## CHARACTERIZATION OF THE EFFECTS OF FUEL AND ENTRAINED SALT ON SOOT MORPHOLOGY

by

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## Abstract

Soot is an important contributor to climate change and has negative effects on human health. These impacts depend on the morphological properties which influence the optical properties, mobility and surface area available to adsorb other contaminants. Different combustion sources may produce soot with different morphologies and thus, different environmental and health impacts. Three soot sources were studied: a dual-fuel natural gas marine engine and two laboratory gas flares. The ship studied operated on its normal route during the measurement campaign and was run both in dual-fuel mode, and diesel-only mode to serve as a comparison. Dual-fuel mode produced substantially less soot, ~96% less, than diesel-only mode at all loads except idle. Soot morphology appeared to be independent of operating load but did vary slightly based on fuelling mode. Dual-fuel mode produced on average smaller aggregates than diesel-only mode however, the small dual-fuel mode aggregates tended to have slightly larger primary particles when compared to diesel-only generated aggregates. Overall the differences in morphology are small compared to the reduction in the amount of soot produced. Gas flaring is used in the oil and gas industry to dispose of gas. The laboratory flares studied were designed to simulate conditions which would be found in the upstream oil and gas industry. Raman spectroscopy showed that the heavier fuels had more graphitic nanostructures and transmission electron microscopy (TEM) and mobility size distributions showed that the aggregates tended to be larger. The relationship between the primary particle size and the aggregate size, did not depend on the fuel. During hydraulic fracturing operations, it is likely that the flowback fluids become entrained in the flare fuels resulting in liquids with inorganic salts becoming part of the combustion process. The morphology of the soot did not change due to the salt however, most of the soot particles became internally mixed with the salt. Unlike soot, salt tends to be an effective cloud condensation nucleus (CCN) and the large number of salt particles will likely influence local cloud formation. Furthermore, the salt particles which attach to the soot may turn the soot itself into an effective CCN.

## Lay Summary

Soot is recognized to be an important contributor to climate change and has negative effects on human health, but its shape determines the size of the effect. This work evaluates the effect of fuel and salt on the shape of soot from three different sources: a dual-fuel marine engine, a gas flare and a gas flare with liquid additives. Natural gas fuelling resulted in ~96% less soot than diesel fuelling with small but statistically significant changes in shape. 'Heavy' fuels produced more soot with slightly larger sizes but no changes in shape compared to 'lighter' fuels. Water in the fuel reduced the soot production but had no effect on shape. The addition of salt again, did not change the shape however most of the soot was attached with the salt. The mixed particles may have effects on clouds different from that of soot alone.

## Preface

This research is the original intellectual product of the author, Una Trivanovic, with the guidance and mentorship of Dr. Steven Rogak. The three chapters in this work are based on one published work and two in-preparation manuscripts. Figure 1.2 is reproduced from the 2013 Intergovernmental Panel on Climate Change report with permission.

A version of Chapter 2 has been published as: Una Trivanovic, Joel C. Corbin, Weihan Peng, Jiacheng Yang, Patrick Kirchen, J. Wayne Miller, Prem Lobo, Stéphanie Gagné, Steven N. Rogak. Size and morphology of soot produced by a dual-fuel marine engine (2019) Journal of Aerosol Science. The supplemental information published for this article is Appendix B: of this thesis. The paper is reproduced here with permission from Elsevier. The experiments were organized by Dr. Stéphanie Gagné, the primary investigator from the National Research Council of Canada (NRC). The dilution tunnel was designed and set up by Weihan Peng, Dr. Jiacheng Yang and Professor J. Wayne Miller from the University of California Riverside. Transmission electron microscope (TEM) images and high-resolution TEM (HRTEM) images were taken by me and Dr. Alberto Baldelli, a post-doctoral researcher from the University of British Columbia (UBC) with training and assistance from the University of British Columbia (UBC) Bioimaging Facility technician, Bradford Ross. TEM grids were collected by Miayan Yeremi a PhD student from UBC, Brett Smith a technician from the NRC and me. Image analysis was performed, by me and Yiling Kang an Undergraduate Student Research Award (USRA) student working under my supervision. The image analysis algorithm was developed by Dr. Ramin Dastanpour who was a post-doctoral researcher when I started at UBC. Grids were collected using a thermophoretic sampler (TPS) developed at UBC by Jeff Farnese a USRA student. Scanning Mobility Particle Sizer (SMPS) data in was captured and analyzed by Dr. Joel Corbin, an NRC research officer. Dr. Prem Lobo from the NRC and Professor Patrick Kirchen from UBC provided technical discussion and helped to revise the manuscript. Other data from this measurement campaign not included in this thesis was published as: Joel C. Corbin, Weihan Peng, Jiacheng Yang, David E. Sommer, Una Trivanovic, Patrick Kirchen, J. Wayne Miller, Steven Rogak, David R. Cocker, Gregory J. Smallwood, Prem Lobo, Stéphanie Gagné. Characterization of particulate matter emitted by a marine engine operated liquefied natural diesel with gas and fuels Atmospheric Environment (2019)doi: https://doi.org/10.1016/j.atmosenv.2019.117030.

A version of Chapter 3 is under preparation for submission as: **Una Trivanovic**, Timothy A. Sipkens, Mohsen Kazemimanesh, Alberto Baldelli, A. Melina Jefferson, Bradley M. Conrad, Matthew R. Johnson, Joel C. Corbin, Jason S. Olfert, Steven N. Rogak. Morphology and size of soot from turbulent diffusion flames as a function of fuel and water addition. The supplemental information for this article is Appendix C: of this thesis. The experiments were organized as part of the FlareNet strategic network. Experiments were performed at the Carleton University Flare Facility. The experimental set-up was performed by Bradley Conrad, Professor Matthew Johnson and Melina Jefferson from Carleton University. TEM images were taken by me and Alberto Baldelli. TEM and Raman grids were collected by Miayan Yeremi and Keyhan Babaee, an MASc student at UBC, using the same TPS. Image analysis was performed, using the same Matlab code, by me and Yeshun Samuel Ma, a USRA student under my supervision. SMPS data was collected

by Dr. Mohsen Kazemimanesh, a PhD student from the University of Alberta. Raman spectroscopy and peak deconvolution was performed by Dr. Alberto Baldelli. Versions of the figures in this Chapter were created by Dr. Timothy Sipkens, a post-doctoral researcher from UBC.

The experiments in Chapter 4 were conducted at the University of Alberta as part of a large collaborative study. The experimental set up was performed by Olanrewaju Bello, a PhD student from the University of Alberta. SMPS and data was captured by Dr. Timothy Sipkens. TEM and Raman grids were collected by me. Raman spectroscopy and peak deconvolution was performed by Dr. Alberto Baldelli. Versions of the figures in this Chapter were created by Dr. Timothy Sipkens. I performed the TEM analysis.

A version of Appendix B was published as: Alberto Baldelli, **Una Trivanovic**, Steven N. Rogak. Electron tomography of soot for validation of 2D image processing and observation of new structural features (2019) 53 (5) 575-582 DOI: 10.1080/02786826.2019.1578860. The paper is reproduced here with permission from Taylor and Francis. Dr. Alberto Baldelli performed the 3D tomographic reconstructions with the help of Bradford Ross in the UBC Bioimaging Facility. 2D image analysis was performed by Yiling Kang and me. 3D model layer construction was performed by Yiling Kang.

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# List of Symbols

da	Projected-area-equivalent diameter
$D_{lpha}$	Projected-area exponent
$D_{\mathrm{f}}$	Fractal dimension
$D_{\mathrm{TEM}}$	TEM power law exponent
$d_{ m m}$	Electric mobility diameter
$d_{ m p}$	Primary particle diameter
<i>d</i> <sub>p,100</sub>	Primary particle diameter of a 100 nm aggregate
d <sub>va</sub>	Sauter mean diameter of the primary particles
ka	Power law prefactor
ko	Fractal prefactor
Ν	Number of primary particles
$R_{ m g}$	Radius of gyration
ρ	Material density
$ ho_{ m eff}$	Effective density
$ ho_{ m eff,100}$	Effective density of a 100 nm aggregate
σ	Standard deviation

# List of Abbreviations

BC	Black Carbon
Card	Cardium shale formation simulated flowback fluid
CB	Carbon Black
CCN	Cloud Condensation Nucleus
C:H	Carbon to Hydrogen Ratio
CH <sub>4</sub>	Methane
CI	Confidence Interval
CI engine	Compression Ignition Engine
$CO_2$	Carbon Dioxide
CPC	Condensation Particle Counter
СРМА	Centrifugal Particle Mass Analyzer
D/G	Disorder to Graphitization Ratio
DLCA	Diffusion Limited Cluster Aggregation
DMA	Differential Mobility Analyzer
Duve	Duvernay shale formation flowback fluid
DW	Deionized Water
ECA	Emission Control Areas
ESEM	Environmental Scanning Electron Microscopy
ETEM	Environmental Transmission Electron Microscopy
GDI	Gasoline Direct Injection
GHG	Greenhouse Gas
HRTEM	High Resolution Transmission Electron Microscopy
ICN	Ice Condensation Nucleus
IMO	International Maritime Organization
IPCC	Intergovernmental Panel on Climate Change
LNG	Liquefied Natural Gas
MAC	Mass Absorption Cross-section
MSC	Mass Scattering Cross-section
NaCl	Sodium Chloride
NG	Natural Gas
NO <sub>x</sub>	Nitrogen Oxides
PM	Particulate Matter
PM 2.5	Particulate Matter less than 2.5
SI engine	Spark Ignition Engine
SLPM	Standard Litres Per Minute
SMPS	Scanning Mobility Particle Sizer
SO <sub>x</sub>	Sulphur Oxides
TEM	Transmission Electron Microscopy
TPS	Thermophoretic Sampler
ULSD	Ultra-Low Sulfur Diesel
WHO	World Health Organization

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I would also like to thank Dr. Joel Corbin, from the National Research Council of Canada (NRC), for his technical support, scientific discussions and mentorship. He has played a role in either analyzing, discussing or measuring data in every chapter of this thesis. I was also fortunate enough to collaborate with Professor Patrick Kirchen (UBC), Dr. Stéphanie Gagné (NRC) and Dr. Prem Lobo (NRC) who helped polish Chapter 2 of this thesis into my first, first-authored journal publication.

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Much of the work in Chapters 3 and 4 was done in collaboration with the University of Alberta (UA) so I would like to thank Professor Jason Olfert (UA) for hosting us in his lab for the experiments described in Chapter 4, helping to design the experiments and extinguishing (metaphorical) fires during the campaign. I would also like to thank Dr. Mohsen Kazemimanesh (UA) for his collaboration on this work.

The TEM image analysis in this thesis is a painstaking process so I would like to acknowledge Yiling Kang and Samuel Ma, UBC USRA students, for their help analyzing the images as well as Dr. Alberto Baldelli who took some of the images in addition to helping with analysis. I would also like to thank Bradford Ross, UBC bioimaging facility technician, for training me to use the TEM and always helping me when something inevitably went wrong. I would also like to thank Dr. Adam Boies from the University of Cambridge for hosting me as a Mitacs Globalink Intern.

Finally, I would like to thank my friends and family near and far for supporting me in everything I do and visiting me when I decide to move half way around the world.

# Dedication

To my parents, who have support me in everything I do.

# Chapter 1 : Introduction 1.1 Background

Soot is a particle produced by a variety of combustion processes due to incomplete combustion of hydrocarbons. It has established negative health effects [1]–[3] and is an important contributor to climate change [4], [5] where it is typically referred to as black carbon (BC) by the climate community. It is also an important industrial material called carbon black (CB) which is used in black pigments and tires. Soot is a carbonaceous aerosol composed of spherical primary particles which aggregate to form a semi-fractal structure on the order of hundreds of nanometers in diameter. Figure 1.1 shows three transmission electron microscope (TEM) images of typical soot particles. Even from a single source, particles can range from nearly a micron in size with thousands of primary particles (Figure 1.1a) to hundreds of nanometers in size with hundreds of primary particles (Figure 1.1b) to less than 100 nm in size with ~ 5 primary particles (Figure 1.1c). Characterizing particle morphology can improve understanding of the magnitude of the health and climate risks, potentially aid in source identification and develop methods for eliminating or measuring particles to reduce their impact. Despite years of research, soot formation is not well understood [6] although there are two proposed mechanisms for soot formation widely cited in the literature [7], [8].



Figure 1.1: TEM images of typical soot particles illustrating the wide range of possible morphologies, a) and c) are from a gas flare, b) is from a marine engine burning natural gas with a diesel pilot.

A fractal is an object which has a self-similar pattern at different scales. This concept was made famous with a description of the coast of Britain [9] where it was shown that the length of the coast depended on the length of the 'measuring stick'. The rate at which the length of the coast changed with respect to the size of the measurement became the fractal dimension,  $D_{\rm f}$ , now widely used to quantify these types of complex structures. Aggregated particles such as soot are considered 'semi-fractal' or 'fractal-like' because they do not meet the mathematical requirements for a fractal. They only exhibit self-similarity over a limited range of scales with the upper limit being some measure of aggregate size and the lower limit being a measure of primary particle size [10]. Fractal dimension for aggregates such as soot can be defined either as the fractal dimension for a population of aggregates or an individual aggregate. When estimating fractal dimension from transmission electron microscopy (TEM), the projected area of a feature is assumed to be

proportional to the mass of the feature thus the reported value is really the mass-fractal dimension. The mass fractal dimension is a 3-dimensional property and as such, using TEM to estimate this quantity can induce errors due to shielding which is discussed further in Appendix A:. Aggregates with few (less than 100) primary particles may be more susceptible to errors due to shielding resulting in an under estimation of  $D_f$  but this error decreases with increasing aggregate size [10]. Previous literature on the morphology of soot explored the fractal dimension of soot in great detail in part because the fractal dimension can be used in the equation [11]:

$$N = k_o \left( R_g / d_p \right)^{D_f} \tag{1}$$

Where *N* is the number of particles,  $k_0$  is the fractal prefactor,  $R_g$  is the radius of gyration (a measure of aggregate size) and  $d_p$  is the primary particle diameter. This equation offers a complete mathematical description of the aggregate. If  $D_f$  and  $k_0$  of the particle population are known, then the other properties can be inferred however, these values are not usually known [12]. This equation also relates particle morphology to its light scattering properties [11]. Finally, the fractal dimension alone (without the prefactor) of a particle population can be correlated to an aggregation model. Diffusion limited cluster aggregation (DLCA) has effectively described soot morphology and produces a  $D_f \sim 1.8$  [13], [14] making  $D_f \sim 1.8$  the generally accepted value for the fractal dimension of soot.

#### 1.1.1 Health and climate effects of soot

The negative health effects of soot were documented as early as 1775 when it was identified as the cause of cancer in chimney sweeps [15]. Since then particulate matter (PM) in air pollution, of which soot is an important component, has been linked to a suite of health problems including cardiovascular effects [2], [16], lung disease [3], [17] and more recently declines in mental health [18]. The world health organisation (WHO) estimates that annually 3 million deaths world wide can be attributed to air pollution [19] and even in 'clean' areas modest reductions in PM 2.5, particulate matter less than 2.5  $\mu$ m in diameter, could have large health benefits [20]. However, the particle morphology plays a role in its toxicity. Specifically, surface area is correlated to the primary particle diameter ( $d_p$ ), has been shown to be the most important metric when assessing acute nanoparticle toxicity [21], while the mobility diameter ( $d_m$ ) determines where in the lungs particles are deposited [22], [23]. Early epidemiological studies showed a relationship between PM mass concentration and health effects prompting many air quality standards to be measured on this basis (e.g. PM 2.5 standards which place limits in terms of mg/m<sup>3</sup>) but more recent data suggests that number based concentration may be a more important measure [5], highlighting the importance of understanding particle morphology.

All aerosols play a role in the climate through mechanisms such as cloud interactions however soot, or BC, is special in that it is one of the few aerosols that is recognized to have a net warming effect on the planet [4]. BC plays a complex role in the atmosphere, in part due to its short atmospheric lifetime (a few days to weeks [4]) and the multiple mechanisms through which it warms the atmosphere. Four different climate effects have been proposed: direct effects (scattering and absorption of solar radiation), indirect effects (changes to cloud physics), indirect surface albedo effect (deposition on snow and ice increasing melting) and semi-direct effects (altered humidity profiles in the atmosphere effect cloud formation) [5]. Reducing BC emissions to address climate change can be particularly attractive in developing countries which emit a large portion of the world's BC emissions but a small proportion of the world's greenhouse gas (GHG) emissions [24]. Addressing BC emissions has the dual benefit of addressing climate change and poor air quality at the same time and is often co-emitted with other pollutants and GHGs. Again, particle morphology determines the magnitude of its climate effects. Mass absorption cross-section (MAC) and mass scattering cross-section (MSC) are the two the most important quantities when assessing the climate warming potential as the balance between the two determines whether a particle has a net warming or cooling effect and are used in climate models [25], [26]. While measuring morphology does not replace directly measuring the optical properties, it is the physical basis for these properties and influences the optical properties [27]. For many measurement techniques, the morphology of the soot must be assumed in order to measure the optical properties making it an essential component of assessing the climate effects.

#### 1.1.2 Soot sources investigated

While soot is produced by many different combustion systems, two are investigated here: a marine engine and gas flares. While marine engines have been studied in the past, the particular type of engine studied here, a dual-fuel natural gas engine, has not previously had its soot emissions characterized beyond measuring the over-all quantity of soot. Gas flares on the other hand, although used extensively in the oil and gas industry to dispose of waste gas not economical to capture, have not been carefully studied in the past. Poor characterization of the emissions from gas flares makes it difficult to regulate and assess the actual climate and health impact. Both of these sources are particularly important in the Arctic where soot has an even greater impact on the climate [28]. Oil and gas operations in the Arctic and increasing marine traffic through the Arctic are important contributors to Arctic climate change [29]. The Arctic has become more attractive as a shipping route due to recent decreases in sea ice [30] and recently there have been political debates over opening up the Arctic to more oil and gas drilling [31] in addition Russia, the country with the largest gas flaring volumes [32], is expected to continue expanding its oil and gas operations [33]. A thorough understanding of the emissions from these sources is critical to weighing the risks associated with these options against the alternatives and soot is an important piece of this risk assessment.

