The Pennsylvania State University
The Graduate School
Department of Energy and Mineral Engineering

PHYSICAL AND CHEMICAL CHARACTERIZATION OF GASOLINE PARTICULATES AND DIFFERENCES RELATIVE TO DIESEL SOOT

A Thesis in
Energy and Mineral Engineering
by
Chethan Kumar Gaddam

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The thesis of Chethan Kumar Gaddam was reviewed and approved* by the following

Randy L. Vander Wal  
Associate Professor of Energy and Mineral Engineering, Materials Science and Engineering and Mechanical Engineering  
Thesis Advisor

Yaw D. Yeboah  
Professor of Energy and Mineral Engineering  
Head of the Department of Energy and Mineral Engineering

André L. Boehman  
Professor of Fuel Science, Materials Science and Engineering and Mechanical Engineering

*Signatures are on file in the Graduate School
ABSTRACT

The research reported here involves a detailed investigation of primary particle size, aggregate size and morphology, primary particle nanostructure (fringe length and tortuosity), surface and bulk chemical composition of the soot generated from a spark-ignited, direct-injection (SIDI) engine at different operating conditions and compare the TEM results to an on road medium duty diesel engine which is of different size class. The comparison is not to find or demonstrate a statistically significant difference but to identify values indicative of differences observed via TEM.

The SIDI engine used in this research is a fuel-neutral, single-cylinder, four-stroke research engine which is built into a Ricardo Hydra block. The engine is a 549 [cc] with a flat-top piston, fueled by Tier II EEE. Working in collaboration with GM and PNNL, a clean baseline engine operating condition was established and repeatability at this condition was ascertained. This baseline condition is specified as 2100 rpm, 350 kPa IMEP, 280 [°bTDC] end of injection (EOI), and 25 [°bTDC] ignition timing. A matrix of operation conditions was established which included the following engine operational changes:

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Characterization techniques involved physical structure (microscopy) and chemistry (spectroscopy), both electron and optical based. Physical size and structure characterization that include aggregate size and morphology, primary particle size and internal nanostructure, were analyzed by TEM and subsequent image analyses. Thermogravimetric analysis (TGA) partial oxidation runs were conducted with intermediate study by HRTEM to estimate the degree of burnout for but one sample. Chemical characterization included organic and elemental content quantification as analyzed by X-ray photoelectron spectroscopy (XPS), volumetric-averaged functional group identification by Fourier transform infrared spectroscopy – Attenuated total reflectance (FTIR-ATR).

The TEM measurements showed that there is more primary particle size variation for SIDI samples. The aggregates formed for the conditions with lesser mixing appeared to be more compact with a higher level of tortuosity. Significantly FTIR provided a volumetric measure of the chemical composition as manifested by the functional groups. XPS showed that there are significant differences in composition between the five different engine-operating conditions. High resolution spectra over the C 1s regions showed that the soot particulates surface mostly consisted of graphitic carbon with some organic content. Corresponding relative peak intensities suggest that organics observed by FTIR-ATR are not concentrated in a surface film. Taken with FTIR-ATR measurements, this serves as strong evidence for matrix distributed organic content. A small (< 20%) surface oxygen content was observed by XPS, consistent with FTIR suggesting that the organic content is mainly alkyl hydrocarbons rather than oxygenated
species. Compared to diesel engine produced soots, aggregate fractal morphologies (both fractal dimension and root form factor) were significantly lower while primary particle sizes were of similar size range. The composite of these analyses illustrates the heterogeneity of species incorporated into soot particles implies a non-uniform growth environment with respect to time, temperature, and gas-phase chemistry during the combustion cycle.
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Above all, I would like to dedicate my M.S. thesis to my dear father whose sacrifices made my dream come true.

