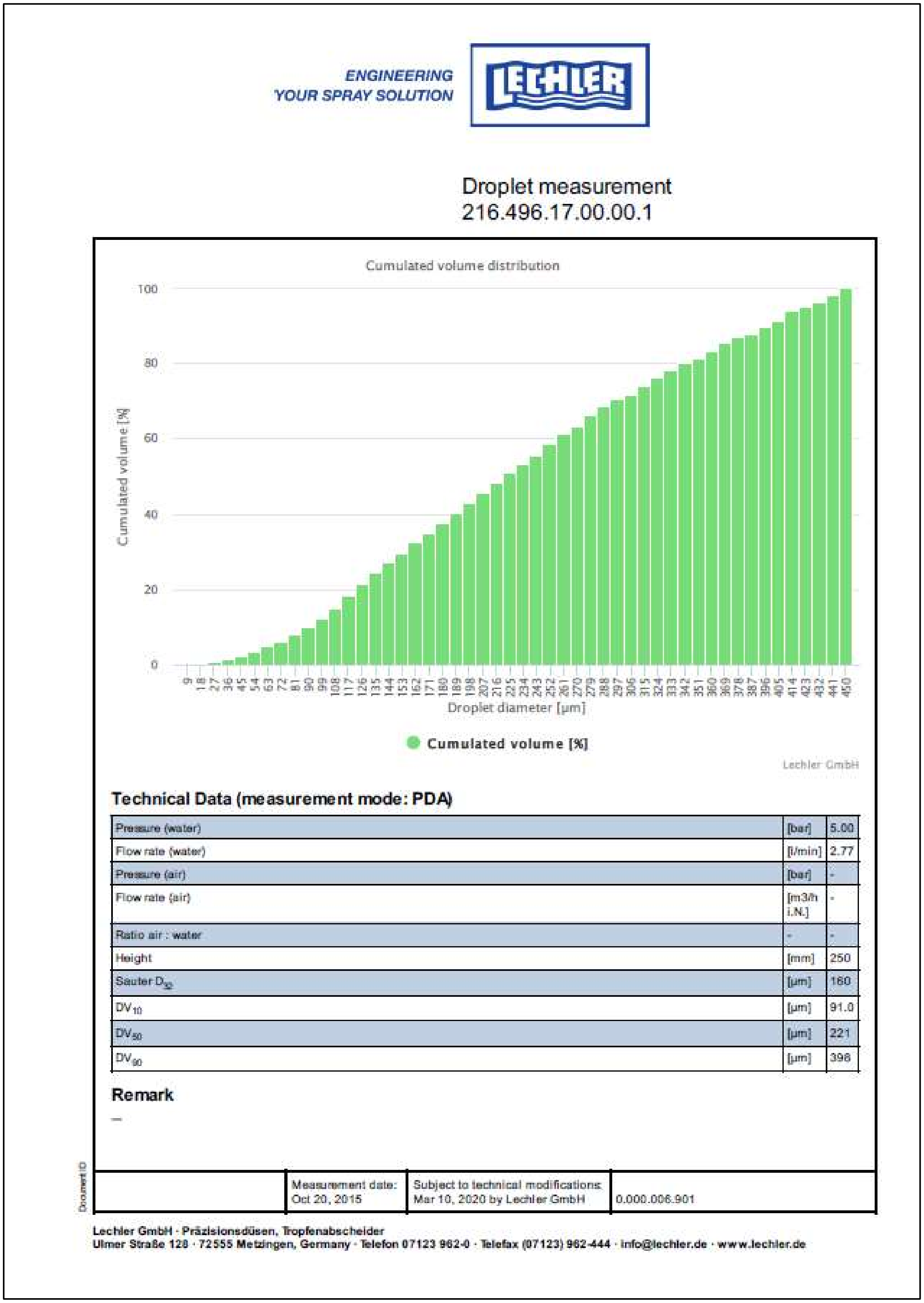

Droplet measurement
216.496.17.00.00.1

Technical Data (measurement mode: PDA)

Pressure (water)	[bar]	5.00
Flow rate (water)	[l/min]	2.77
Pressure (air)	[bar]	-
Flow rate (air)	[m3/h i.N.]	-
Ratio air : water	-	-
Height	[mm]	250
Sauter D_{32}	[µm]	160
DV_{10}	[µm]	91.0
DV_{50}	[µm]	221
DV_{90}	[µm]	398

Remark

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	Measurement date: Oct 20, 2015	Subject to technical modifications Mar 10, 2020 by Lechler GmbH	0.000.006.901

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