#### **1.2 Motivation**

The recent Intergovernmental Panel on Climate Change (IPCC) special report listed aerosols as the largest contributors to uncertainty in the remaining global carbon dioxide (CO<sub>2</sub>) budget [34] in part due to the use of Mie theory for assessing the direct effects of BC which assumes spherical particles [4] and due to the extremely complex indirect climate effects of aerosols including soot [35]. Figure 1.2, reproduced from the 2013 IPCC report on climate change [36], illustrates this. Uncertainties on the 'Aerosols' and 'Changes in clouds due to aerosols' bars are considerably larger than any of the others to the extent that even the sign of the 'Aerosols' effect is in question, depending on both the positive contribution of soot and the negative contribution of other aerosols. Thus, understanding particle morphology in the context of both its

direct and indirect climate effects has the potential to drastically improve climate models in addition to assessing individual source impacts for regulatory purposes.



Figure 1.2: Figure from the 2013 IPCC report quantifying changes in global radiative forcing due to human activities since 1750. Reproduced with permission.

Regulation of emissions for both climate and air quality purposes requires robust, easy-touse methods for measuring emissions. The studies discussed in this thesis were largely done in controlled environments with laboratory grade equipment, many experienced individuals and months of data processing and analysis. This level of characterization is too costly and not necessary for simply monitoring emissions however the morphological characteristics measured here are essential for the development of simpler, less involved yet reliable measurements. Optical methods are widely used for online aerosol measurement in everything from laboratory grade instruments to household smoke detectors [37]. Similar to the uncertainties in climate models due to the widely used simplifying assumption of spherical particles, optical instruments such as smoke detectors require knowledge of particle morphology for accurate measurements [37]. Even laboratory grade instruments, which do not rely on optical properties but rather particle mobility, can disagree due to the influence of particle morphology [38].

One of the challenges of characterizing soot morphology is the wide range of morphologies produced by the different sources and even within just one source as shown in Figure 1.1, where a) and c) are from the same source. Transmission electron microscopy (TEM), is an attractive method for quantifying morphology as it gives a level of detail that is nearly impossible to achieve with an online measurement. The drawback being that, given the polydisperse nature of soot

populations, an extremely large number of particles must be analyzed to extract statistically significant information. Recent advancements in image processing techniques have allowed for the application of TEM to much larger data-sets than in the past and has led to researchers in the field to try to build automated image analysis codes for soot. One such algorithm is applied here developed by Dastanpour, Boone and Rogak [39]. Appendix A: is a validation of the accuracy of this code when accounting for the fact that soot is a 3-dimensional object being assessed through 2-dimensional images. The findings in Appendix A: confirm that while the code doesn't have systematic biases with respect to projection angle, it does have some variability. Furthermore, one single number often doesn't accurately represent the range of morphologies within an aerosol population. Throughout this thesis methods described by Olfert and Rogak [40] are employed to describe the range of soot particles rather than reporting one median value for primary particle size of a soot population.

#### **1.3 Thesis Outline**

This purpose of this thesis is to quantify differences in soot morphology changes in fuel composition or liquid additives. It applies advancements in image processing [39] and new methods for summarizing the wide range of particle morphologies within a single population [40] to soot from realistic sources which haven't been carefully characterized in the past. This will provide a theoretical basis necessary for developing instrumentation for regulatory purposes and in assessing the potential climate and health impacts.

Chapter 2 describes a study on soot from a commercial, in-use dual-fuel marine engine which can operate either on natural gas (NG) with a small diesel pilot or completely on diesel. NG engines produce significantly less soot than a diesel engine however the quantity is not negligible and has not previously been characterized as NG engines gain popularity. Experiments conducted by Corbin et al. [41] suggest that the soot from the dual-fuel engine originates from the diesel pilot, rather than the pre-mixed natural gas.

In Chapter 3 a laboratory gas flare located at the Carleton University Flare Facility is studied. The flare is a large turbulent diffusion flame. These experiments were conducted with a wide range of different fuels representative of the global oil and gas industry under the same combustion conditions. Here, it is expected that changes in soot morphology are due to the fuel, not combustion conditions.

Finally, Chapter 4 examines soot produced from flames with entrained liquid additives representative of flowback fluids from hydraulic fracturing. A preliminary study was performed on the same gas flare located in the Carleton University Flare Facility followed by a more focused study at the University of Alberta with a slightly smaller flare. The purpose of these experiments was to examine the effect of inorganic salts and liquids on the morphology of soot. The mixing state of the soot and salt particles are carefully considered.

Chapter 5 summarizes the results from the different studies and provides recommendations for future work. While the intermediate chapters focus on the technical findings from the experimental work, this chapter will explore the implications those technical findings may have on the climate and health.

# Chapter 2 : Size and morphology of soot produced by a dual-fuel marine engine

## **2.1 Introduction**

The International Maritime Organization (IMO) develops international regulations and recommendations to prevent pollution of the marine environment. Increasingly stringent IMO regulations on emissions from shipping have turned natural gas (NG) into an attractive fuel for commercial transportation. Compared to other fossil fuels NG has lower particulate matter (PM) and potentially lower nitrous oxides ( $NO_x$ ) emissions in addition to eliminating sulphur oxide ( $SO_x$ ) emissions. Currently the IMO regulates SO<sub>x</sub>, NO<sub>x</sub> and PM emissions. In 2020 a worldwide cap on sulphur content in fuel will come into place (reducing the acceptable sulphur content in fuels from 3.5% mass/mass to 0.5 m/m), while in Emission Control Areas (ECAs) sulphur is already limited to 0.1% m/m. The ECAs designated by the IMO comprise an important portion of world trade including: the Baltic Sea area, the North Sea area, the North American area and the United States Caribbean Sea area. NG also promises lower carbon dioxide (CO<sub>2</sub>) emissions, however due to increased methane (CH<sub>4</sub>) emissions it may not lead to a net reduction in greenhouse gas (GHG) effects, depending on the time period over which these emissions are evaluated and engine operation [42]. Beyond its potential for emission reductions it is also typically cheaper than diesel and is available worldwide [43]. The PM emissions are partially comprised of soot or black carbon (BC). Unlike GHGs, the effect of BC on the environment is much more complex and regional than GHGs. The Arctic is particularly sensitive to BC emissions as particles deposit on the surface of snow and ice altering surface albedo and increasing the rate of melting [44]. Furthermore, BC emitted at lower altitudes has greater climate forcing in the Arctic [28]. For these reasons, BC from marine applications is particularly important as marine traffic in the Arctic may increase in the future due to the reduction in sea ice, making these areas more navigable. The negative health effects of BC are also of concern in port cities [45]. In addition, the morphology of soot particles can be used to gain insights into the combustion conditions [46], [47] and enable further improvements of these conditions. In the case of natural gas, improved combustion would decrease methane emissions and render the fuel even more attractive on a GHG emissions basis.

The IMO does not regulate BC and as such, very little information exists on marine engine BC. Previous studies on NG engines have focused on the volatile fraction of PM emissions [48], [49] or simply on PM quantity [50], [51]. While NG engines typically produce dramatically less soot than other fuels, the quantity, especially in accumulation is non-negligible and is likely to increase in the coming decades. Thus, it is important that we understand the morphology of these particles and how they were formed. To the authors' knowledge no previous publications have described particle morphology from dual-fuel natural gas engines.

In this study the primary particle sizes, aggregate size distributions, and nano-structure of PM catalytically denuded at 350 °C from a dual-fuel marine engine is presented and discussed. The engine studied here was designed and tuned to be operated specifically on liquefied NG (LNG), although diesel-only operation is possible. Soot morphology from both LNG and diesel-only operation were studied using transmission electron microscopy (TEM), high resolution TEM (HRTEM) and a scanning mobility particle sizer (SMPS). Effective density was inferred from primary particle size and aggregate size. TEM was used to explain the observed non-lognormal SMPS size distributions. Total PM emissions and their environmental impact are described by

Corbin et al. [41]. Methane emissions and reduction strategies, as measured directly from the exhaust stream are described by Sommer et al. [42]. Although most of the particles in this study were soot, the SMPS size distributions may also include some organic PM and thus, the terms PM and soot are both used throughout this chapter.

#### **2.2 Methods**

#### 2.2.1 Sample collection

The soot emissions described in this work were collected aboard a commercial in-use vessel equipped with two 4320 kWh, dual-fuel, four-stroke, nine-cylinder, compression ignition engines. While these engines can run on either diesel or NG, they were specifically designed to run on NG, unlike many other NG powered vehicles which are retrofitted diesel engines. In order to ignite the NG by compression, a small quantity of diesel pilot is used. At engine loads above 50%, the diesel pilot provides only ~2% of the total energy. Below 50% load the proportion of energy provided by the diesel pilot remains below ~10% with the exception of idle, when the diesel pilot makes up a higher proportion of the provided energy. Measurements were performed during the vessel's normal commercial operation from a single engine. For each measurement the load was set at the desired level for around 30 minutes while the second engine supplied any additional power required by the vessel. Measurements were taken across a range of engine loads including idle for both NG and diesel-only mode. Ultra-low sulphur diesel (ULSD) fuel was used, and the LNG was composed of primarily methane (91-95%).

Emissions were sampled from the exhaust stack at temperatures above ~350 °C and routed with a heated sampling line maintained at ~55 °C to a partial dilution tunnel meeting ISO-8178 standards and described by Gysel et al.[52]. The exhaust was diluted 6-fold using dry air and was distributed to a suite of diagnostic emissions instrumentation described elsewhere [41]; and only the TEM and SMPS data are discussed here. Background-subtracted  $CO_2$  concentrations were used to determine the dilution ratio.

A TSI SMPS (model numbers 3088, 3082, 3081 and 3776) with an X-ray charger was used in conjunction with a 350 °C catalytic stripper (Catalytic Instruments GmbH, Germany, model CS015) to remove volatile PM. A mobility-diameter range of approximately 6 – 170 nm was used for most measurements; however, the size distributions were monitored, and the range adjusted if indications of larger particles were present. Scans of up to 200 seconds were used to ensure adequate scan time; the median scan time was 20 seconds. The SMPS was generally operated with sample and sheath flows of 0.3 and 3.0 standard litres per minute (SLPM), respectively, with occasional scans conducted at 1.5 and 15 SLPM. Data were inverted by the software algorithms built into the TSI 3082, which does not account for aggregate-specific effects [53] and may therefore be biased low by about 20% for the estimation of soot number concentrations [54].

The length of the sampling line from the manifold to the instruments was between 2 to 4 m. Particle losses within the CS015 are particularly relevant for the SMPS and were corrected for using a manufacturer-provided particle penetration function, which was itself derived through a combination of theory and experiment (personal communication, Catalytic Instruments, 2018). Particle penetration through our sampling system was modelled and discussed by Corbin et al.

[41], with the conclusion that particles with mobility diameters of 10, 20, 40, and 100 nm would have been measured with 73, 85, 91, and 95 % efficiency, respectively. Since the vast majority of soot particles were larger than 40 nm, no correction for these losses was implemented and the concentration of very-small (<10 nm) particles shown in Figure 2.5 below should be considered a lower bound

Soot was deposited onto 3 mm carbon type-B copper TEM grids (01813, 300 mesh, Ted Pella) using either a custom thermophoretic sampler (TPS) developed at the University of British Columbia (UBC) or an ESPnano (Model 100, Wa., USA) which functions on the principle of electrostatic precipitation [55]. A  $\sim$  2 m long sampling line was used to extract 1 lpm of flow from the sampling manifold in a closed loop with the TPS using 300 ccm from this line for sample collection. This allowed the flow to continue undisturbed when the TPS was not running. A schematic of the sampling system can be found in Appendix B: (Figure B.1). During diesel-only operation grids were collected for  $\sim$  30 s at idle, 25% load, 50% load or 75% load. During LNG operation, total soot produced was over an order of magnitude less than diesel, and thus required sampling times of  $\sim$  30 min. The engine load was not as consistent for the entire duration of the long sampling periods. For this reason, loads when the engine was operating on LNG were separated into idle, low ( $\sim$  30% load), medium (40% to 60% load) and high (70% to 90% load) categories.

#### 2.2.2 Transmission electron microscopy and image analysis

TEM images were taken with a Hitachi H7600 transmission electron microscope located in the UBC Bioimaging Facility. The H7600 TEM allows for 0.35 nm point to point resolution. Images were taken with 80 kx – 150 kx magnification and an accelerating voltage of 80 kV. A total of 383 TEM images were taken, resulting in the analysis of 736 individual particles using a previously-validated automated image processing algorithm described by Dastanpour, Boone and Rogak [39]. This algorithm binarizes TEM images automatically using Otsu's algorithm for thresholding and rolling ball transformation allowing projected-area-equivalent diameter to be calculated and then uses the Pair Correlation Method (PCM) to estimate average primary particle diameter ( $d_p$ ) as follows. The PCM assumes that the variation in  $d_p$  within an aggregate is small compared to the variation between different aggregates. Instead of measuring individual primary particles, the PCM estimates the average  $d_p$  within an aggregate with the pair correlation function, a weighted average of the binary image density at a given radius, tuned for TEM images of soot. Thus, the  $d_p$  reported for each aggregate does not account for polydispersity within the aggregate but rather it is an estimate of the average  $d_p$ .

For high resolution (HR) TEM exhaust, PM was deposited onto 3 mm lacey formvar/carbon copper TEM grids (01885, 400 mesh, Ted Pella) using the thermophoretic sampler. Images were taken with a FEI Tecnai G2, located in the UBC Bioimaging Facility, which is capable of up to 700 kx magnification with point resolution of 0.27 nm. Images were taken with an acceleration voltage of 80 kV.

#### 2.3 Calculated parameters

Soot primary particle size has typically been reported as a single median diameter for the entire soot population studied. However, soot, even from a single source exhibits a wide range of aggregate and primary particle sizes making a single number a poor representation of the entire population. Furthermore, it has been observed that across a range of different soot sources, the primary particle size does not vary significantly within a given aggregate, but does vary significantly between aggregates of different size [47]. In other words, primary particle size  $(d_p)$  is correlated to aggregate projected-area-equivalent diameter (da). Olfert and Rogak [40] showed that this relationship can be described with a power law in the form:

$$d_{\rm p} = d_{\rm p,100} \left(\frac{d_{\rm a}}{100 \,\rm nm}\right)^{D_{\rm TEM}} \tag{2.1}$$

where  $D_{\text{TEM}}$  is the power law exponent, and  $d_{p,100}$  is the primary particle size for an aggregate with a projected-area-equivalent diameter of 100 nm. The use of  $d_{p,100}$  in Equation 1 results in a physically meaningful power-law prefactor, as it is common to observe 100 nm soot aggregates. This decouples changes in primary particle size due to changes in aggregate size from more intrinsic changes in primary particle size across the entire population. In Equation 1, the parameters  $D_{\text{TEM}}$  and  $d_{p,100}$  were fit linearly in logarithmic space using  $d_a$  and  $d_p$  data from the TEM image analysis. The Matlab linear regression function was used to provide 95% confidence intervals on the fit parameters. We also compare values from the fit to a more conventional median diameter from a lognormal fit also preformed in Matlab using the built-in fitdist function.

A complementary equation was developed by Eggersdorfer et al. [56] to relate the mobility diameter of the particles,  $d_{\rm m}$ , to the effective density,  $\rho_{\rm eff}$ , assuming monodisperse aggregates with spherical primary particles in point contact. This equation uses the Sauter mean diameter of the primary particles,  $d_{\rm va}$ , which are assumed to be approximately equivalent to the primary particle size from TEM,  $d_{\rm va} \sim d_{\rm p}$ . Assuming that the effective density is a function of the primary particle size, the effective density of a 100 nm mobility diameter particle,  $\rho_{\rm eff,100}$ , can be calculated as:

$$\rho_{eff,100} = k_a \rho \left(\frac{d_{va,100}[nm]}{100 nm}\right)^{3-2D_a}$$
(2.2)

. . .

where  $\rho$ , the material density of soot, is taken to be 1800 kg/m<sup>3</sup> ± 10% [25], [57], as discussed further below.  $D_{\alpha}$  and  $k_a$  are the projected-area exponent and the prefactor respectively. These quantities have been experimentally calibrated by Dastanpour et al. [58] as  $D_{\alpha}=1.1$  and  $k_a=1.13$  for soot from internal combustion engines. The mass mobility exponent,  $D_m$ , can be related to  $D_{\text{TEM}}$ with the following relationship [58]:

$$\rho_{eff} = \left(\rho_{eff,100}\right) \left(\frac{d_m}{100 \, nm}\right)^{D_m - 3} \tag{2.4}$$

The choice in  $k_a$ , and to a greater extend  $D_a$ , have a significant effect on the final calculated values of  $\rho_{\text{eff},100}$  and  $D_{\text{m}}$ . The values recommended by Dastanpour et al. [58] were calibrated using soot from a dual-fuel natural gas engine and from a gasoline direct injection (GDI) engine. Both

engines were examined across a wide range of operating conditions and different fuels. In addition, these values have also been applied with success on soot from gas flares by Kazemimanesh et al. [59]. This makes it likely that these values will work for the engine studied here, supported by the similarity between effective densities calculated here and measured effective density from previous literature discussed in Section 2.3.1. The assumption that  $d_m \sim d_a$  is strictly valid only in the free molecular flow regime (particle is much smaller than the gas mean free path), but for typical fractal aggregates, errors in the transition regime are on the order of 10% [60], [61]. A 10% change in aggregate size corresponds to a ~ 5% change in estimated effective density and a ~ 3% change in estimated primary particle size. Furthermore, this small error is partly compensated by the choice of  $D_a$  and  $k_a$ , obtained by comparing TEM measurements and effective density measurements using the same assumptions as used here.

#### 2.3 Results and discussion

#### 2.3.1 Microscopy

Typical TEM images from NG and diesel-only operation at different loads are presented in Figure 2.1. The dashed red circles in Figure 2.1a show approximately the "projected-areaequivalent diameter"  $d_a$  (bigger) and "primary particle diameter"  $d_p$  (smaller) used throughout this work. During diesel-only operation TEM grid samples were collected at idle, 25% load, 50% load or 75% load.