“Thank you so much dad for everything. No one else believed in me as much as you did”
Nomenclature

Acronyms

A/F  Air to Fuel Ratio
ATR  Attenuated Total Reflectance
CI   Compression Ignition
CO   Carbon Monoxide
CO₂  Carbon Dioxide
CRL  Collaborative Research Laboratory, University of Wisconsin
DC   Direct Current
DISI  Direct Injection, Spark Ignition
DMA  Differential Mobility Analyzer
DR   Dilution Ratio
EC   Evaporative Chamber
EGR  Exhaust Gas Recirculation
EI   Emissions Index
EOI  End of Injection
EPA  Environmental Protection Agency
ERC  Engine Research Center, University of Wisconsin
FTIR-ATR  Fourier Transform Infrared Spectroscopy – Attenuated Total Reflectance
FD   Fractal Dimension
GDI  Gasoline Direct Injection
GM   General Motors
HC   Hydrocarbon
HCCI  Homogeneous Charge Compression Ignition
HRTEM High-resolution Transmission Electron Microscopy
ID   Inner Diameter
IMEP  Indicated Mean Effective Pressure
MBT  Maximum Brake Torque
MHGD  Micro-Hollow Glow Discharge
NO   Nitrogen Monoxide
NO₂  Nitrogen Dioxide
N₂O  Nitrous Oxide
NOₓ  Nitrogen Oxide
PAH  Polycyclic Aromatic Hydrocarbons
PFI  Port Fuel Injection
PNNL Pacific Northwest National Laboratory
RFF  Root Form Factor
SMPS  Scanning Mobility Particle Sizer
SOF   Soluble Organic Fraction
SPLAT II second-generation Single Particle Laser Ablation Time-of-Flight mass spectrometer
TD    Thermodenuder
TGA   Thermogravimetric Analyzer
TEM   Transmission Electron Microscope
VPR   Volatile Particle Removal
XPS   X-ray Photoelectron Spectroscopy

Various acronyms for gasoline direct injection technology that are encountered in the worldwide literature

DGI   Direct Gasoline Injection
DIG   Direct Injection Gasoline
DI-G  Direct Injection Gasoline
DISI  Direct-Injection Spark-Ignited
GDI   Gasoline Direct Injection
G-DI  Gasoline Direct Injection
SIDI  Spark-Ignited Direct-Injection

Variables

\( \rho \)  Density of a fluid
\( \Phi \)  Equivalence ratio
\( \sigma_y \)  True mean of the transformed random variable \( Y = \ln X \)
\( \mu_y \)  Variance of the transformed random variable \( Y = \ln X \)
\( d_p \)  Depth of penetration
\( \lambda \)  Wavelength
\( \bar{x} \)  Arithematic mean of primary particle diameter
\( \sigma_p \)  Standard deviation of primary particle diameter
\( \eta \)  Coefficient of variation
\( D_f \)  Fractal Dimension
\( d_g \)  Gyration diameter
Chapter 1

INTRODUCTION

1.1. Motivation

Internal combustion (IC) engines are major sources of particulate matter in the atmosphere because a significant fraction of the total emission inventories in urban areas appears to be associated with transportation vehicles. While there are many more spark-ignition (gasoline) engines on the roads, compression-ignition (diesel) engines are under scrutiny because of their relatively high particle mass emissions.

The evolution and continuous improvement of the spark ignition, direct-injection (SIDI) engine has brought about more attention due to the potential in combining the positive qualities of compression-ignition (CI) and spark-ignition (SI) engines. One of the main disadvantages of SIDI engines is their significant higher PM emission compared to conventional port-fuel injection (PFI) engines.

Today’s regulations are mostly based upon total particle mass [1]. However, much research has suggested that number-based particulate regulations be issued in the light of evidence that nanoparticles, despite their negligible contribution to total mass, may also impose a great hazard to both the environment and human beings [2]. Emissions reductions and fuel economy improvements without the trade-off of performance are a priority for automobile buyers. As the technology penetrates the marketplace and particulate standards continue to evolve, original engine manufacturer’s (OEM) want to anticipate requirements of future aftertreatment systems: (1) they want to know when
filtration might be required, which depends on the quantity and size of the particulates, as well as the nature of the regulations in force at a given time, and (2) if particulate filtration will be required on these vehicles, OEMs would like clues to allow the quickest possible adaptation of existing Diesel Particulate Filter technology.

European number standards include specifications for treatment of the exhaust prior to counting. Raw diesel exhaust can contain significant numbers of droplets made up entirely of organics, as well as significant coatings of organics on the soot particles. The standards therefore include procedures to remove some of this volatile content, which can significantly alter the size and shape distributions. This can make the difference between meeting and failing to meet the number standards.