Figure 2.1: TEM images from a) NG at idle, b) NG at low load, c) NG at medium load, d) diesel at 25% load, e) diesel at 50% load, and f) diesel at 75% load.

Figure 2.1b shows power law fits, as described by equation (1), derived from the data points in Figure 2.1a which are the average primary particle size,  $d_p$ , and corresponding aggregate size,  $d_a$ , of all particles imaged, collected using both the thermophoretic sampler and the electrostatic precipitator described in Section 2.2.1. No differences were observed between soot collected using the two methods. Solid red lines denote soot from NG operation while dashed blue lines denote soot from diesel-only operation. Shaded areas represent the 95% confidence intervals on the fits. The dotted black line is the "universal fit" described by Olfert and Rogak [40], the fit for data from numerous studies on soot from non-premixed flames. The primary particles sizes for aggregates the primary particle sizes converge. This difference would be hidden if only the most common primary particle size was reported, which is a more conventional approach to reporting TEM data for soot.



Figure 2.2: Results from TEM data for all load conditions combined. NG is shown in solid red, diesel is shown in dashed or open blue, the universal fit from Olfert and Rogak (2019) is represented with a black dotted line. a) shows individual data points representing the average primary particle size within an aggregate which were fitted with the lines in b). Shading represents the 95% confidence intervals on the fits.

The fits in Figure 2.2b suggest that for aggregates below approximately 200 nm in diameter, NG tends to produce particles with slightly larger primary particles than diesel only operation. For larger aggregate particles the fits for NG and diesel-only operation converge to

similar values for their primary particle size. As aggregates approach 1µm in projected-areaequivalent diameter, the measured  $d_p$  starts to deviate from the power law fit shown in Appendix B: (**Error! Reference source not found.**). This is true for both fueling options and is characterized by the larger confidence intervals at large aggregate sizes. It is not surprising that the power law fit would not be valid for all sizes as there is likely a limit to how large primary particles can grow for a given engine and/or engine condition. Alternatively, for diesel-only operation, those aggregates approaching 1µm in size may represent the few that were able to undergo coagulation resulting in lower average primary particle size compared to aggregate size due to a wider distribution in primary particle sizes within the aggregate. Coagulation rates for both fueling conditions are discussed in Appendix B: (Section B.4 Coagulation). It is also possible that these large aggregates are in reality multiple smaller aggregates which have landed in the same location on the grid again lowering the average primary particle size for aggregates of that size. As the large aggregates represent a very small number of the total particles collected, they do not have a strong influence on the fit.

Conventionally, these data are represented as histograms of the primary particle sizes and aggregate sizes. Figure 2.3 shows histograms of  $d_p$  (dashed lines) and  $d_a$  (solid bars) with lognormal fits (grey solid lines) to serve as a comparison to past studies. Particles were selected for imaging to provide a broad range of sizes, not to provide an accurate size distribution. It is likely that smaller particles were under-sampled during imaging. Furthermore, both the thermophoretic sampler and the ESPnano tend to lose collection efficiency at smaller sizes. The exact collection efficiency for the thermophoretic sampler is not characterized, while the approximate lower limit for the ESPnano is reported as ~ 20 nm [62]. So, while informative, the size distributions from TEM do not accurately represent particles in the smaller size ranges and should only be interpreted as a convolution of the true particle size distribution with the instrumental sampling efficiency and image-processing detection efficiency.



Figure 2.3: Histograms of the projected-area-equivalent diameter (da), solid bars, and primary particle size (dp), dashed lines, from TEM analysis with lognormal fits, solid grey lines. The blue, left-hand graph represents diesel-only operation, the red, right-hand graph represents NG operation.

The sampling biases described likely account for the discrepancy between the TEM size distributions and the SMPS mobility size distributions presented later in Section 2.3.2. However, the SMPS and TEM measurements are consistent in indicating that the aggregates from NG operation have a smaller median size than those from diesel-only operation. The primary particle distribution for diesel shows a wider distribution than the NG primary particle distribution.

Table 1 lists numerical values to the fits shown in Figure 2.2 and the calculated effective density as described by equations (2), (3) and (4), where  $\rho_{eff,100}$  is the effective density for a 100 nm aggregate and  $D_{\rm m}$  is the mass-mobility exponent. The reported effective density is not the median effective density because it has not been weighted by the particle number distribution (not measured robustly by TEM) though the reported parameters could be used to calculate effective density. Figure 4 compares the effective density calculated from our TEM data with effective density measurements reviewed by Olfert and Rogak [40] showing that it does represent the effective density of a typical particle. Comparing to the universal fits proposed by Olfert and Rogak [40] both diesel-only operation and NG operation exhibited higher primary particle sizes,  $d_{p,100}$ and correspondingly higher effective densities,  $\rho_{\rm eff,100}$ . This is consistent with the effective density data for compression ignition (CI) engines reviewed in Olfert and Rogak [40] and the diesel-only fit falling in the middle of the compression ignition engine results shown in Figure 2.4. Of the seven CI engine studies which were included in the review, one was a natural gas engine with a diesel pilot [63]. As the 'universal fit' falls on the low end of the CI engine results, the higher effective density observed in this study may not be unique to this engine, but rather a feature of compression ignition engines as a group.



Figure 2.4:Measured effective density data from Olfert and Rogak (2019) for compression ignition engines (denoted with an x) and non-compression ignition engine sources (denoted with open circles) compared to the universal fit (black dashed line), the diesel-only.

The value of  $\rho_{eff,100}$  is sensitive to the material density of soot used in Equation 2. As noted above, we used  $\rho = 1800 \text{ kg/m}^3 \pm 10\%$  [25], [57]. This value is the recommended density of mature soot, as defined by Michelsen [6]. Mature soot is the highly-graphitic carbonaceous material which does not decompose during the lower-temperature "organic" stages of thermal-optical analysis, and which would therefore have a "low organic content" or "low OC" according to Ouf et al. [57], as demonstrated by the data of Török et al. [64]. ). It is essential to realize that the material referred to as "OC" by Ouf et al. [57] is not comparable to the volatile organic compounds which the term "OC" is typically understood to mean. Rather, this material represents the thermal decomposition (pyrolysis) products of less-graphitic carbon, which have been demonstrated to evolve in an inert atmosphere at temperatures above approximately 400 °C [65] are representative of the diesel/natural-gas combustion studied. Table 2.1 summarizes the data from Figure 2.2, Figure 2.3 and Figure 2.4 and disaggregates the data for different engine loads. No trends due to engine load were seen so this data was not shown in the figures for simplicity. Conversely, the data for dieselonly and NG operation are similar but with differences which are still statistically significant. Pvalues from a t-test are listed in Table B.2 of Appendix B: for each condition. The one exception to this case is the "NG idle" category which fits more closely with the diesel-only operation data points than it does with the NG operation data points. Physically this is not surprising since at idle the proportion of diesel pilot to NG is higher than when it is under load implying that the combustion conditions are approaching that of diesel-only operation. Table 2.1 also illustrates the advantage of reporting a power-law fit to describe the population rather than a median diameter. Comparing the median diameters shows only a 9% difference between the diesel-only and NG operation  $d_p$  while comparing  $d_{p,100}$  shows a 20% difference. If the most common primary particle size is used, the difference between the two disappears all together. Differences in primary particle size are masked by differences in aggregate size and sampling bias when median diameter is used. Despite this, the median primary particle size from a lognormal fit can be recovered almost exactly when the median aggregate size is inserted into equation (1). Using the median projected-areadiameter for NG (191 nm) and diesel-only (215 nm) results in primary particle sizes of 33.4 nm and 30.5 nm respectively. This is nearly identical to the median primary particle sizes from a lognormal fit reported in Table 2.1,  $34 \pm 1.6$  nm and  $31 \pm 1.1$  nm respectively. The SMPS data in Figure 2.5 shows that in reality, the median diameter for NG and diesel are likely smaller than ~ 200 nm which is not unexpected as thermophoretic samplers tend to oversample large aggregates [66]. Thus,  $d_{p,100}$  is a robust way of highlighting the differences between the two fuelling cases, less sensitive to sampling artifacts or the choice of averaging approach.

Table 2.1: A comparison of median projected-area-equivalent diameter  $(d_a)$  and median primary particle size  $(d_p)$  from lognormal fits of the data to fits from TEM and calculated effective density and the "Universal Fit" proposed by Olfert and Rogak (2019).  $d_a$ : projected-area-equivalent diameter,  $d_p$ : primary-particle diameter,  $d_{p,100}$ : primary particle diameter of a 100 nm aggregate,  $D_{TEM}$ : power law fit exponent,  $\sigma_8$ : geometric standard deviation,  $\rho_{eff,100}$ : effective density of a 100 nm aggregate,  $D_m$ : mass mobility exponent.

	Lognormal Median TEM Values		TEM Power Law Fit		Calculated Effective Density		
Category	d <sub>a</sub> (nm)	$d_{\rm p}$ (nm)	$d_{\rm p,100}^{1}(\rm nm)$	$D_{\mathrm{TEM}}{}^1$	$\sigma_{ m g}$	${D_{\mathrm{m}}}^1$	$ ho_{\rm eff,100}^{1}$ (kg/m <sup>3</sup> )
Diesel 75%	$233\pm31$	$33 \pm 1.1$	$27 \pm 3.6$	$0.29\pm0.12$	1.32	$2.4\pm0.10$	$704 \pm 76$
Diesel 50%	$191\pm34$	$28\pm3.2$	$21 \pm 2.3$	$0.46\pm0.11$	1.38	$2.6\pm0.09$	$582\pm51$
Diesel 25%	$230\pm38$	$32 \pm 3.2$	$23 \pm 3.1$	$0.38\pm0.12$	1.40	$2.5\pm0.10$	$627\pm69$
Diesel Idle	204 ± 30	$29\pm3.0$	$22 \pm 2.8$	$0.41\pm0.13$	1.43	$2.5\pm0.10$	$604 \pm 63$
All Diesel	215 ± 17	31 ± 1.6	22 ± 1.5	$0.41 \pm 0.06$	1.40	$2.5\pm0.05$	$612 \pm 32$
NG High	$197 \pm 26$	$35 \pm 2.3$	29 ± 2.4	$0.27\pm0.08$	1.33	$2.4\pm0.06$	$763\pm50$
NG Medium	186 ± 19	$32 \pm 1.6$	$26 \pm 1.5$	$0.30\pm0.06$	1.34	$2.4\pm0.05$	$698\pm31$
NG Low	$197\pm26$	$36 \pm 2.5$	$30 \pm 2.7$	$0.29\pm0.10$	1.28	$2.4\pm0.08$	$767\pm57$
NG Idle	212 ± 52	$30 \pm 4.0$	$23 \pm 3.6$	$0.35\pm0.14$	1.35	$2.5 \pm 0.11$	$629 \pm 80$
All NG	191 ± 12	34 ± 1.1	28 ± 1.0	$0.29\pm0.04$	1.33	$2.4\pm0.03$	$729 \pm 21$
Universal Fit	-	-	$17.7 \pm 0.35$	$0.35\pm0.03$	1.33	$2.48\pm0.02$	$510\pm8$

2.3.2 SMPS size distributions

Figure 2.5 shows the SMPS size distributions of PM catalytically denuded at 350 °C. The number concentration has been normalized by kg of  $CO_2$  to compare size distributions at different operating loads and different levels of dilution.  $CO_2$  measurements are described by Corbin et al. [41] and in more detail by Peng et al. (in preparation). The NG size distribution is distinctly different from a typical log-normal distribution and instead has a relatively flat distribution from 10 nm to 100 nm. Diesel on the other hand appears to have two (log-normal) modes, the first (larger) mode occurring around 20 - 30 nm and the second around 100 nm. The TEM images

revealed that the majority of the particles collected, including ones as small as ~30 nm in diameter, were soot is characterized by the fractal aggregate morphology typical of soot. In addition, the size distribution from TEM is also shown with blue and red histograms for diesel-only and NG operation respectively assuming that  $d_m \sim d_a$ . The height of the bars should be interpreted as the relative number of aggregates compared to other bins. It has no true numerical value as it has been arbitrarily placed at a height similar to the SMPS distribution for comparison. The TEM histograms show that no particles below ~ 30 nm in projected-area-equivalent diameter were analyzed with TEM. Thus, our analysis is limited to particles above this size as we can only speculate on the nature of the particles below this point.



Figure 2.5: SMPS size distribution after denuding at 350°C in a catalytic (oxidative) denuder. Solid lines denote NG operation, dashed lines denote diesel only-operation. Percentages represent engine load. The increase in particle number for NG at idle and for diesel at all loads is attributed to incomplete removal of volatiles by the denuder. At all other loads, denuding was complete, as discussed in the text. Histograms represent the size distributions from TEM for comparison. The height of each histogram is arbitrary for illustration.

During NG idle operation, (green solid line in Figure 2.5), it is possible that the catalytic denuder was overloaded and failed to remove all of the volatile PM resulting in the mode at approximately 20 nm. This may also be the case for the diesel size distributions as both idle, and diesel-only operation lead to increased volatile PM. Evidence of this can be seen in Figure 2.1a, where small (10-20nm), poorly defined "spots" can be seen surrounding the soot from NG operation at idle.

With the exception of the idle case, all volatiles were removed from the NG PM. This statement is proven by the fact that decreasing the catalytic stripper temperature did not result in any change to the denuded size distribution [41]. These size distributions exhibit an atypical "flat"

distribution from approximately 10 nm to 100 nm. HRTEM was used to image the nano-structure of particles smaller than the typical soot particle, 50 nm or less. This revealed characteristic onion-like fringes surrounding an amorphous core [67] and supports the hypothesis that these particles are in fact soot. Figure 2.6 shows the microstructure of these "nano" soot particles a) and b) as well as primary particles from a larger soot aggregate c) for comparison.



Figure 2.6: HRTEM images of soot nano-structure. a) and b) are of agglomerates <50nm in size, c) is from a typical, large fractal soot particle for comparison. Straight, amorphous regions in images a) and b) belong to the TEM grid carbon substrate. All images are of particles collected at 30% load during NG operation.

All particles visible by TEM or HRTEM (those larger than ~30 nm) appeared to be soot; no comment can be made for smaller particles. Volatile particles could not be easily imaged as they tend to evaporate when placed under a vacuum or when exposed to the electron beam. Section B.3 Non-typical particles of Appendix B: further details non-typical particles collected on TEM grids including their frequency (Table B.3), sample TEM images (Figure B.3) and HRTEM images (Figure B.4). For these reasons, the plateau in the NG operation SMPS size distributions (Figure B.4) is likely caused by nano-soot particles. In the absence of coagulation (coagulation rate calculations can be found in Appendix B:, Section B.4 Coagulation) there is no reason for these particles to form a distinct mode.

A possible, but as later shown, unlikely explanation for the presence of the nano soot particles is fragmentation. Neoh, Howard and Sarofim [68] observed that, during fuel-lean to slightly fuel-rich soot oxidation, particle number concentration increased while particle size and mass concentrations decreased. This led to the hypothesis that large aggregates were fragmented into smaller aggregates as the particles underwent oxidation. More recently this phenomenon was directly observed by Sediako, Soong, Howe, Kholghy and Thomson [69] using environmental scanning electron microscopy (ESEM) and again at higher resolution by Toth, Jacobsson, Ek and Wiinikka [70] using environmental transmission electron microscopy (ETEM). Two mechanisms for fragmentation are proposed. The first is due to internal burning of primary particles while the second is the result of narrow bridges between primary particles being consumed to the point where the connection is weak enough for the particles to detach. However, it is worth noting that ESEM and ETEM are limited to lower temperatures and pressures and the experiments are conducted over very long time scales compared to those found in an engine. Toth, Jacobsson, Ek and

Wiinikka [70] also observed that the SiN substrate used in the study may have catalyzed the fragmentation observed. Furthermore, the samples collected in this campaign did not contain any of the signs of oxidation which one would expect to find if particles were fragmenting due to oxidation.

#### 2.3.3 Possible effects of combustion conditions on soot morphology

A key feature of NG combustion is the large reduction in the number concentration of soot in comparison to diesel. NG is premixed in the cylinder which is does not favour soot formation. The diesel pilot is then injected into the engine which forms fuel-rich regions well suited to soot formation. This is similar to diesel-only operation however the quantity of diesel is greatly reduced in turn reducing the overall number concentration of soot. Thus, the soot formed during NG operation is attributed to the diesel pilot fuel. Further evidence of this came from a cylinder deactivation experiment described by Corbin et al. [41]. In short, the experiment suggested that soot emissions increased when the ratio of diesel to NG in the cylinders was increased.

In addition to the reduction in number concentration, the morphology of the soot produced by the two conditions have statistically significant differences. Specifically, the smaller aggregate size and larger primary particle size of soot from NG operation when compared to diesel-only operation. The cause of these differences is likely the different conditions under which diesel burns in the two modes, but there are too many differences to provide a simple explanation. Most likely, during NG operation there are fewer soot nucleation sites available so individual primary particles are able to grow to a certain size but have fewer primary particles nearby with which to interact and thus form smaller aggregates with larger primary particles relative to diesel-only operation where many primary particles are available to form larger aggregates.

Given the large particle concentration differences between the two fuelling modes, it would be natural to suppose that coagulation in the exhaust system influences both the morphologies observed and the size distributions obtained by the SMPS. However, considering the undiluted number concentrations, the coagulation timescale is estimated to be 2 s for diesel which is longer than the exhaust residence time of ~ 0.3 s. There might be a small amount of post-combustion coagulation for the diesel-only case but, as soot concentrations for NG operation were substantially lower, none were observed for the NG cases. Estimates of coagulation timescales are described and discussed in further detail in Appendix B:.

#### **2.4 Conclusions**

This study used TEM, HRTEM and SMPS to describe the morphology of catalytically denuded (350 °C) particulate matter from a dual-fuel marine engine operating in both NG mode and diesel-only mode. Power law fits applied to the average primary particle size and projected-area-diameter data extracted from TEM imaging showed statistically significant scaling relations for the two different engine fueling conditions. The power law fits for diesel-only and NG operation are  $d_p = (22 \pm 1.5) \left(\frac{d_a}{100 \text{ nm}}\right)^{0.41\pm0.06}$  and  $d_p = (28 \pm 1.0) \left(\frac{d_a}{100 \text{ nm}}\right)^{0.29\pm0.04}$  respectively, where  $d_p$  is the primary particle diameter in nanometers and  $d_a$  is the aggregate projected-area-equivalent diameter in nanometers. Physically, this means that NG operation

produces smaller aggregates with larger primary particles compared to diesel-only operation. To the authors' knowledge this is the first time a statistically significant difference in scaling relationships has been shown for soot from the same engine operating under different conditions. These relationships were further used to infer effective density, which were comparable to the effective densities of other compression ignition engines reported in the literature. However, they are larger than the proposed universal fit by 22% and 8% for NG operation and diesel-only operation respectively. Accounting for this difference is critical for estimating particle mass emission factors from SMPS size distributions.

The SMPS size distributions corroborated the shift seen in the TEM size distributions showing that smaller aggregates were formed during NG operation. The SMPS size distributions also showed non-lognormal size distributions for NG operation. Despite being a-typical, HRTEM revealed that the particles in the flat region from ~ 20 - 100 nm in the size distribution can still be attributed to soot particles. The source of the soot during NG operation was likely the diesel pilot. That is, for both diesel-only and dual-fuel operation, the fuel producing the soot was the same and the global operating conditions (engine speed and load) were similar. Thus, the differences in morphology for the two fuelling conditions must be attributed to differences in cylinder combustion conditions although the specific mechanisms remain unknown.
# **Chapter 3 : Effects of fuel mixture on the morphology of soot from gas flares**

## **3.1 Introduction**

Gas flaring is ubiquitous in the oil and gas industry where excess gas is burned off, both routinely for gases which are not economic to capture and in emergencies. Globally, gas flaring volumes are not decreasing. In 2012, an estimated 143 billion cubic meters (bcm) of gas was flared [32] while in 2018 this number had risen to 145 bcm [71]. As with many combustion processes, gas flaring produces soot. Similar to ship emissions, gas flaring is of particular concern in the Arctic. Nearly half of soot emissions in the Arctic are estimated to come from gas flaring due to high volumes of flaring in Russia, the North Sea and the Norwegian Sea [72]. Despite this, the environmental effects of flaring have been poorly characterized and often over-looked in the past [73].

Gas flares are large-scale buoyant turbulent flames, which often limits accessibility and has restricted the number of studies that have characterized emissions. Downstream aircraft measurements have been used in the past [74], but these types of studies are expensive and, by necessity, occur far downstream of the actual flaring site where the plume is highly diluted. Optical diagnostics, such as Sky-LOSA [75], [76], can be used in the field, but the diagnostics provide limited information about particle morphology. In fact, this type of optical diagnostic itself relies on assumptions regarding particle morphology and the authors cite the optical properties of soot as the largest source of error in Sky-LOSA measurements.

The following study investigated the effect of industry-representative fuels on the size and morphology of soot generated from a large, buoyant turbulent diffusion flame located at the Carleton University Flare Facility. Emissions from the flare were sent through a dilution tunnel and analyzed with a suite of online and offline instrumentation downstream. Fourteen different fuel compositions, representative of the range observed in the global oil and gas flaring industry, were studied in addition to the effect of entrained water on the resulting particles. The primary particle size, aggregate size, mobility diameter, effective density and Raman D/G ratios are reported as a function of the fuel's volumetric higher heating value (HHVv).

#### **3.2 Methods and materials**



Figure 3.1: A schematic of the experimental setup at the Carleton Flare Facility. High purity gas bottles supply fuel to the burner and emissions are collected by a ventilation hood and distributed to a range of instrumentation.

Soot particles were generated from a buoyant turbulent diffusion flame at the Carleton University Flare Facility, described in detail by Kazemimanesh et al. [59]. A schematic of the overall setup is provided in Figure 3.1. The burner is 2-inches in diameter and all tests are run at a flowrate of 156 standard litres per minute (SLPM) of fuel resulting in an approximately 2 m high flame. Particles are collected by a ventilation hood placed above the flare, naturally providing dilution in the range of  $\sim 20:1$  to  $\sim 120:1$ . Instruments pulled samples from an insulated tunnel connected to the ventilation hood with pumps and flow control built into the equipment.

Fuels were composed of mixtures of methane, ethane, propane, *n*-Butane, nitrogen, carbon dioxide, isopentane, *n*-hexane, and *n*-heptane and were chosen to represent the range of flaring fuels in the global oil and gas industry. The fuel codes, fuel composition, carbon-to-hydrogen ratio (C:H), geographic region, and volumetric higher heating values (HHVv) are listed in Appendix C:. The L9, M9, and H9 fuels span the typical compositions of fuels commonly found in Alberta, Canada; BK-BR and BK-WO represent fuels from the Bakken region in North Dakota, USA; EC-AC, EC-AS and EC-A27 are representative of fuels from Ecuador; RU-KM1, RU-KM2 and RU-FI are representative of fuels from Russia; and NS-M9 is an average fuel composition of 20 platforms in the North Sea. In addition, results in this study are compared to data from Kazemimanesh et al. [59] which are labeled L6, M6 and H6. In this study, the fuels are primarily characterized by their HHVv and span a large range, with the highest HHVv (75.17 MJ/m<sup>3</sup>) being more than twice as large as the lowest HHVv (35.8 MJ/m<sup>3</sup>). HHVv in this case is a theoretical value, calculated based on the target fuel composition. While HHVv does not capture all relevant

information regarding the fuel composition, it is used throughout this study as a proxy for the complex fuel mixtures.

#### 3.2.1 SMPS characterization

Particle mobility distributions were characterized using a scanning mobility particle sizer (SMPS), which consists of a differential mobility analyzer (DMA; TSI Inc., Model 3081) and a condensation particle counter (CPC; TSI Inc., Model 3776). The default inversion approach provided by the TSI software is used to retrieve the distribution of mobility diameters in the aerosol.

#### 3.2.2 Transmission electron microscopy analysis

Transmission electron microscopy analysis was performed using the same techniques described in Section 2.2.2 Transmission electron microscopy and image analysis. Briefly, samples were collected with the a thermophoretic sampler and imaged with a Hitachi H7600 at an accelerating voltage of 80 kV. Images were processed using an automated image analysis algorithm developed by Dastanpour, Boone and Rogak [39], seven fuel cases were analyzed. Between 100 to 200 aggregates per condition were analyzed resulting in 1487 total data points. As in Section 2.2.2 Transmission electron microscopy and image analysis, the data were fit linearly in log-log space to give power-law relationships between the projected-area-equivalent diameter,  $d_a$ , and the primary particle diameter,  $d_p$ . The data were then used to estimate the effective density of the soot using methods developed by Eggersdorfer et al. [56] and tuned for soot by Dastanpour et al. [58].

#### 3.2.3 Raman spectroscopy

Samples for Raman spectroscopy were collected on titanium substrates with the same thermophoretic sampler used to collect the TEM samples. A Renishaw Confocal Raman spectrometer was used with a 785 nm laser point focus at an energy of 0.2 mW, with exposure and integration times set to 10 s and 1 s, respectively. OriginPro (version 2017) was used to deconvolute the Raman spectra with the five-bands method. Three independent spectra were measured and averaged for each sample. The five bands selected for Raman deconvolution were [77]: D4 (1127 cm<sup>-1</sup> to 1208 cm<sup>-1</sup>), D1 (1301 cm<sup>-1</sup> to 1317 cm<sup>-1</sup>), D3 (1489 cm<sup>-1</sup> to 1545 cm<sup>-1</sup>), G (1571 cm<sup>-1</sup> to 1598 cm<sup>-1</sup>), D2 (1610 cm<sup>-1</sup> to 1625 cm<sup>-1</sup>). A detailed description of the Raman analysis is provided by Baldelli and Rogak [78]. Here, the ratio of the D peaks to the G peak is reported as a measure of the level of order or disorder within the nanostructure with larger numbers indicating a more disordered nanostructure.

#### 3.3 Results and discussion

#### 3.3.1 Mobility distribution

Figure 3.2 shows SMPS-derived mobility distributions for the available fuels. For fuels from L9 (HHVv =  $35.8 \text{ MJ/m}^3$ ) to EC-AC (HHVv =  $54.6 \text{ MJ/m}^3$ ), the number concentration and median soot diameter rise with increasing HHVv, indicating the expected trend towards higher soot yields for heavier fuels. These trends diminish for fuels with a HHVv above  $55 \text{ MJ/m}^3$ , where the sooting propensity appeared to saturate. RU-FI (HHVv =  $71.5 \text{ MJ/m}^3$ ) and RU-KM1 (HHVv = 51.4) are exceptions to this trend, with higher soot concentrations compared to other

fuels with similar HHVv. This is likely related to differences in fuel composition which are not easily summarized by the HHVv alone. The HHVv nonetheless correlates with the soot quantity well considering its simplicity.



Figure 3.2: SMPS size distributions of particles produced by 11 different fuel compositions. The line colour is proportional to the HHVv thus lines which are similar in colour are also similar in HHVv. The fuel code is listed with the higher heating value in brackets in units of MJ/m<sup>3</sup>. Larger HHVv tended to produce more particles with a slight increase in median diameter apart from RU-KM1 and RU-FI which did not exactly follow the trend, producing more particles than fuels with larger HHVv.

#### 3.3.2 Microscopy

As in Chapter 2, average primary particle size and aggregate size have been extracted for each particle imaged and are plotted in Figure 3.3a below. Figure 3.3b gives the power law fits derived from these data where  $d_{p,100}$  is the expected size of a 100 nm particle and  $D_{\text{TEM}}$  is the power law exponent. The universal fit [40] is denoted with a dashed line.



Figure 3.3: a) Projected-area-equivalent diameter and average primary particle size of each aggregate analyzed. b) Power law fits for each fuel condition with the 'universal fit' [40] denoted with a dashed line. There is no statistical difference between the fits for the different fuels.

The aggregates collected here are very similar to the universal fit and are not distinguishable from one another when considering the overlap from the 95% confidence intervals which are listed in Table 3.1. The table lists the median primary particle diameter and projected-area-equivalent diameter which were fit to a lognormal distribution using the Matlab function

histfit, as well as the parameters fit in Figure 3.3. Placing the median aggregate diameter derived from the lognormal fit into the power law equations retrieves the lognormal median primary particle diameter almost exactly, within 2% for all cases except for EC-AC27 which matches within 5%. This is not surprising as the same data is used to derive the median primary particle diameter in both cases. If the median primary particle diameter is correlated with HHVv it appears as though higher HHVv produces larger primary particles. However, the aggregate diameter is also increasing with HHVv which accounts for this increase. When primary particles are considered with respect to aggregate size there is no more correlation as illustrated by the consistency in  $d_{p,100}$ in Table 3.1 where again  $d_{p,100}$  is the primary particle diameter of a 100 nm aggregate. Fitting the results for all fuel cases together the combined relationship,  $d_p = 16.3*(d_a/100)^{0.35}$ , is similar to that reported by Kazemimanesh et al. [59],  $d_p = 17.7*(d_a/100)^{0.44}$ . Thus, the fuel has little to no effect on the relationship between  $d_p$  and  $d_a$  in this case.

Table 3.1: A summary of TEM results from select fuels. Median primary particle diameter and projected-area-equivalent diameter using a lognormal fit are compared to power law fits for the same data. Primary particle diameter from the power law fit at the median aggregate size is also listed.

Fuel Code	HHVv [MJ/m <sup>3</sup> ]	Median d <sub>p</sub> [nm]	Median da [nm]	$d_{\rm p,100} \pm 95\%$ CI [nm]	$D_{TEM}\pm95\%~CI$
L6*	35.3	-	-	$16.5\pm0.5$	$0.45\pm0.04$
L9	35.8	15.0	104	$14.8 \pm 1.0$	$0.34\pm0.09$
M9	41.6	16.4	122	$15.0\pm1.0$	$0.44\pm0.07$
H9	47.0	17.7	135	$16.1\pm0.8$	$0.28\pm0.06$
M6*	48.5	-	-	$17.1\pm0.9$	$0.54\pm0.07$
RU-KM1	51.4	17.6	134	$16.5 \pm 1.2$	$0.29\pm0.09$
EC-AC	54.6	20.6	174	$16.7\pm1.6$	$0.38\pm0.09$
H6*	54.7	-	-	$17.9\pm1.0$	$0.52\pm0.07$
BK-BR	61.1	21.5	147	$18.9 \pm 1.4$	$0.32\pm0.09$
EC-AC27	75.2	25.0	262	$16.2\pm2.0$	$0.40\pm0.10$
Universal Fit [40]	-	-	-	$17.7\pm0.35$	$0.35\pm0.03$

\* Fuels where data was adopted from the work of Kazemimanesh et al. [59]

However, these data are significantly different from the dual-fuel engine studied in Chapter 2 shown in Figure 3.4. This is consistent with the data shown in Figure 2.4 where compression ignition data consistently resulted in soot with greater effective density which is analogous to larger primary particles for a given aggregate size as described by the equations in Section 2.3 Calculated parameters. As previously stated the universal fit [40] was calculated using data from a range of premixed, turbulent flame sources including CI engines, spark ignition (SI) engines, and burners. If compression ignition engines truly produce larger primary particles compared to other

sources, then the universal fit could be improved to better predict non-CI engine sources by removing this type of data from the fit.



*Figure 3.4: Power law fits for the marine engine in Chapter 2 (solid purple line) which is different from the 'universal fit'* [40] *(dashed line) and the gas flare in Chapter 3 (solid green line). Shaded areas represent the 95% confidence intervals on the fits.* 

One possible explanation for this is that the elevated pressure in CI engines allows for the growth of larger primary particles. Gigone, Karataş and Gülder observed an increase in primary particle diameter when soot was produced in a pressurized atmosphere [79]. These experiments were conducted with a coflow laminar diffusion flame and cannot be directly applied to turbulent flames due to the drastically different conditions in the two types of flames. However, laminar flames allow for more controlled experiments not possible with turbulent flames. Gigone, Karataş and Gülder [79] observe an increase in median primary particle size from 17.2 nm to 23.6 nm with pressures of 3 bar and 6 bar respectively. They did not report primary particle size as a function of aggregate size however, meaning if the relationship observed by Olfert and Rogak [40] holds true for laminar flames these results could be attributed to a change in aggregate size. SI engines which did not show any relative increases in primary particle size, while operating at lower pressures than CI engines, still have pressures which are much greater than the 3 bar change in pressure studied here. If a change as small as 3 bar could induce an increase in primary particle size, then one would expect to see increased primary particle sizes for SI engines as well. More work is needed to explain the root causes of the increase in primary particle diameter observed here, either supporting the pressure hypothesis or finding alternative explanations. Nonetheless, the results in Figure 3.4 clearly show that the 'universal fit' [40] represents the flare data well but is distinctly different from the marine engine data.

#### 3.3.2 Raman spectroscopy

Raman D1/G ratios are plotted as a function of a fuel's volumetric higher heating value in Figure 3.5. Fuels which are described in this study are denoted with open circles, those from Kazemimanesh et al. are denoted with solid circles [59]. Error bars represent the standard deviation of results of three spectra from the same sample. For all four ratios, the graphitization increases with HHVv meaning the disorder, D, peak is decreasing while the graphitization, G, peak is increasing. Similar trends were seen for the D2/G, D3/G and D4/G ratios which can be found in Appendix C:.



Figure 3.5: D1/G ratios of Raman samples as a function of the fuel's volumetric higher heating value. Fuels which are considered in this study are denoted with open circles. Solid circles denote results from the study by Kazemimanesh et al. [59]. D1/G ratios for cases with water addition are shown with blue squares.

Baldelli and Rogak studied soot produced by a small laminar ethylene flame size selected with different ELPI+ impactor stages where larger aggregates, which had on average larger primary particles, had lower D/G ratios [80]. Specifically, the D1/G ratio decreased from 13 to 9 as  $d_p$  increased from ~ 16 to 25 nm. For the flare soot, the D1/G ratio decreases from ~ 11 to 5 as median primary particle increases from 15 to 25 nm (the increase associated with larger HHVv, Table 3.1). Possibly the size of the primary particle influences the Raman spectra, but likely the flame residence time and fuel composition result in slightly different trends.

#### **3.4 Conclusions**

The effect of a wide range of flare fuel mixtures, representative of the global oil and gas industry, on soot morphology was investigated. Fuel composition resulted in significant differences in soot aggregate size and number concentration, with little effect on the structure of the aggregates. Fuels with a greater HHVv produce, on average, larger aggregates in greater quantities than fuels with a lower HHVv. This corresponds to an increase in primary particle size, consistent with previous findings [59]. If the primary particle size for a single aggregate size ( $d_{p,100}$  for aggregates 100 nm in diameter) is considered, then the average primary particle sizes for all of the fuel cases is the same to within a few nanometers. Unlike for the marine engine, the 'universal fit' [40] summarizes the morphology of the soot studied here very well. This suggests that perhaps the universal fit is not universal, but it could be applied categorically.

The nanostructure of soot, assessed using D/G ratios from Raman spectroscopy, was found to become more graphitic for fuels with greater HHVv. This change is associated with an increase in the average primary particle size, roughly consistent with previous observations for size-segregated soot from a small ethylene burner [80]. Overall, HHVv does remarkably well as a method of tracking the differences between otherwise complex fuel mixtures.