1.2. Objective

Thus the very unusual soots of SIDI, based on morphology and nanostructure motivated the detailed interrogation via complimentary spectroscopy and microscopy techniques. The present work addresses the impacts of engine operating conditions of an SIDI engine on the size, morphology, nanostructure, surface organic and elemental content and volumetric averaged functional group identification of the gasoline particulate matter (soot). EPA tier II EEE gasoline is the test fuel used in this work. For comparison of similarities and differences, the soot generated from SIDI engine is compared to soot generated from a medium duty diesel engine (ULSD fuel).

1.3. Outline

The results obtained while completing this experimental objective are described and summarized in this thesis. Chapter 2 provides background information and review of
literature for the various aspects that shall be covered. Next, Chapter 3 describes the experimental setups that include the test SIDI engine and a medium duty diesel engine, PM collection and test fuels followed by a small summary for each of the characterization techniques that are used. Chapter 4 illustrates the various soot characterization methods applied to quantify TEM images at different length scales. Chapter 5 describes the results for the objectives mentioned earlier followed by subsequent detailed discussion. Conclusion and recommendations for future work are described in Chapter 6. The Appendix includes mainly statistical analyses and miscellaneous data.
Chapter 2

LITERATURE REVIEW

This chapter gives a brief literature review of various aspects regarding the measurement of particulate emissions from vehicles. It starts with the introduction of PM-related and gasoline legislation, which is followed by a brief description of the engine itself. The effects of engine operating conditions on size, morphology, nanostructure and chemical composition are discussed.

2.1. Legislation Review

2.1.1. PM-related Legislation

In the last two decades, port-fuel injection (PFI) engines have been nearly ubiquitous, accounting for over 99% of all light-duty vehicle engines sold in the United States each year between 1996 and 2007 (Environmental Protection Agency (EPA)) [3]. Since that time, SIDI technology has been incorporated in U.S. production vehicles as manufacturers strive to meet new fuel economy standards. SIDI vehicles composed 2.3% of light duty gasoline vehicles in 2008 and 8.5% in 2010, EPA 2010. The percentage of gasoline vehicles with SIDI engines is expected to continue to increase rapidly with a projection of 60% of all new vehicles by 2016 in the U.S. (California Air Resources Board (CARB), 2010).

New emissions standard Euro 5a, which was enacted in September 2009, regulates the PM mass (g/km) emissions standard for diesel and SIDI vehicles. To meet the PN (#/ km) regulation for diesel powered vehicles in Euro 5b, DPFs with higher
efficiencies will be required [4]. Moreover, the introduction of Euro 6 over the New European Driving Cycle (NEDC) will lead to the implementation of a PN limit for all SI passenger vehicles, as shown in Table 1.

Table 2.1 Past, current and proposed European emission standards (*SIDI engine only, **all gasoline engines) [5]

<table>
<thead>
<tr>
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<th>Gasoline</th>
<th>Diesel</th>
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<td></td>
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<td>Euro 5a</td>
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<td>100</td>
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<td>5*</td>
</tr>
<tr>
<td>THC (mg/km)</td>
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</tbody>
</table>

Because motor vehicles are a major contributor to both air pollution and greenhouse gas (GHG) emissions, the California Air Resources Board (CARB) is proposing the establishment of new PM emissions standards for light-duty vehicles as part of the Low Emission Vehicle (LEV) III program. These standards propose that, beginning in 2014, all vehicles subject to LEV III-SULEV requirements must comply with at least one of the following two standards: 1) A Federal Test Procedure (FTP)-weighted PM mass emissions limit of 0.006 g/mi by 2014 and of 0.003 g/mi by 2017, 2) A FTP-weighted solid particle number (SPN) emissions limit of $6.0 \times 10^{12}$ particles/mi by 2014 and of $3.0 \times 10^{12}$ particles/mi by 2017 [5].
2.1.2. Adverse health effects of gasoline exhaust particles

Elevated particle emissions are of public health concern, especially for those living near major highways. Epidemiological studies indicate children living close to highways are more likely to develop asthma and reduced lung function [6]. A toxicological study carried out near a major Los Angeles freeway found a significant increase in coronary artery lesions for mice exposed to ultrafine particles (diameter < 100 nm; UFP) relative to the effect of larger size particles [7]. Exposure to PFI vehicle-emitted UFP has been associated with increased oxidative stress in rat lung, heart and liver tissue [8]. In addition, greater inflammatory cytokines were induced in human lung cells by SIDI than diesel particles for similar number concentration exposures [9]. Because gasoline exhaust particles are associated with significant adverse health effects, the particle emissions of SIDI engines may be regulated in the future in the European Union and possibly in the State of California (CARB, 2010) [10]. California is the only U.S. state with the authority to set stricter than federal automobile emissions standards and has sometimes influenced nationwide standards [11].