# Chapter 4 : Effects of inorganic salts on the morphology of soot from gas flares

# 4.1 Introduction

Hydraulic fracturing, commonly known as fracking, is an oil and gas extraction method in which hydraulic fluids are injected into shale formations at high pressure to release oil or gas reserves [81]. This creates a scenario where the hydraulic fluids are likely to become entrained in the flare fuel. Preliminary studies showed that these fluids may have significant impacts on the emissions from the flares, sodium chloride (NaCl) being a particularly important component [82]. The salts and other elements which undergo combustion along with the hydrocarbons in the fuel have the potential to affect soot formation, aggregation and nanostructure. Laboratory studies of small premixed flames have shown that small amounts of alkali metals, specifically sodium, potassium and caesium, reduce the mass concentration of soot produced but increase the number of soot particles produced [83]. More recently Moallemi, Kazemimanesh, Kostiuk and Olfert [84] observed a similar phenomenon when NaCl was added to a small premixed flame, specifically soot number concentration increased in regions of the flame where coagulation is likely to occur. They suggest that the addition of NaCl reduced coagulation between soot particles. In addition to the effects that changes in soot morphology can have on its climate warming potential, the mixing state of the soot and salt particles can also influence a particle's optical properties. Modelling has shown that salts can have a 'lensing' effect when soot is internally mixed with salt particles. This means that the salt can act as a lens magnifying the light absorption of the soot particles with the largest effect occurring when soot is completely immersed in the salt [85].

## 4.2 Methods and materials

Two separate experiments were performed to study the effects of flowback fluids on soot. The first was conducted alongside the experiments in Chapter 3Chapter 2 with the same experimental set up with one real and several simulated flowback fluids. Follow up experiments were conducted at the University of Alberta to further investigate the effect of sodium chloride solutions with varying salt concentrations on soot.

#### 4.2.1 Carleton university flare facility experiments

An atomizer was used to introduce liquid droplets into the burner shown in Figure 3.1 from the previous chapter. Four liquids were used: deionized water (DW), sodium chloride dissolved in deionized water, 'Cardium' liquid (card) and 'Duvernay' liquid (duve). Salt concentrations were 0, 150 g/L, 4.1 g/L and 145 g/L respectively. The Cardium liquid is a simulated flowback fluid representative of the Cardium shale formation in Alberta, Canada. The Duvernay liquid is the one real flowback fluid taken from the Duvernay shale formation in Alberta, Canada. In both liquids, sodium chloride is one of the main components with lower levels of potassium, calcium and other elements. The full elemental composition of the fluids is listed in Appendix C:. These liquids were added to the L9, M9 and H9 fuels described in Chapter 3 with the same fuel flow rates (156 SLPM) and both 13 mL/min and 2 mL/min liquid additive flowrates. As before, Raman spectroscopy and SMPS scans were performed and particles were collected on TEM grids for microscopy. The

automated code used in Chapter 2 and Chapter 3 could not distinguish between salt and soot particles and thus could not be applied to TEM images with salt added but was applied with the same methods to assess differences between the dry and deionized water cases. 546 aggregates were analyzed for the three cases. For the salt added cases, particles were manually classified as 'salt alone', 'soot alone' or 'mixed' particles as shown in Figure 4.1. Details of the methods used to determine if a soot particle was mixed with a salt particle are described in Appendix E:. Briefly, particles were classified as salt or mixed when there was a clearly cubic structure, a diffraction pattern or if the particle was unstable under the electron beam. Soot by contrast is an aggregate of spherical particles, does not cause diffraction patterns and is stable under the electron beam.



a) Cardium

b) NaCl

Figure 4.1: TEM images of particles collected from the Carleton University Flare Facility with liquids added to the flame. a) is an example image from the Cardium solution case while b) is an example image from the NaCl solution case. Annotations denote the three particle categories: salt alone, soot alone and mixed particles.

#### 4.2.2 University of Alberta experimental set-up

The experiments conducted at the University of Alberta were performed with a laboratory buoyant turbulent diffusion flame with an approximately 1 m flame height. The flame at the University of Alberta was smaller, with only 10 SLPM of fuel compared to 156 SLPM in the previous experiments. Figure 4.2 illustrates the experimental set up. A suite of instruments for optical, physical and chemical analysis are shown in the figure although the TEM and Raman spectroscopy samples collected with the thermophoretic sampler will be the focus. Propane was the only fuel used and varying amounts of sodium chloride dissolved in deionized water were added to the fuel. Tests were performed with no liquid added and salt solutions with 0.01, 0.03, 0.1, 0.3, 1.0 and 3.0 weight % salt with a flowrate of  $8.9 \pm 0.25$  mL/min. This is equivalent to ratios of salt to fuel ranging from  $1.81 \times 10^{-7}$  g/g to  $5.42 \times 10^{-5}$  g/g. In comparison, the Carleton University experiments had ratios of salt to fuel ranging from  $1.07 \times 10^{-7}$  g/g to  $2.54 \times 10^{-5}$  g/g.



Figure 4.2: Experimental set up at the University of Alberta. Propane and salt solutions are supplied to the burner and collected with a ventilation hood to distribute to the suite of instrumentation.

## 4.3 Results and discussion

#### 4.3.1 Results from Carleton University

An SMPS was used to measure the distribution of particle sizes from the flames. Trends were the same for all three fuel types, a) L9, b) M9 and c) H9. Deionized water reduced the particle concentration slightly, the greatest difference was in the L9 case. In every case, the addition of salt solutions increased the total particle number concentration by over an order of magnitude. The Cardium cases all have bimodal distributions, with one peak at ~ 100 nm where the dry soot peak is, and the second at a size below ~ 40 nm. In each case when the liquid flow rate is reduced, the peak shifts slightly to smaller mobility diameters. This suggests that the smaller peak is primarily salt particles while the larger is soot and lower salt concentrations result in smaller salt particles. Qualitatively this can be seen in the TEM images in Figure 4.1, the Cardium solution (4.1 g/L) in a) has visually smaller salt particles than the NaCl solution (150 g/L) in b). Thus, for the NaCl and Duvernay cases in Figure 4.3, the salt particles have mobility sizes similar to that of soot creating a single mode in the distribution instead of a bimodal distribution.



Figure 4.3: SMPS size distributions for particles from flames produced with a) L9 fuel, b) M9 fuel and c) H9 fuel. Solid lines denote dry flames, dashed lines denote the different liquid additive cases each of which are annotated.

Manual classification of the TEM images revealed that while there are many salt particles on their own, a majority of soot particles were mixed with salt. The exact percentages of particles in each category is tabulated in Table 4.1. Effectively, half of particles are salt alone, half are mixed, and the small remaining balance is soot alone.

Liquid Additivo	Average	# of Particles		
Liquid Additive	Salt Alone	Mixed Particles	Soot Alone	Analyzed
Cardium	44.0%	48.5%	7.6%	798
NaCl	51.9%	46.8%	1.3%	527
All	48.0%	47.6%	4.4%	1325

Table 4.1: Average percentage of particles manually counted from TEM images.

Visually the grids have a lot of material on them suggesting that particles may not truly be mixed, but rather they fell on the same point on the grid by chance. The images were used to estimate the probability that particles would fall on the same point on the grid and it was found that 47% of particles are expected to appear overlapped due to oversampling. This is nearly the same as the total frequency of mixed particles. Conversely, this could also be due to coagulation post-flame. Rough coagulation calculations show that ~ 61% and ~ 51% of soot particles should be mixed with salt based on the concentrations and sampling residence time. Details of both overlap and coagulation calculations can be found in Appendix D:. Thus, further experiments described in Section 4.3.2 Results from the University of Alberta were conducted to conclusively determine the mixing state of the particles.

The automated image analysis code was able to analyze image from the water addition cases, the results of which are shown below in Figure 4.4. Dashed lines represent cases with water addition while solid lines represent dry fuel cases. Similar to the results in Figure 3.3, there does not seem to be a statistically significant difference in the relationship between projected-area-equivalent diameter and average primary particle diameter due to the addition of water. The 95% confidence intervals on the fits are tabulated in Table 4.2 and illustrate the significant overlap between the different cases and as observed in the SMPS data, a slight reduction in median projected-area-equivalent diameter and a corresponding decrease in median primary particle diameter. The one exception to this is the L9 case where the median diameter is slightly higher for the water addition case however, given the similarity between the projected-area-equivalent diameters this can likely just be attributed to noise in the data.

Table 4.2: Tabulated values for the power law fits of the L9, M9 and H9 fuels with and without the addition of deionized water. Lognormal fits of the distributions were used to determine the median primary particle diameter and median projected-area-equivalent diameter.

Fuel Code	HHVv [MJ/m <sup>3</sup> ]	Median d <sub>p</sub> [nm]	Median d <sub>a</sub> [nm]	$d_{\rm p,100} \pm 95\%$ CI [nm]	$D_{TEM} \pm 95\%~CI$
L9 + Water	25.9	16.3	97	$16.5 \pm 1.1$	$0.36 \pm 0.08$
L9	35.8	15.0	104	$14.8 \pm 1.0$	$0.34\pm0.09$
M9 + Water	41 C	14.8	102	$14.7\pm0.7$	$0.31\pm0.06$
M9	41.6	16.4	122	$15.0 \pm 1.0$	$0.44 \pm 0.07$
H9 + Water	47.0	16.0	131	$14.7\pm0.8$	$0.28\pm0.06$
H9		17.7	135	$16.1 \pm 0.8$	$0.28\pm0.06$



Figure 4.4: Projected-area-equivalent diameter versus average primary particle diameter for L9, M9 and H9 fuels with and without water addition.

Raman spectroscopy was performed with the same procedure described in Chapter 3 and as before, the D1/G ratios are shown here with the D2/G, D3/G and D4/G ratios in Appendix C:. The solid circles represent the dry fuel cases, the same data shown in Figure 3.5. Open circles represent the different liquid additives. The Cardium points do consistently have slightly higher

D/G ratios than the other solutions however, given the error bars, this does not appear to be significant. The error bars represent the standard deviation of three different Raman spectra from each sample. Thus, the liquid additives did not appear to have any effect on the Raman D/G ratios.



Figure 4.5: Raman D1/G ratios from the L9, M9 and H9 fuels. Solid circles denote the dry cases as a comparison between the liquid additive cases which are denoted with open circles.

#### 4.3.2 Results from the University of Alberta

As the University of Alberta experiments were more focused studying one fuel, one solution and an even distribution of salt concentrations. Figure 4.6 confirms the patterns which are less evident in Figure 4.3. The addition of water reduces the amount of soot produced with a slight reduction in median particle size. In this case the reduction in the number concentration of the soot is more significant than in the Carleton University results. This is likely due to the fact that the ratio of water to fuel is significantly higher in the experiments conducted at the University of Alberta. At the lowest salt concentration, 0.03%, a clear bimodal distribution is produced with one peak at ~ 22 nm with the second directly above the water addition distribution at ~ 100 nm. The smaller peak shifts to higher mobility diameters with increasing salt concentration until only one peak is evident. This peak is confirmed to be salt particles from the TEM where the median projected-area-equivalent diameter of the salt was 36 nm, 41 nm, 56 nm and 78 nm for 0.1%, 0.3%, 1.0% and 3.0% salt respectively. In comparison the small particle modes for the same salt cases in Figure 4.6 are at approximately 27 nm, 38 nm, 50 nm and 80 nm respectively. This confirms that

increasing the salt concentration in the liquid solution results in larger salt particles and the smaller size peaks are a result of the salt.



Figure 4.6: SMPS mobility size distributions for propane: dry, with deionized water and 0.03%, 0.1%, 0.3%, 1.0% and 3.0% salt.

The Raman D/G ratios, as before, showed no trend with salt quantity suggesting that the presence of NaCl does not influence soot nanostructure. There is a slight decrease in D1/G at the higher salt concentrations but again, the error bars in Figure 4.7, which represent the standard deviation of three different Raman spectra from each sample, suggest that the result is not significant. The error bars are quite large in this case, potentially because this flame produced relatively low soot concentrations compared to the previous study which can cause background noise. This is consistent with the data from Figure 3.5 where the lower HHVv fuels which produced less soot had larger error bars than the high HHVv fuels which produced large soot quantities.

The HHVv of the propane used in this study was not directly measured however it is  $\sim 96 \text{ MJ/m}^3[86]$ . This is higher than any of the fuels measured in Chapter 3 yet the D1/G ratio for dry propane is 9.0 which is approximately the same as the M6 fuel which had an HHVv of 48 MJ/m<sup>3</sup>. The reason that propane does not follow the trend observed in Chapter 3 is not clear however some speculations can be made. First, the HHVv of the complex fuel mixtures from Chapter 3 are determined by both the amount of heavy alkanes (increase HHVv) and the amount of inert gases such as carbon dioxide and nitrogen (decrease HHVv). The propane burned in this chapter did not contain inert gases which could be one of the factors determining the D/G ratios which isn't well captured by the HHVv.



Figure 4.7: Raman D1/G ratios for propane with no liquid additives, water, 0.03%, 0.1%, 0.3%, 1.0% and 3.0% salt. Error bars denote one standard deviation.

Finally, TEM girds which were sparsely loaded to avoid the probability of 'artificially' mixed particles due to overlap were manually categorized into soot alone and mixed particles as before. Due to the high ratio of salt to soot particles (from Figure 4.6), the number of salt particles alone were not counted. This would have required many additional hours of microscopy work in order to image a representative number of soot and salt particles. Assuming the smaller mobility diameter peak in the SMPS distributions is salt, there are roughly two orders of magnitude more salt particles than soot particles, requiring a corresponding 100 times increase in microscopy time. For this reason, during the imaging soot particles were intentionally searched for on the grid for imaging rather than using the normal procedure described in Appendix E:. While the lower grid loading did lead to a larger number of 'soot alone' particles than previously observed, a majority of the soot particles found were still mixed with the salt confirming that a majority of the soot particles are internally mixed with salt.

Salt Quantity	% of Soot Particles Alone	% of Soot Particles Mixed
0.1%	34%	66%
0.3%	24%	76%
1.0%	14%	86%
3.0%	28%	72%

Table 4.3: Ratio of soot particles which are alone or mixed with salt with respect to salt quantity.

Due to the lower loading on the grids, it is easier to qualitatively assess particle morphology. Figure 4.8 shows typical images of soot from a) 0.1% salt, b) 1.0% salt and c) 3.0% salt. Some of the salt particles in the images have been annotated. The images are all at the same

scale. The cases with lower salt concentrations typically only have only a few small salt particles decorating the soot particles. As the salt concentration increases, it becomes more common to see a greater number of salt particle imbedded in the soot rather than simply touching the outside. Sometimes, as in Figure 4.8 c), the salt particles appear to join two otherwise separate soot particles together.



*Figure 4.8: Typical TEM images of soot from the flares with NaCl solution at concentrations of a) 0.1% salt, b) 1.0% salt and c) 3.0%. Embedded salt particles are annotated.* 

The data presented in this chapter suggests that soot forms with little influence from the presence of salt while the salt forms later in the flame. Initially, the NaCl should be completely dissociated in a water solution and while the temperature of the flame was not directly measured here, the propane flame most likely reaches temperatures well above both the melting (1074 K) and boiling (1686 K) points of bulk NaCl [84] suggesting that salt particles won't be able to form solid particles until after the flame while soot forms inside the flame. In addition, small particles may have lower boiling and melting temperatures than the bulk material [84] which further contributes to the hypothesis that the salt particles form after the soot. These experiments had considerably lower particle number concentrations compared to the experiments described in Section 4.3.1 Results from Carleton University resulting in much lower coagulation rates. In these experiments the ratio of soot particles which coagulated with salt are 2.2%, 6.3%, 5.4%, 8.3% and 9.7% for the 0.03%, 0.1%, 0.3%, 1.0% and 3.0% salt cases respectively. These calculations rely on many estimated values and cannot account for coagulation that occurs in the region between the tip of the flame and the beginning of the ventilation hood. However, given the high salt concentrations there should also be evidence of coagulation between salt particles. Counting the number of monomer salt particles and dimer or, rarely, polymer salt from the TEM, resulted in coagulation rates of 0% (no coagulated salts were observed), 3.7%, 12.2% and 18.7% for 0.1%, 0.3%, 1.0% and 3.0% salt concentrations respectively. These observed rates are similar (within a factor of 2) to the expected coagulation between salt particles which suggests that the coagulation calculations for soot-salt mixing is also within the right range. All observed and calculated coagulation rates are tabulated in Table 4.4. These rates are much lower than the frequency of the mixed soot particles. This may suggest that there is a mechanism other than simple post-flame coagulation resulting in the high frequency of mixed soot particles. Soot may act as a nucleation site for the nascent salt particles although soot particles have been shown to be poor nucleation sites for salt in atmospheric conditions [87]. Of course, the atmosphere is an extremely different

environment from a turbulent flame, so it is conceivable that in the elevated temperatures of a flame or post flame region, salt ions use soot as a site for heterogeneous nucleation. These are interesting results which warrant further investigation to determine the exact cause of the mixing.

Salt Concentration	% of Mixed Soot (TEM)	Calculated % of Soot-Salt Mixing	% of Coagulated Salt (TEM)	Calculated % of Salt-Salt Mixing
3.0%	66%	9.7%	18.7%	9.2%
1.0%	76%	8.3%	12.2%	6.8%
0.3%	86%	5.4%	3.7%	3.8%
0.1%	72%	6.3%	0	3.6%
0.03%	-	2.2%	-	1.3%

Table 4.4: Observed mixing rates of particles from TEM rates and expected coagulation rates estimated from the particle concentration, particle sizes and residence time.

#### 4.4 Conclusions

Two separate experiments at different facilities were conducted in order to probe the effect of inorganic salts on soot morphology. While there are some differences between the two experiments, the results from the second set of experiments generally confirm the hypotheses that were developed as a result of the data from the first, more complex set of experiments. From the Raman spectra, the addition of water, or dissolved salts did not appear to have any impact on soot nanostructure. TEM showed that soot particles are internally mixed with salt particles a majority of the time. This mixing does not appear to be due to post-flame coagulation. The exact mechanism for the internal mixing of soot and salt should be investigated further. The mixing state could have implications for the climate impact of the soot particles as it may have effects on the particle's optical properties and ice/cloud nucleation properties. Modelling work has suggested that internally mixed salt does enhance the absorption properties of soot. However, the lensing effect is small when soot is not completely embedded in the salt [85]. Particle size distributions showed that the addition of water reduced the amount of soot formed, but as little as 0.0027 g/min of salt (0.03 wt% salt with an 8.9 mL/min liquid flowrate) resulted in 1.5 x  $10^6$  #/cm<sup>3</sup> more particles than the water addition cases.