Compared with particulate mass, the number concentration may pose a greater threat to human health and the environment in light of previous research results on the impact of particulates. Based on Stokes’ law, the rate at which particles settle increases with the square of their diameter, hence the rate at which fine particles settle is fairly low and they usually remain airborne for days. In addition, they can easily pass through the human respiratory filtering system and deposit deep in the lungs. The ultrafine particles (< 100 nm in mean diameter) and the nano-sized particles (< 50 nm diameter) are
considered to be potentially dangerous due to their capability to enter deep into the respiratory tract which is consistent with what have found in their research.

Apart from gasoline and diesel, ethanol and bio-diesel blends, which are seen as a clean and CO2-efficient fuel and which produces smaller particles, are becoming more and more promising.

2.2. Spark Ignited, Direct Injection Engine

Direct Injection (DI) fueling for gasoline engines is an enabling technology for the development of vehicles with better fuel economy. In combination with turbocharging, gasoline DI fueling significantly improves engine power, which allows the engine displacement volume to be reduced for a given application (downsizing), even while the engine performance improves [12]. When the engine is downsized, the engine friction is reduced and the engine operates at higher engine loads for a larger fraction of the operating map, as quantified by the brake mean effective pressure (BMEP), which results in more efficient operation. In addition, gasoline DI fueling reduces the tendency of a fuel to knock because of enhanced charge cooling, allowing the compression ratio to be increased for higher efficiency. As a result, fuel economy can be increased for vehicles with DI fueling compared to engines with port fuel injection (PFI) technology. The major difference between the PFI engine and the SIDI engine is in the mixture preparation strategies, which are illustrated schematically in Figure 2.1.
DI gasoline engines are being rapidly incorporated into new vehicles in the United States. PFI technology has been nearly ubiquitous in light-duty vehicles over the past 2 decades, accounting for over 99% of all light-duty vehicles sold in the United States each year between 1996 and 2007 [3]. Since that time, gasoline DI fueling has begun to emerge, accounting for 2.3% of light-duty gasoline vehicles in 2008 and rising to 8.5% in 2010. The percentage of vehicles with gasoline DI technology in the United States is expected to continue increasing rapidly, with a projection of 60% of all new vehicles by 2016 [3].

While gasoline DI technology is beneficial for fuel economy, it produces an increase in particulate matter emissions in comparison to PFI engines. Aakko and Nylund
[14] reported that the particle mass emissions for a gasoline DI vehicle were on order of magnitude higher than for a PFI vehicle for the European 70/220/EEC drive cycle. Similarly, the particle number emissions were roughly a factor of 5 higher for the DI vehicle than for the PFI vehicle, although direct comparison of these is difficult because different vehicle drive cycles were used. A report issued by the California Air Quality Board [10] estimates that, on average, particle mass emissions are increased somewhere between 2 and 20 times for gasoline DI engines compared to PFI. Relatively high SIDI particle emissions have prompted several studies on the effects of engine operating parameters [12], [15–17] and fuel composition [18], [19] on particle characteristics.

Recent research in PM measurement has focused on the fact that, during cold start and at high acceleration points, SIDI engines can emit a significantly higher PN concentration in comparison with diesel engines equipped with a diesel particulate filter (DPF). These emissions are in the ultra-fine-particle and nanoparticle range, in contrast to the larger particles from diesel engines [12], [13].

Reductions in particle emissions from DI engines are being pursued with a number of different strategies. Moore et al. [20] show that increased charge motion achieved through deactivation of one of the intake valves is effective in reducing soot emissions, as quantified by the filter smoke number (FSN). Hedge et al. [21] show that exhaust gas recirculation (EGR) is effective at reducing particle emissions at part-load operation while simultaneously improving fuel consumption, likely through a reduction in throttling losses. With DI fueling strategies being relatively new to production engines, further improvements to fuel injection hardware and engine operating strategies may allow for further reductions in particle emissions.
2.2.1. SIDI Operations

In the SIDI engine (also referred to as gasoline direct injection (GDI)), fuel is injected directly into the combustion chamber where it is ignited by a spark plug. The SIDI engine could be considered a cross between a traditional gasoline port fuel injected (PFI) spark ignition, Otto cycle, and a compression ignition (CI), direct injection, Diesel cycle.