# **Chapter 5 : Conclusions and recommendations**

The physical morphology of soot from three separate experimental campaigns on two different types of turbulent, non-premixed flames are described in this thesis: a marine engine and gas flares.

#### **5.1 Conclusions**

#### 5.1.1 Effects on soot morphology

Four types of possible effects on soot morphology were probed here: combustion conditions, fuel type, water addition and salt addition.

Combustion conditions appear to have by far the greatest effect on the relationship between aggregate size and primary particle size. In Chapter 2 a small but statistically significant difference is found in the  $d_p - d_a$  relationships of soot produced by a dual-fuel engine operating in either dualfuel mode, where natural gas is premixed in the engine and a non-premixed diesel pilot is used to ignite the NG, and in diesel-only mode with no natural gas combustion. While this may appear to be a difference in fuel type, it is effectively a difference in combustion conditions as the soot produced by the engine in dual-fuel mode is suspected to be due to the diesel pilot not the premixed natural gas [41]. Previous studies have also observed changes in soot primary particle size with engine operating condition however the changes may be attributed to changes in aggregate size as the two quantities have not been coupled in the past [88], [89]. Aside from the small difference between the two engine operating conditions, the difference between the marine engine and the gas flare studied are very large. Compression ignition data reviewed by Olfert and Rogak [40] was similar to that of the CI engine studied here which all tended to have larger primary particles for a given size compared to other sources including spark ignition engines. On the other hand the non-CI engine data from Olfert and Rogak [40] fits well to the gas flare data regardless of fuel type.

Fuel type substantially influenced the size of the aggregates which, per the  $d_p - d_a$  relationships, resulted in corresponding changes in primary particle sizes. The Raman spectra of the soot was also influenced by fuel type however based on past observations [80] this can likely also be attributed to changes in median aggregate size. The volumetric higher heating value of a fuel proved to be a remarkably good predictor of aggregate size; the higher the HHVv of a fuel the larger the aggregates. Heavier fuels also resulted in larger quantities of soot.

The addition of water reduced the amount of soot and slightly decreased the median mobility diameter. Salt, even in very small quantities, produced a huge number of very small salt particles. Due to the high concentration and difference in particle size, they tend to readily coagulate with soot particles such that a majority of soot particles leaving the flame have at least a small amount of internally mixed salt. The salt itself did not affect any of the other aspects of soot morphology studied here.

#### 5.1.2 Implications

While soot from any one source is highly varied, there appear to be some trends within populations. Specifically, CI engines produce larger primary particles for a given aggregate size when compared to other sources. Fuel volumetric higher heating value also showed a correlation between aggregate size and particle concentration although this would need to be investigated for a wider range of soot sources to see if the relationship still applies. For devices such as Sky-LOSA [38], [39] prior knowledge of the fuel type, or the use of a low-cost sensor which can estimate median aggregate size the 'universal fit' [43] (or a modified version for CI-engines) could be used to improve the accuracy of the instrument or perhaps apply corrections after measurement.

Primary particle size is an important factor in the optical properties of an aggregate, more so than the number of primary particles in the aggregate. Sorensen [11] showed that larger primary particles lead to a larger single scattering albedo compared to increases in the number of primary particles (proportionate to aggregate size) which eventually reaches an asymptote. This would suggest that aggregates with larger primary particles such as CI engines are less absorbing than soot from other sources with smaller primary particles. However, the climate effects of such changes are likely outweighed by any substantial change in the amount of soot produced for example when comparing the difference between the lightest fuel, L9 and the heaviest fuel studied RU-FI, Figure 3.2.

Small amounts of aqueous salt in combustion systems could result in emissions which drastically alter cloud composition in the area. Soot is not considered to be a good cloud condensation nucleus (CCN) [90] or ice condensation nucleus (ICN) [91], although atmospheric aging has been shown to enhance its CCN propensity [92]. On the other hand, salt is considered to be an effective CCN [93]. This means, that the inclusions of salt could turn the soot into effective CCN particles in addition to the release of individual salt particles into the atmosphere.

#### 5.2 Limitations and recommendations for future work

The work presented here naturally has limitations. The most obvious limitation is the small number of sources studied, one engine and two gas flares. While the data in both cases seems to agree well with data from the literature it is difficult to generalize based on this and the results should be extrapolated with a degree of caution.

Much of the analysis performed here relies on automated image analysis of transmission electron microscope images. This type of analysis is sensitive to the settings used by the microscopist, the particles selected by the microscopist, the application of the image analysis code and the sampling of the particles themselves methods for which are described in detail in Appendix E:. While the methods used here seemed to be reproducible by different users within the same lab, and agrees well with manual analysis, it may not work well outside of the lab. Attempts to use similar image analysis codes produced by other groups have illustrated the difficulty of sharing this type of method between labs. Thus, while comparing datasets examined with the same methods is robust, it may be hard to compare directly to other studies. There is a need in the community to develop a standard method for calibrating image analysis codes and presenting TEM data in order to effectively compare results from different studies. Thus, a pressing piece of future work would be a standardization of TEM image analysis within the community. There are too many soot sources for any one group to asses them all but the ability to compare between groups would allow for more corroboration of the deviation of CI engine soot from the 'universal fit' [40] observed here. While it is difficult to convert an entire community, a good first step would be a common 'test-image' set that algorithms could be tested against and possibly a review paper on the topic.

While one of the stated goals of this work is to assess the climate impacts of different soot particles, optical properties were not directly measured in this study which are the most relevant properties for the climate. The optical properties are fundamentally based on the morphology of the particles however there are many factors contribute to the optical properties of soot and a direct measurement would be an important addition to this analysis. Optical properties were measured in the Chapter 4 experiments and will be a part of the ongoing work on this topic. This is particularly important for the effect of salt on soot as modelling has suggested that salt may enhance the optical properties of soot although the extent of this depends on the way in which the two are mixed [85]. In addition, the particles studied here are freshly emitted. This is relevant for the local health effects however, in the atmosphere, the particles would quickly undergo processing which would change the morphology of the particles. To truly understand the climate effects, the morphology in the atmosphere should also be considered. For measurement purposes freshly emitted soot is still important. For example in the case of Sky-LOSA [75], [76] the instrument uses the optical properties of soot to determine the quantity being emitted from the flame directly. The characteristics described here lay the foundation for future on this topic involving either experimental or computational models for atmospheric aging of soot the soot studied here. Finally, the mechanism for the internal mixing of soot and salt observed should be investigated in addition to exploring the range of conditions under which it may occur.

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# Appendix A: Electron tomography of soot for validation of 2D image processing and observation of new structural features<sup>1</sup> A.1 Introduction

Measuring the properties of soot aggregates is fundamental to the understanding of their impact, the prediction of emission rates and the climate forcing effects of black carbon particles [1]. The morphology of the aggregates is one the main properties of interest for understanding the soot formation process and its impact on health and the environment [2]. Combustion-generated soot is generally an aggregate of primary particles that exhibits a fractal-like structure. Transmission electron microscopy (TEM) remains one of the best techniques for characterizing this structure but produces images that are two-dimensional (2D) projections of the true three-dimensional (3D) structure. Measurements of aggregate area, primary particle size, aspect ratio, and fractal dimension are prone to artifacts due to shielding or orientation biases. If images of two aggregates are found to have differing geometric properties, it is not clear how much of the discrepancy is due to true differences in the 3D structures or is simply due to orientation effects. Orientation might be biased by the collection process and procedure [3], or it might be random [4, 5].

A few researchers have studied the projection artifacts using computer-simulated aggregates [6]. This has been especially useful in understanding how the fractal dimension of images is related to the true 3D fractal dimension [7, 8, 9], and the relationship between projected area and total surface area. However, the simulated aggregates are composed of spherical primary particles [10]. Despite the success of the Diffusion-Limited Cluster Aggregation model in producing soot aggregates that appear similar to 2D images of real soot, it is unclear whether the simulated soot aggregates capture all relevant structural features. Even if the simulated soot aggregate has an accurate structure, real TEM images contain noise and limited contrast, which, despite recent developments [11], is difficult to reproduce in simulated images.

Projection artifacts can be studied using real images from a microscope with a tilting stage. Gray et al. used two view angles to create stereographic visualizations of aggregates to facilitate accurate counting of primary particles [12]. It was found that counting the number of primary particles in diesel aggregates was  $36 \pm 5\%$  greater when using stereopsis when compared to viewing 2D TEM images. Many modern microscopes have the capability of imaging particles at many angles such that computed tomography can be used to reconstruct the 3D aggregate. A few studies have analyzed 3D images of soot or nanoparticles aggregates [13, 14, 15, 16 17 18 19]. These studies found that properties such as geometric surface area, volume, radius of gyration and number of primary particles are substantially different for the 3D object and its 2D projection [14, 17, 18, 20]. However, properly calibrated processing of 2D images can be used to derive 3D quantities [21].

<sup>&</sup>lt;sup>1</sup> A version of this appendix has been published: "Aerosol Science & Technology: Electron tomography of soot for validation of 2D image processing and observation of new structural features." 53 (5), 575-582. Copyright 2019. Taylor & Francis. Reprinted with permission.

Two properties that are physically important are the projected area (usually well correlated with particle drag) and primary particle diameter (central to fractal models of aggregates). Projection artifacts in these quantities have not been studied but might exist if aggregate sampling results in strongly biased orientations. Often measurements of aggregate area and primary particle size show great scatter (e.g. [22]), and it has been impossible to disaggregate the contributions to this variance from image processing artifacts, projection artifacts, and true particle-particle differences.

Also, prior work does not mention the presence or absence of structural features that cannot be detected in 2D images, such as ring structures that might form during partial restructuring of aggregates during or after growth. In fact, the first tomographic video that we obtained showed such rings, which was an important factor in pursing this research.

#### A.2 Materials and methods

#### A.2.1 Generation of soot

The soot studied here was generated at the Carleton University Vertical Flare Facility in the Energy and Emissions Research Lab. Details of the methods and the 3 fuel blends "L6," "M6," "H6" are described in the online supplementary information of [23]. Flares had an exit velocity of 0.5 m/s and were up to 3 m tall. Detailed characterization of soot from this facility is described by Kazemimanesh et al. [24]. Although it cannot be expected to represent all soot sources, it does seem to be typical in terms of the aggregate size, primary particle size, and Raman spectra.

For simplicity in the following sections the aggregates are named using letters as no trend between the soot morphology and the production conditions has been found. Measurements of effective density (mass-mobility exponent 2.55) and EC/TC ratios (>90%) confirmed that this was typical uncoated soot suitable as a model material for the purposes of the present study.

#### A.2.2 Collection of soot

Particles were collected using a portable thermophoretic sampler, developed at the University of British Columbia. Particles were deposited onto 3 mm lacey formvar/carbon copper TEM grids (01881, 200 mesh, Ted Pella). Two of the particles in this study were collected on carbon type-B copper TEM grids (01840, 200 mesh, Ted Pella). However, these grids resulted in reduced resolution due to a more limited tilt angle at higher magnifications and to the presence of a carbon film which reduced the transmittance of the beam.

#### A.2.3 Imaging

Images of the soot aggregates were taken with a High-Resolution Transmission Electron Microscope (HRTEM) (FEI Tecnai G2), located in the Bioimaging Facility at the University of British Columbia. The device allows a magnification range of up to 700 kx, a point resolution (nm) 0.27, and a flexible high tension (20, 40, 80, 120, 160, 200 kV). Images at each plane were recorded using a magnification of approximately 100 kx, depending on the soot aggregate size, and a tension of 80 kV. Each soot aggregate has been exposed to the beam for about 450 s. Previous literature references showed that shorter time can be enough to initiate an oxidation process in soot nanoparticles. Although, a higher voltage is used, 300 kV. Furthermore, changes are visible in a

size range below 2 nm [24]. The TEM grid was placed on a holder, which was able to tilt from an angle of  $-60^{\circ}$  to  $+50^{\circ}$ . An image of the soot aggregate was taken at each rotation degree between the ranges of -60 to -20 and +20 to  $+50^{\circ}$ , and at each  $2^{\circ}$  between the range of -20 and  $+20^{\circ}$ . A total of 91 images each soot aggregate were taken. Nine soot aggregates were imaged.

#### A.2.4 Image processing

The 2D images used to create the tomographic reconstructions were used individually to test the effect of orientation on particle measurements. Three different 2D image processing algorithms were applied. The focus of this study was the automated algorithm described by Dastanpour, Boone, and Rogak which employs the pair correlation method (PCM) for estimating average primary particle size in an aggregate [22]. As a comparison another automated code employing a Hough transformation for estimating primary particle size was tested [26]. Manual sizing was employed as the robust albeit tedious reference method (details in the SI). Each aggregate had approximately 90 images taken with 1–2 degree changes between images. Approximately 30 images per aggregate were analyzed with each image processing code.

#### A.2.5 Tomographic reconstruction

The 91 images taken per soot aggregate were processed using Inspect 3D [27]. The Simultaneous Iterative Reconstruction Technique (SIRT) was used for the volume reconstruction. SIRT is a well-established technique used for tomography [28, 29, 30]. The SIRT method reprojects from the current estimation of the tomogram by adding up densities along projection lines through the tomogram, taking the difference between the original projection data and this reprojection at each pixel [31]. This difference shows the amount of error in the current estimation; in the next iteration the error is distributed among the pixels along the ray contributing to it [31, 32,33].

#### A.2.6 Construction of a printable solid model

Z-direction image stacks were used to create a 3D model using the tomographic image processing program IMOD [34]. Z-direction stacks were loaded into the 3dmod tool where the "join" drawing tool was used to manually draw contours around the particle slices. Each aggregate contained between 800 and 1100 z-direction sections and approximately 1 out of 10 sections were manually contoured. Once a sufficient stack of contours has been created, the mesh tool was used to create a solid model. The model could then be exported as a .stl file. Due to the manual contouring, the models often had sharp edges which were smoothed with Amira's surface simplification algorithm, which collapses as edges to points on the surface mesh, as long as the original surface points remain close to the triangulated surface mesh. A detailed explanation of the process used to produce the 3D printable .stl files and the final files, are contained in the SI of [23].

We first consider the effect of projection angle on 2D image analysis results for seven soot aggregates lettered "A" through "G"<sup>2</sup> Figure A.1 shows a series of three different viewing angles

<sup>&</sup>lt;sup>2</sup> Nine aggregates were tomograpically imaged, but two of the aggregates had large portions which fell outside of the imaged area making it impossible to reliably measure aggregate area and aspect ratio.

for three different soot aggregates illustrating substantially different morphology at different projection angles. One of the most obvious differences is the change in aspect ratio across the tilt angles.



Figure A.1: Two-dimensional images of three soot aggregates at three different inclination angles. Top: aggregate A; middle: aggregate F; bottom: aggregate G.

Figure A.2 shows the variations in primary particle diameter, projected area-equivalent diameter, and aspect ratio, with projection angle.



Figure A.2: Primary particle diameter (a), Normalized area equivalent diameter (b), and particle aspect ratio (c) are shown for seven soot aggregates (A, B, C, D, E, F, and G).

Figure A.2a depicts only the results from the PCM method to determine average primary particle size, a graph comparing the different methods can be found in the SI of [23]. As the stage is rotated from  $-60^{\circ}$  to  $+50^{\circ}$ , the average primary particle size fluctuates around its mean value but shows no correlation with angle or aspect ratio Figure A.2c. This implies that, even if there are orientation biases in the sampling process, it is unlikely to affect the mean primary particle size. It
is possible that in a larger sample or with different collection procedures a trend in particle orientation might become visible. Previous studies have suggested that thermophoresis, which was used to collect the particles studied here, can preferentially orient the particles [3, 34]. Other studies assume thermophoresis results in random particle orientation [4, 5]. Likely, the magnitude of the temperature gradient (relatively small in the sampler used here) would influence such orientation biases.

Figure A.2b shows the area-equivalent diameter normalized by the maximum areaequivalent diameter of each soot aggregate. For several aggregates, larger area is correlated with lower aspect ratio. This implies that these aggregates have a bounding envelope that is more oblate than prolate. However, not all aggregates exhibited the same behavior and given the small sample size, we do not know how typical this is. The diameters in Figure B.2b are normalized by the maximum value so that the average must be less than unity. For most aggregates, the normalized *diameter* at 0 degrees is not far from the average, so we see no obvious bias with angle. The maximum variation in diameter is about 15%, corresponding to a variation in area of roughly 30%. For aggregates with uniform primary particle size, the variations in area should be indicative of the number of countable primary particles. Thus, our variations with angle appear to be lower than Gray's earlier report that counts from 2D images were 36% too low.

Table A.1 summarizes the mean and standard deviation of image-derived parameters obtained by the three image processing codes. In this very small sample of aggregates we do not see an increase of primary particle diameter with projected–area, predicted by the correlation of Dastanpour and Rogak [36]; this is unsurprising given that the geometric standard deviation of primary particle size around the previously reported correlation was 1.3 to 1.4.

Aggregate number	Method	Primary Particle Diameter (nm)	Area-Equivalent Diameter (nm)	Aspect Ratio
	PCM	$31.8 \pm 4.4$	$169 \pm 9$	$1.23 \pm 0.11$
А	Manual	$25.2\pm3.4$	$167 \pm 10$	$1.40\pm0.23$
_	PCM	$32.1\pm4.5$	$167 \pm 7$	$1.30\pm0.18$
В	Manual	$25.8\pm4.2$	$171\pm9$	$1.74\pm0.14$
С	PCM	$33.6\pm3.0$	$675 \pm 28$	$1.09\pm0.05$
D	PCM	$36.2\pm2.6$	$453\pm22$	$1.20\pm0.05$
	PCM	$34.0 \pm 1.4$	$348\pm22$	$1.49\pm0.18$
Е	Manual	$26.7\pm3.4$	$_{349} \pm 23$	$1.41 \pm 0.16$
	Hough	$32.0 \pm 1.2$		
	PCM	$37.4\pm6.0$	$367 \pm 15$	$1.13\pm0.09$
F	Manual	$30.6\pm4.8$	$369 \pm 9$	$1.74\pm0.20$
	PCM	$38.3 \pm 3.3$	$293 \pm 10$	$1.50\pm0.17$
G	Manual	$33.8\pm4.4$	$292 \pm 9$	$1.36\pm0.17$

Table A.1: Image analysis results including manual, PCM, and Hough transformation algorithm comparisons given as the mean  $\pm$  the standard deviation of the results across the series of angles for a particular aggregate.