The fuel injection systems of early SIDI engines were derived from the basic diesel injection system. For example, the Texaco T CCS engine [9] utilized a diesel-type injector that produced a spray with relatively poor atomization and fuel–air mixing quality, and with high penetration rates relative to sprays from current pressure-swirl atomizers. The Ford PROCO engine [14] used an outwardly opening pintle atomizer with vibration to enhance the fuel atomization; however, the poppet opening pressure was on the order of 2.0 MPa, which is quite low.

SIDI engines can be divided into two different mixture preparation strategy types: stratified charge and homogeneous charge as shown in Figure 2.2. Homogeneous charge refers to a consistently blended, homogeneous, stoichiometric mixture of air and fuel ($\Phi=1$) throughout the combustion chamber. This can be achieved by injecting fuel early in the cycle, during the intake stroke, before compression [13]. The lean burn, stratified charge occurs when fuel is injected late during the compression stroke, resulting in a variable fuel and air mixture throughout the combustion chamber with equivalence ratio ranging $1.5 > \Phi > 0$ (air) at the time of combustion. In this case, the fuel-air mixing time is too short in order for the mixture to become homogeneous throughout the cylinder.
2.3. PM of the Internal combustion engine

2.3.1. Particle Formation Mechanism

PM is defined as all substances, other than unbound water, that are present in exhaust gas in the solid (ash, carbon) or liquid phases. Engine particulates consist of combustion-generated, solid carbon particles, commonly referred to as soot, that result from agglomeration or cracking, and upon which some organic compounds have been adsorbed. The carbon particles become coated with condensed and adsorbed organic compounds, including unburned hydrocarbons and oxygenated hydrocarbons [13], [23], [24].

Internal combustion engines have been identified as a significant source of ultrafine PM. A significant proportion of diesel emissions particles have diameters smaller than 100 nm, whereas particles emitted from gasoline-powered engines are
generally less than 80 nm in diameter. Typically, these particles are a complex mixture of solid and more-volatile particles [5], [13], [25]. Figure 2.3 shows the typical particles.

![Typical particles](image)

Figure 2.3 Some typical particles depicted schematically: coarse mode, nucleation mode, and accumulation mode [24]

The number, size and growth rates of these more-volatile particles depend on variables that affect condensation, such as the dilution rate, temperature, residence time, surface area of pre-existing particles, and humidity [26]. The highest PNs are found in the nucleation mode, with particle diameters smaller than 0.1 µm. However, the percentage of the mass represented by this mode is low (1-20%). Most of the particulate mass is found in the accumulation mode, with particle diameters between 0.1 µm and 1.0 µm. The coarse mode, with particle sizes larger than 1.0 µm, represents 5–20% of the particulate mass, but the particle number in this mode is minor [27].
A number of previous investigators have studied particle formation mechanisms in SIDI engines through both optical techniques and modeling. Moore et al. [20] show that, at advanced injection timing, liquid fuel spray impinges on the piston and the corresponding computational fluid dynamics (CFD) modeling illustrates that liquid fuel accumulation on the piston remains well after the injection event is completed. Sabathil et al. used an optically instrumented spark plug to spatially resolve the regions of soot luminosity in-cylinder. It was found that the regions of soot luminosity correspond to the bowl feature on the piston, agreeing with the findings of liquid fuel accumulation by Moore et al. Thus, fuel spray impinging on the piston during the intake stroke remains in liquid form through the compression stroke and into the combustion event, where fuel-rich pool fires can form particle emissions.

For liquid fuel to survive on the piston post-injection until combustion, the heat transfer to the liquid fuel, in either droplet or liquid film form, is insufficient to fully vaporize the fuel. The heat-transfer requirement is highly dependent upon the oxygen content of the fuel [12]. In general, the average fuel mass injected per cycle for conventional gasoline is 25 mg/stroke. The latent heat of vaporization values for the injected fuel based on Heywood [28] is around 7 Joules.

2.3.2. PM emissions from SIDI engines

Recent studies report that the particulate number (PN) concentration from SI engines increases significantly with high loads, aggressive acceleration and cold start conditions [5], [29].

Much of the research indicates that SIDI engines produce significantly more
particulates than conventional PFI engines, especially during the cold start phase and during stratified operation[13]. Therefore, for the first time a general reduction in the particulate-matter limit for spark-ignition direct injection engines is being combined with plans to introduce a limit on the PN for SIDI engines.