The variations of primary particle size with projection angle were characterized by a standard deviation up to 4 nm or 16%. While the Hough transformation method implemented by Kook et al. and the manual sizing gave consistent bias relative to the PCM results, all methods showed nearly identical variation with projection angle (SI of [23]). The relative bias between the methods is likely due to details of the image quality as the PCM code and the Kook code use different methods to handle the grayscale images. The PCM code was originally tuned against manual sizing for zero bias over hundreds of particles, but typically would give 14% higher or lower values than manual sizing. In this study the PCM code regularly overestimated the manual results. This is attributed to lower than normal image quality of these projections when compared to conventional TEM projections. Primary particles are more affected by the image definition; a low resolution does not allow the PCM code to easily identify the overlapping areas or the primary particles edges. A detailed description of the algorithm's methods is included in the SI of [23]. There is a notable difference in the mean aspect ratios calculated with the PCM code and the manual code due to a difference in the way the length and width of a particle are defined (see SI of [23]). However, the quantity of interest is the standard deviation of the values analyzed across inclination angles which is comparable for both methods. The PCM and manual method use the same algorithm to determine the projected area-equivalent diameter. The results are not identical as human judgment is used in the thresholding of the grayscale image, resulting in slightly different binary images.

The videos and solid reconstructions, which can be found in the SI of [23], exhibited some features that could not have been determined from 2D images. For example, the videos sometimes show that a small separate particle underneath a large aggregate; in the 2D images it is often impossible to tell that the small particle is distinct from the large aggregate.

The videos and tomography also revealed the presence of ring structures. Figure A.3 shows an example of the 3D solid model rendering of a soot aggregate, with a ring structure highlighted in green. Eight of the nine aggregates examined exhibited ring structures. The only aggregate that did not exhibit a ring structure was aggregate B, which is one of the smallest aggregates, while larger aggregates sometimes contained many ring structures. The rings present in soot aggregates are hidden at certain angles, and even if visible, cannot be distinguished (in 2D) from individual branches that overlap at a given viewing angle. For example, the 3D imaging revealed cases where large aggregates overlapped smaller (unattached) soot aggregates that did not appear distinct in an ordinary projection. Evidence of this can be found in the video of aggregate D in the SI of [23]. Given that the 3D model creation resulted in slightly smoothed (and perhaps thickened) structures, one might wonder if the rings are artificially closed by the modeling. However, the videos in the SI involve no such modeling yet exhibit the ring structures clearly.



*Figure A.3: Two 3-D models of soot from 3 different angles. The observed ring structure is highlighted in green. Top: Aggregate A, Bottom: Aggregate E.* 

Early studies simulating the aggregation process [37] suggested that when the particleparticle sticking probability is reduced substantially, denser aggregates result. However, 2D TEM images of fresh soot typically have the appearance of the simulated aggregates produced with perfect sticking. On the other hand, studies have shown that condensation of liquids or electric fields [38] can cause substantial restructuring of aggregates. However, the flare-derived soot examined here appears to be free from any coatings, through the formation and dilution process, as indicated by an effective density typical of fresh soot [39]. The ring structures we observe are relatively subtler and would require only small rotations at the contact points between primary particles. Our imaging cannot determine whether such rotations occur during the soot formation, during dilution, or post sampling. However, it seems likely that restructuring could occur during formation, when the temperatures are high, and the primary particles have not yet become "welded" by further surface growth.

### A.3 Conclusions

This study showed that average primary particle size, projected area-equivalent diameter and aspect ratio can be reasonably estimated from 2D projections, at least for "typical" dry, fractallike soot aggregates with a substantial number of primary particles. Different image processing algorithms, including manual measurements, produced slightly different measurements, but none were strongly dependent on orientation angle or projected aspect ratio. Primary particle size varied by less than 16% as projection angled changed, while projected area-equivalent diameter varied by only 6% across projection angles. Only seven aggregates were analyzed in detail, but the magnitude of the variations were very similar for all aggregates, so perhaps the sample size is representative, at least for aggregates with many primary particles. With the small sample size, we were not able to see any orientation biases from sampling, but even if there are preferential orientations, the impact on the measurements of primary particle size or projected area measurements should be very small, based on the discussion above. As automated image processing methods improve, it will be possible to strengthen the conclusions with larger sample sizes.

However, there are some inherently 3D features that are visible only using tomography. For example, the 3D imaging revealed cases where large aggregates overlapped smaller (unattached) aggregates that did not appear distinct in an ordinary projection. As another example, the tomographic videos and solid models highlighted the presence of ring structures in most of the aggregates—suggestive of aggregate restructuring after aggregation. As far as we know, this has not been observed experimentally before, but it would be a natural consequence of weak bonds between newly-connected primary particles. These ring structures are clearly visible in the videos produced directly from the tomographic imaging, without any of the expensive solid model creation needed to produce, for example, 3D printed soot models.

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# Appendix B:Supplemental information for Chapter 23B.1 Sampling configuration

Figure B.1 is a schematic of the sampling configuration used to obtain the data discussed in this study. Some instruments which were also sampling from the manifold during the measurement campaign, but which were not described in this study are not shown for simplicity.



Figure B.1: Schematic of sampling configuration, not to scale. Bold, highlighted instruments denote instruments which provided data directly discussed in the main publication. A 'T' denotes a tee flow splitter and a 'Y' denotes a wye flow splitter or mixers. Dashed lines denote temporary connections. TPS is the thermophoretic sampler. All sampling lines were connected closer to the end of the sampling manifold but are shown all along the length for drawing space consideration.

<sup>&</sup>lt;sup>3</sup> A version of this Appendix was published as the supplemental information for the article: "Journal of Aerosol Science: Size and morphology of soot produced by a dual-fuel marine engine." 135, 105448. Crown Copyright 2019. Published by Elsevier. Reprinted with permission.

### **B.2** Particle morphology

Figure B.2 represents the individual aggregate data which makes up Figure 2.2 in the main publication plotted in log space.



Figure B.2: Points represent the projected area equivalent diameter and average primary particle diameter for every aggregate imaged. The left-hand side represents particles from diesel-only operation and the right-hand side represents particles from NG operation with their respective fits and the Olfert and Rogak (2019) universal fit.

In addition to the confidence intervals on the fit, confidence intervals were calculated primary particles binned by aggregate size. Size bins were evenly spaced in natural logarithm space. All calculations were done in natural logarithm space and converted only for presentation. The primary particle size 95% confidence intervals were calculated as  $\alpha_{95\%} = \frac{2*\sigma}{\sqrt{N}}$  where  $\sigma$  is the standard deviation and *N* is the number of aggregates in the size bin.

Table B.1 summarizes the size bin limits, the mean sizes and the upper and lower limits of the confidence intervals. This same information is plotted in **Error! Reference source not found.** 

Aggregate Size Bin	NG Pri	mary Part (nm)	icle Size	Number	ber Diesel Primary Particle Size (nm)			Number
(nm)	Lower Limit	Mean	Upper Limit	Points	Lower Limit	Mean	Upper Limit	Points
27 - 37	-	-	-	0	-	15	-	1
37 - 49	17	19	22	5	8.3	16	29	2
49 - 67	21	23	26	18	12	16	21	4
67 -90	25	25	28	36	18	21	25	16
90 - 122	26	28	29	80	21	24	27	36
122 -164	30	33	35	64	24	27	30	38
164 - 221	34	36	38	70	27	30	33	38
221 - 299	35	38	41	65	32	36	39	46
299 - 403	37	39	42	47	34	36	39	48
403 - 545	40	43	46	39	37	41	44	24
545 - 735	42	45	48	20	38	43	50	8
735 – 992	45	49	53	12	40	46	52	8
992 -	40	45	50	3	-	-	-	0

Table B.1: A summary of aggregate size bins, primary particle mean values and confidence intervals.



Table B.1 plotted against with the power law fits presented in the main publication. b) normalized number of particles in size bin which makes up the points in Figure B.2 a).

T-tests were performed to determine whether or not different operating conditions produced significantly different primary particle size distributions or aggregate size distributions based on the null hypothesis that the two conditions have the same mean value. None of the aggregate size distributions were significantly different. Only the total NG and diesel-only primary

particle size distributions were significantly different. Based on 95% confidence intervals some of the NG loads may be considered slightly different but are no longer significant based on 99% confidence intervals. The results are listed in Table B.2.

Condition 1	Condition 2	Primary particle p-value	Aggregate p-value
All Diesel	All NG	0.0007	0.0716
Diesel 75%	Diesel 50%	0.0685	0.3360
Diesel 25%	Diesel 50%	0.2261	0.2730
Diesel 25%	Diesel 75%	0.5602	0.7302
Diesel idle	Diesel 75%	0.0902	0.5132
Diesel idle	Diesel 25%	0.2991	0.4068
Diesel idle	Diesel 50%	0.7723	0.8313
NG high	NG medium	0.0212	0.8242
NG high	NG low	0.8757	0.6834
NG high	NG idle	0.0370	0.4018
NG low	NG idle	0.0189	0.4018
NG medium	NG idle	0.4755	0.2855
NG idle	Diesel idle	0.9268	0.5802

Table B.2: P-values from t-tests for hypothesis testing with the null hypothesis that the two conditions have the same mean.

## **B.3** Non-typical particles

B.3.1 Non-typical soot particles

While uncommon, a not insignificant number of non-typical particles were found during diesel operation particularly at higher loads. The source of these particles was not thoroughly investigated but they are included here for completeness. Figure B.3 shows examples of TEM images of these particles.



Figure B.3: TEM images of non-typical particles observed during high load diesel operation.

These particles were only observed on diesel-only operation TEM grids and they occurred more often at higher loads as illustrated in Table B.3. They were observed on grids collected using thermophoresis and electrostatic precipitation. These numbers could be slightly higher as particles which were difficult to categorize as either typical soot or clearly non-typical were not included in the frequency estimation.

Load Category	Frequency of non- typical particles
75%	12%
50%	2.8%
25%	1.4%
Idle	0%
Total	5.3%

Table B.3: Frequency of non-typical particles as a percentage of total particles sampled for diesel-only operation

HRTEM images of these particles revealed nanostructures which are surprisingly similar to that of a typical soot particle. Figure B.4 shows the nanostructure of a non-typical particle while S4b shows the nanostructure of a typical soot particle collected from the same engine running on diesel only.



Figure B.4: HRTEM images of nanostructure from a) non-typical particles described above and b) a normal soot aggregate produced by the same engine.

#### B.3.2 Non-soot particles

On girds collected using the ESPnano, evidence of liquids (e.g. lube oil) and potentially metals were seen. The reason this was seen on grids collected via the ESPnano but not the thermophoretic sampler (TPS) may be that the TPS operates at a higher tempreature than the ESPnano effectively stripping these materials from the deposited aerosol.

## **B.4** Coagulation

After leaving the turbocharger, the exhaust (at ~ 350 °C) travelled approximately 10 meters to an exhaust port on the side of the engine at which point it entered the dilution tunnel where a 6-fold dilution of clean air was added. In order to investigate the likelihood that soot particles were able to undergo coagulation during this time the residence time of the exhaust was compared to the characteristic timescale for coagulation of the exhaust. The characteristic timescale for coagulation,  $\tau_c$ , is defined as "the time necessary for reduction of the initial number concentration to half its original value" [1]. The exhaust had an approximately 24-inch diameter ( $A = 0.292 \text{ m}^2$  area) and a flowrate (Q) of 10 m<sup>3</sup>/s. Thus, the estimated residence time (t) was calculated as t = (LA)/Q where L is the exhaust distance travelled.

As soot particles are complex, non-spherical particles the kernel function, K, was calculated using methods described by Rogak and Flagan [2]. Parameters used in the calculation are listed in Table B.4.

Description	Parameter	Value
Molecular weight of air	$M_{ m air}$	28.97 g/mol
Universal Gas Constant	R	8.31 J/mol-K
Exhaust Pressure	Р	101 kPa
Exhaust Temperature	Т	350°C
Gas Viscosity of Air at 350°C	$\mu_{ m air}$	3.16x10 <sup>-5</sup> Pa-s
Mobility Diameter	$d_{ m m}$	30 nm
Particle Density	ρ	$1800 \text{ kg/m}^3$
Boltzman Constant	k	$1.38 \times 10^{-23} \text{ m}^2 \text{kg/s}^2 \text{K}$

Table B.4: Parameters used to calculate the characteristic timescale for coagulation.

For simplicity, the assumption was made that all of the particles had the same mobility diameter. In order to get the most conservative estimate,  $d_{\rm m} = 30$  nm was chosen as it yields roughly the largest coagulation kernel. Thus, the collision diameter,  $d_{\rm c}$ , becomes 60 nm (2 $d_{\rm m}$ ) and the volume equivalent diameter ( $d_{\rm v}$ ) becomes 1.41x10<sup>-23</sup> m<sup>3</sup>.

From Seinfeld and Pandis [1] the mean free path of air ( $\lambda_{air}$ ), Knudsen number (*K*n), Cunningham correction factor (*C*<sub>c</sub>) and the diffusivity (*D*) for 30 nm particles were calculated:

$$\lambda_{air} = \frac{2\mu_{air}}{P\sqrt{\frac{8M_{air}}{\pi RT}}}$$
(1)

$$Kn = \frac{2\lambda_{air}}{d_m} \tag{2}$$

$$C_{c} = 1 + Kn \left( 1.257 + 0.4exp\left(\frac{-1.1}{K_{n}}\right) \right)$$
(3)

$$D = \frac{kTC_c}{3\pi\mu_{air}d_m} \tag{4}$$

Using these quantities, the diffusion mean free path ( $\lambda_{1,2}$ ), diffusion Knudsen number ( $Kn_D$ ) and the transition correction factor can be calculated as described by Rogak and Flagan [2].

$$\lambda_{1,2} = \frac{2(D+D)}{\sqrt{\frac{12kT}{\pi^2 \rho} (2d_v^{-3})}}$$
(5)

$$Kn_D = \frac{2\lambda_{1,2}}{d_c + d_c} \tag{6}$$

$$\beta = \frac{1 + K_{nD}}{1 + 2K_{nD}(1 + K_{nD})} \tag{7}$$

The transition-regime kernel function was calculated as [2]:

$$K = 2\pi (d_c + d_c)(D + D)\beta$$
(8)

Then, given the initial number concentration ( $N_0$ ),  $\tau_c$  can be calculated [1].

$$\tau_c = \frac{2}{6KN_0} \tag{9}$$

Using these equations and the described assumptions, the estimated residence time of the exhaust before entering the dilution tunnel is 0.3 s while  $\tau_c = 2.2$  s for an initial concentration of  $N_0 = 5.5 \times 10^6$  particles/cm<sup>3</sup>, the maximum concentration for diesel-only operation from the scanning mobility particle sizer (SMPS) data. As discussed in the main text, this suggests that while a small amount of coagulation may be possible it is unlikely to have had an impact on the majority of the particles. For NG, the concentration of soot is over an order of magnitude lower and thus coagulation between soot particles is highly unlikely. However, NG operation did result in extremely high total particulate matter (PM) concentrations due to the increase in organics. The maximum total number concentration (un-denuded) for NG was  $N_0 = 3.0 \times 10^7$  particles/cm<sup>3</sup> which results in a  $\tau_c = 0.4$  s. At this concentration some soot-organic coagulation would be expected. If this had occurred there should be evidence of morphological changes in the soot, specifically compacted particles after evaporating the volatiles (either in the catalytic stripper or in the vacuum of the transmission electron microscope (TEM)). This would be particularly evident at idle during NG operation as this resulted in the highest concentration of organics. No evidence of such morphological changes were seen. For these reasons, coagulation outside of the engine is unlikely to have played a substantial role in the data studied here.

# **B.5 References**

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# Appendix C:Supplemental information for Chapter 3C.1 Detailed fuel composition

Fuel code	L9	M9	NS-M9	H9	RU-KM2	RU-KM1
C:H	0.264	0.274	0.281	0.293	0.299	0.312
HHVv [MJ/m <sup>3</sup> ]	35.8	41.6	43.2	47.0	48.5	51.4
Region	Canada	Canada	North Sea	Canada	Russia	Russia
[Composition by	Volume %]					
Methane	92.4	86.4	82.5	75.7	77.1	74.0
Ethane	0.32	6.83	8.09	11.5	5.29	3.08
Propane	0.09	2.36	4.06	6.06	8.24	7.87
n-Butane	0.40	0.97	1.53	2.60	4.28	6.79
Nitrogen	1.54	1.62	1.43	1.70	1.56	1.90
Carbon Dioxide	5.16	1.22	1.70	1.22	1.76	2.85
iso Pentane	0.06	0.33	0.51	0.78	1.24	2.35
n-Hexane	0.03	0.13	0.07	0.23	0.21	0.43
n-Heptane	0.04	0.19	0.13	0.24	0.37	0.77
Fuel code	EC-AC	BK-WO	BK-BR	EC-AS1	RU-FI	EC-A27
C:H	0.364	0.311	0.331	0.349	0.346	0.369
HHVv [MJ/m3]	54.6	52.3	61.1	60.9	71.5	75.2
Region	Ecuador	USA	USA	Ecuador	Russia	Ecuador
[Composition by	Volume %]					
Methane	46.4	57.8	49.1	54.0	51.9	39.6
Ethane	7.93	20.0	21.0	7.47	9.81	7.93
Propane	11.1	11.4	15.0	11.4	16.9	16.44
n-Butane	6.78	3.81	6.72	8.61	10.3	14.33
Nitrogen	8.03	5.22	3.66	1.03	0.95	3.27
Carbon Dioxide	12.4	0.57	0.70	6.18	0.15	5.55
iso Pentane	2.95	0.93	2.15	3.87	4.68	6.61
n-Hexane	1.17	0.22	0.59	1.34	2.93	2.00
n-Heptane	3.31	0.15	1.06	3.06	2.41	4.24

Table C.1: Detailed composition of fuels used in the Chapter 3

# C.2 Raman D/G ratios

For simplicity, only the D1/G ratios of the Raman spectra were shown in the main text as a measure of disorder in the nanostructure. D2/G, D3/G and D4/G ratios showed the same trends and are shown here. The D2/G shows only a very weak correlation with HHVv, while D3/G and D4/G have a stronger relationship. The same information is tabulated in Table C.2.

Fuel Code	HHVv [MJ/m <sup>3</sup> ]	$D1/G \pm 1\sigma$	$D2/G \pm 1\sigma$	$D3/G \pm 1\sigma$	$D4/G \pm 1\sigma$
L6*	35.3	12.4 ± 1.39	$0.80 \pm 0.30$	$1.66\pm0.57$	$1.36\pm0.59$
L9	35.8	$11.4 \pm 1.01$	$0.86 \pm 0.11$	$1.66\pm0.16$	$1.22\pm0.12$
L9 with water	35.8	$11.5\pm0.99$	$0.82\pm0.10$	$1.66\pm0.21$	$1.22\pm0.12$
M9	41.6	$10.3\pm0.80$	$0.71\pm0.09$	$1.50\pm0.13$	$1.17\pm0.10$
M9 with water	41.6	$10.5\pm0.81$	$0.73\pm0.06$	$1.56\pm0.13$	$1.14\pm0.11$
H9	47.0	$8.38\pm0.72$	$0.67\pm0.09$	$0.92\pm0.09$	$0.74\pm0.07$
H9 with water	47.0	$8.31\pm0.51$	$0.76\pm0.06$	$0.94\pm0.06$	$0.63\pm0.08$
M6*	48.5	$8.92\pm0.90$	$0.68\pm0.13$	$1.40\pm0.16$	$1.11\pm0.14$
RU-KM1	51.4	$8.21 \pm 0.71$	$0.65\pm0.09$	$0.97\pm0.10$	$0.68\pm0.07$
EC-AC	54.6	$7.69\pm0.54$	$0.62\pm0.07$	$0.89\pm0.08$	$0.64\pm0.08$
H6*	54.7	$7.32\pm0.55$	$0.59\pm0.24$	$0.90\pm0.21$	$0.62\pm0.20$
BK-WO	57.8	$7.88 \pm 0.51$	$0.63\pm0.07$	$1.00\pm0.08$	$0.70\pm0.10$
EC-AS1	60.9	$6.22\pm0.54$	$0.522\pm0.04$	$0.60\pm0.04$	$0.57\pm0.01$
BK-BR	61.1	$6.12\pm0.83$	$0.43\pm0.08$	$0.57\pm0.08$	$0.52\pm0.03$
RU-FI	71.5	$5.41\pm0.28$	$0.45\pm0.05$	$0.48\pm0.05$	$0.44\pm0.06$
EC-A27	75.2	$5.37\pm0.33$	$0.36\pm0.06$	$0.43\pm0.04$	$0.44 \pm 0.04$

Table C.2: Tabulated D/G ratios for all fuels studied sorted by HHVv.



Figure C.1: D2/G, D3/G and D4/G ratios from Raman spectra as a function of HHVv.

# Appendix D: Supplemental information for Chapter 4 D.1 Flowback fluid composition

The composition of the liquids added to the flames in Chapter 4 and the resulting aerosols are listed in Table D.1. The liquid composition was measured using x-ray diffraction (XRD) for 15 chemical elements or compounds: Na, Cl, Li, B, Mg, S, K, Ca, Mn, Fe, SO<sub>4</sub>, Br, HCO<sub>3</sub>, Sr, Ba. The aerosol composition was measured using x-ray fluorescence (XRF) analysis in which the sample is analyzed for eight chemical elements: Na, Cl, K, Ca, Fe, S, Mg and Ba. A Micromatter Rigaku NEX CG EDXRF spectrometer was used and calibrated using the NIST traceable calibration. Some of the difference in composition can be attributed to the fact that XRD can detect more elements than XRF. The two methods do give roughly the same results suggesting that the elements that went into the flame also came out of the flame.

	Sodium	Chloride	Care	dium	Duve	ernay
	Liquid	Aerosol	Liquid	Aerosol	Liquid	Aerosol
Na	39.34%	38.60%	34.07%	36.23%	33.53%	31.65%
Cl	60.66%	58.66%	41.77%	58.34%	59.36%	59.36%
Li	-	-	-	-	0.02%	-
В	-	-	-	-	0.05%	-
Mg	-	2.23%	0.07%	2.30%	0.43%	2.37%
S	-	0.48%	-	1.11%	0.06%	0.49%
Κ	-	0.03%	0.80%	1.01%	1.11%	1.43%
Ca	-	-	1.10%	1.02%	4.78%	4.64%
Mn	-	-	-	-	0.005%	-
Fe	-	-	0.22%	-	0.13%	0.06%
$SO_4$	-	-	7.72%	-	-	-
Br	-	-	-	-	0.13%	-
HCO <sub>3</sub>	-	-	14.20%	-	0.16%	-
Sr	-	-	-	-	0.48%	-
Ba	-	-	0.05%	-	0.01%	-

Table D.1: Liquid additive chemical compositions from the Carleton University experiments described in Chapter 4. The liquid composition was measured using X while the aerosol composition was measured using XRF. The two methods have some limits in what elements can be measured accounting for some of the differences in composition.

#### **D.2 TEM particle overlap calculations**

If aerosol flows are sampled for too long, TEM grids can easily become overloaded making it possible to distinguish two separate particles which fell in the same location on the grid from an internally mixed particle that would be in the same state if released into the atmosphere. In order to determine if this was the case with the grids studied in Section 4.3.1 Results from Carleton University. ImageJ was used to determine the total area of each image, A<sub>total</sub>, the are in the image covered in salt, A<sub>salt</sub>, the number of soot particles in the image, N<sub>soot</sub>, and the total number of salt particles in the image, N<sub>salt</sub>. The average soot projected-area-equivalent diameter,  $d_a$ , was obtained from the image analysis reported in Chapter 3. The collision equivalent diameter, cd, of a salt and soot was then calculated as:

$$c_d = \frac{4}{\pi} * \sqrt{\frac{A_{salt}}{N_{salt}}} + d_a \tag{D.1}$$

Next, the overlap probability was calculated as:

overlap probability = 
$$N_{salt} \left( \frac{\frac{\pi}{4} c_d^2}{A_{total}} \right) * 100$$
 (D.2)

#### **D.3** Coagulation calculations

Coagulation calculations were done using the same equations described in Appendix B: with slight modifications to estimate the fraction of soot 'lost' to salt. The two calculations diverge once the coagulation kernel, K, has been calculated. From the coagulation kernel the rate of coagulation between the two populations can be calculated as:

$$\frac{dN_s}{dt} = K * N_{soot} * N_{salt} * 0.5 \tag{D.3}$$

Where  $N_{soot}$  is the number of soot particles measured during the water addition cases, and  $N_{salt}$  is the estimated salt concentration based on the increase in particle number concentration between the salt case and the water addition case. Finally, the number of soot particles 'lost' to salt is:

mixed fraction 
$$= \frac{dN_s}{dt} \div N_{soot} * t$$
 (D.4)

Where *t* is the estimated residence time from the ventilation hood to the thermophoretic sampler. Salt mobility diameters were estimated from the peaks of the small particle modes in the SMPS data from Figure 4.3 and Figure 4.6. The sizes used were 25 nm for the Cardium solution and 100 nm for the NaCl and Duvernay solutions. For the University of Alberta experiments the sizes were 22 nm, 27 nm, 38 nm, 50 nm and 80 nm for 0.03%, 0.1% 0.3% 1.0% and 3.0% salt respectively. Table D.2 lists the fixed parameters used in the calculations while Table D.3 lists the variables which may have differed between the Carleton University and University of Alberta experiments. Finally, Table D.4 lists the coagulation results from both campaigns.

Description	Parameter	Value
Molecular weight of air	$M_{ m air}$	28.97 g/mol
Universal Gas Constant	R	8.31 J/mol-K
Exhaust Pressure	Р	101 kPa
Exhaust Temperature	T	300 °C
Gas Viscosity of Air at 300°C	$\mu_{ m air}$	3.00x10 <sup>-5</sup> Pa-s
Soot Density	$ ho_{ m soot}$	$1750 \text{ kg/m}^3$
Salt Density	$ ho_{ m salt}$	500 kg/m <sup>3</sup>
Boltzman Constant	k	$1.38 \times 10^{-23} \text{ m}^2 \text{kg/s}^2 \text{K}$

Table D.2: Parameters used in the coagulation calculations described in Chapter 4.

Table D.3: Variables for coagulation calculations which varied between the Carleton University experiments and the University of Alberta experiments. When a range is listed it represents the lowest and highest values used for the calculations within that campaign due to differences between test points.

Description	Parameter	<b>Carleton Value</b>	U of A Value
Residence time	t	5.5 s	22 s
Soot Size	d <sub>m,soot</sub>	92 nm	100 nm
Salt Size	d <sub>m,salt</sub>	25 to 105 nm	22 to 125 nm
Soot Concentration	$N_{soot}$	$2.0 \text{ x } 10^7 \text{ #/cm}^3$	$1.10 \text{ x } 10^5 \text{ #/cm}^3$
Salt Concentration	N <sub>salt</sub>	$1.8 \text{ x } 10^8 \text{ #/cm}^3$	$(1.54 \text{ to } 12.9) \text{ x } 10^6 \text{ #/cm}^3$

Table D.4: Calculated coagulation rates for the Carleton University and University of Alberta experimental campaigns.

Campaign	Test Point	<b>Coagulation Rate</b>
	NaCl	61%
Carleton University	Duvernay	61%
	Cardium	41%
	3.0%	9.7%
	1.0%	8.3%
University of	0.3%	5.4%
moenta	0.1%	6.3%
	0.03%	2.2%

# Appendix E:Microscopy methodsE.1 Introduction

Microscopy can often feel like more of an art than a science as each user has preferred methods, tips and tricks and each machine has its own intricacies. In this thesis, all of the imaging was preformed at the UBC Bioimaging Facility. All conventional transmission electron microscopy (TEM) was performed on a Hitachi H7600 with an 80 kV accelerating voltage. The high-resolution TEM (HRTEM) imaging and tomographic reconstructions discussed in Appendix B were performed on an FEI G20 with an 80 kV accelerating voltage. I took a majority of the images with the remainder of the imaging conducted by Dr. Alberto Baldelli.

As a material, soot and other carbonaceous particles are easy to image using electron microscopy because they are conducting and thus do not require a coating, they are not easily damaged by the electron beam and due to the amorphous structure do not have distinct diffraction patterns. Other materials, such as salts or semi-volatile components of engine exhaust, are susceptible to these problems and must be imaged with more care. Regardless of the material, care should be taken to randomly select particles. For example, it is easy to over-select large particles as they are eye-catching and easy to find on the TEM grid resulting in biased results. The following sections will discuss the techniques, methods and materials used to conduct the microscopy throughout this thesis.

# **E.2 Grid Selection**

The very first step in any type of electron microscopy is the selection of an appropriate grid. Many types of grids exist but only two types were used in this thesis: 3 mm carbon type-B copper TEM grids (01840, 200 mesh, Ted Pella) and 3 mm lacey formvar/carbon copper TEM grids (01881, 200 mesh, Ted Pella) which furthermore will be referred to as carbon film grids and lacey grids respectively. Carbon film grids consist of a copper grid (mesh referring to the size of the grids in this case 200  $\mu$ m) with an extremely thin layer of carbon on top. Lacey grids on the other hand still have a copper grid for support but on top of the grid is a formvar/carbon web with empty space in-between the supports. In both cases, the samples should be collected on the 'carbon' side of the grid. This side of the grid has a black sheen while the back of the grid it can still be imaged as the electron beam is transmitted through the entire sample regardless of orientation however there may be a reduction in image quality. Figure E.1 shows the difference between the two grids.



Figure E.1: TEM images taken from soot collected on a) a carbon film grid and b) a lacey grid.

For TEM, carbon film grids are generally preferable because the images have a smooth background with nothing touching the particle. This is essential for automated image processing because the algorithm cannot differentiate between particle and formvar support. However, lacey grids are preferable for two applications discussed in this thesis: HRTEM and tomography. HRTEM is usually used to image the nanostructure of soot particles which requires resolution of the individual graphene layers making up the primary particles. At this scale, the thin carbon film in the background makes the background noisy and can distort the nanoscale fringes that are being imaged. For tomography, the microscope stage is tilted, and the beam is no longer perpendicular to the grid. At the extreme angles, the electron beam becomes attenuated by the film thus restricting the range through which the stage can be tilted. This dramatically reduces the quality of the tomographic reconstruction. In both cases, the lacey grids allow for an empty background improving the resolution of the final image. Alternatively, holey carbon grids are very similar to lacey carbon grids and could be easily confused. Holey grids have much thicker formvar/carbon section with only small holes in the middle suitable for capturing particles too small for the lacey grid. Holey grids were not used because soot is typically large enough for the lacey web and holey grids reduce the chances of particles being suspended in space between supports as would be required for applications where a carbon film is not suitable.

#### E.3 Determining an Appropriate Sampling Time

One of the biggest experimental challenges with microscopy is determining an appropriate sampling time. A sampling time which is too long will result in a grid which has many overlapping particles making it impossible to discern the true size and shape of individual particles. A short sampling time will either result in no, or very few particles making the time needed for imaging extremely long or, the flow may not have time to reach steady operation resulting in a biased sample. Each device and experimental system will have an ideal sampling time and if possible, it is best to take a few test samples with different sampling times, check the loading with a TEM and then adjust the sampling time for the rest of the measurements accordingly. This optimal sampling time should be benchmarked with another online sensor, which can allow the user to adjust sampling time if something changes, such as a black carbon sensor or an SMPS if the flow consists of particles other than soot.

#### E.4 Avoiding bias during imaging and magnification required for PCM

There are many systematic ways to avoid bias during imaging and more important than the method selected is consistency. The method described here was used in Chapter 3 and Chapter 4 of this thesis. Carefully selecting particles at random allows for a reconstruction of the particle size distribution from the TEM images an example of which shown in Figure E.2 using data from two different fuels described in Chapter 3, EC-AC on the left and H9 on the right.



Figure E.2: Comparison between the SMPS particle size distribution (continuous, dashed lines) and TEM reconstruction (histogram, solid lines) of the size distribution using the imaging method described here.

The histograms reconstructed from TEM agree well with the SMPS data collected for the same sample however in both cases it is evident that there is a slight shift towards larder particle sizes despite efforts to be unbiased. Over 2000 TEM images were analyzed as a part of this thesis and the smallest particle observed was 19 nm. It is possible that the sampling device (a custom, UBC made thermophoretic sampler) has a lower limit beyond which it is unable to capture particles or has very large losses. In addition, the image analysis algorithm has a hard time picking up very small particles which have very low contrast when compared to the background which further contributes to this lower limit. Despite these limitations, for the sizes typical of soot (~ 100 nm median diameter) the agreement between the TEM results and the SMPS are quite good further taking into consideration the two very different methods for measuring particle size. The methodology is as follows:

- 1. Particles should be selected from different points on the grid. The centre and four corners are typically chosen except in cases where one or more of these locations is overloaded.
- 2. Select a random copper support grid in the section you are imaging.
- 3. Zoom into a point just off the copper support at approximately 100 kx magnification, the preferred magnification for primary particle and aggregate sizing.
- 4. Pan across the grid in a straight line from the point you've selected and image *every* particle encountered. If needed, zoom out to fully capture particles which do not fit into the image fully or zoom in to capture details on very small particles. Return to 100 kx before continuing to pan in a straight line.
- 5. Repeat this procedure for all five locations on the grid.

6. If scaling between  $d_p$  and  $d_a$  is of interest, intentionally seek out particles far from the median (very large or very small particles) at the end of the imaging process. Add a comment to the images that these are not randomly selected.

#### E.5 Imaging grids with salt and soot

Salt is difficult to image because it evaporates under the electron beam and is crystalline causing diffraction patterns. Salt will evaporate at a faster rate on carbon film grids compared to lacey grids, when the voltage is increased and when the magnification is increased. Reducing the accelerating voltage will reduce the contrast/quality of the final image and wasn't observed to dramatically improve the evaporation time thus this approach was not used. Instead, the area of interest is chosen at a very low magnification, then after zooming into an area near-by, the focus can be adjusted. Once the magnification and focus are adjusted the beam was moved to a new, unaffected area and an image was immediately taken. The damage from the electron beam was observed to be very localized making it easy to find an unaffected area.

The crystalline structure of salt results in a diffraction pattern which could be used for analysis of the salt itself, although this technique was not employed here. Typically, it is undesirable to have artifacts from the diffraction in the image and it was observed that imaging with the aperture in greatly reduced diffraction artifacts. When imaging soot alone the aperture makes little to no difference although typically it is recommended to image with the aperture in. In some cases, however, it is desirable to differentiate between salt and soot and in these cases the diffraction can confirm that a salt is present. In these cases, it is best to remove the aperture. Adjusting the focus can also help to uncover diffraction patterns.

Another method for differentiating between soot and salt is to watch for volatility under the electron beam. In these cases, it may be desirable to place the area in question under very high magnification and wait to see what happens. However, after very long exposure at high magnification even the soot may be damaged by the electron beam. If the suspected salt does not begin to evaporate under the beam relatively quickly (less than ~ 30 s) it is better to attempt to use diffraction patterns to discern soot from salt. Figure E.3 shows an example of a) a mixed soot/salt particle b) the diffraction artifact from the salt particle and c) the same mixed particle after being exposed to the electron beam. In image a) it is not evident that there is any salt present. Removing the aperture and putting the particle slightly out of focus reveals one of the salt particles in image b) and after some time exposed to the electron beam three salt particles become evident in image c) due to the obvious change in their structure/transparency.



Figure E.3: Ways to identify a mixed soot/salt particle. a) a mixed particle, b) the diffraction pattern caused by the salt when the aperture is removed or the particle is out of focus, c) the mixed particle after extended exposure to the electron beam.