Particles are a result of incomplete combustion and poor mixture formation in the combustion chamber. In particular, fuel wetting of the cylinder wall is mainly responsible for particle formation during the cold start and transient phase in SIDI engines. In addition to optimizing combustion chamber and piston bowl shape, the intake flow motion as well as the fuel injection control strategy must be optimized to avoid wall wetting and to enhance mixture preparation [22].

Various gasoline engine combustion systems were used to identify the impact of advanced engine technologies on PN distributions. Among SIDI vehicles, particle numbers from the lean burn SIDI vehicle were larger than those from the stoichiometric SIDI vehicle. Compared to a DI diesel vehicle without an after-treatment system, the lean burn SIDI vehicle showed a total particle number approximately one tenth of that of the DI diesel vehicle, whereas the PN of the stoichiometric SIDI vehicle was approximately one hundredth of the DI diesel vehicle value [30].

Recent measurements of tailpipe PN emissions show that conventional SIDI light-duty passenger engines cannot comply with a limitation of $6 \times 10^{11}$ #/km. To achieve compliance, two different approaches are feasible: 1) Engine hardware modification and EMS improvement, 2) Exhaust after-treatment with a gasoline particulate filter (GPF) [11], [22], [30].
2.4. Effect of engine operating parameters on the PM emissions

There are many parameters that can be changed in order to alter the performance that in-turn will effect the emissions in a SIDI engine. These parameters include injection timing, spark timing, injection pressure, global A/F, engine load as well as the temperature of the intake air, oil, and coolant. Only the effects of variations in Injection timing, Global A/F ratio and Load are discussed in this section, because of the relevance to this study.

2.4.1. Injection timing

Injection timing plays a significant role in mixture preparation for DISI engines. As described earlier, there are two main mixture strategies: stratified charge (late end of injection (EOI)) and homogeneous charge (early EOI). Homogeneous mixtures allow for high torque and high power output to be achieved. A downfall to homogeneous charge is that since the fuel is injected earlier, there is more time for fuel droplets to interact with the hot wall and enter into crevice volumes, which can potentially increase emissions and soot. During early injection, fuel could also impinge on the surface of the piston forming a fuel film layer which results with an increase in emissions and soot. Homogeneous charge operation also uses more fuel than the lean burn, stratified charge operation.
The results of the EOI changes are shown in Figure 2.4 and are compared to the average baseline data as reported by Farron et al [22]. In general, the lean burn, stratified charge fuel-air mixture is globally lean, but some fuel-rich pockets within the combustion chamber at ignition time are possible, due to the reduction in mixing time in comparison to homogeneous charge. With charge stratification, unthrottled, part-load operation, with equivalence ratio range $\Phi < 1$, high efficiency and low fuel consumption is achieved. With stratified charge, fuel is injected and directed into certain areas of the combustion chamber where the fuel/air concentration is greater at the time of spark. In this case, in comparison to homogeneous charge, less fuel can be used in order to initiate combustion at the time of spark.
2.4.2. Global A/F ratio

The study by Kaiser, et al. [31] included an A/F sweep for a DISI stratified operation with the results shown Figure 2.5. Results from this study are similar to results reported elsewhere [22]. As shown in Figure 2.5, there is a dramatic reduction in CO with increasing A/F while NO\textsubscript{x} and HC increase only slightly, but hover around a constant concentration.

Figure 2.5 Emissions from stratified charge operation for changing A/F [22]
Figure 2.6 Rich and Lean in comparison to the baseline [22]

The particulate size distribution plots for the A/F changes are shown in Figure 2.6. A decrease in A/F allows for an increase in fuel-rich zones in the combustion chamber. A rich mixture around the spark plug at the time of ignition can cause the formation of soot. Fuel film on the cylinder walls from an accumulation of combustion chamber deposit at rich operating conditions can also lead to an increase in soot. An increase in particulate may be observed because of this increase in soot at rich operating conditions.

2.4.3. Load

Injection strategy is dependent upon engine load. As mentioned earlier, at lower loads, lean burn, stratified charge late injection is desired while at higher loads,
homogeneous charge early injection is desired in order to maintain the full use potential for fuel economy benefits.

Engine load also affects the engine emissions. A study performed by Kaiser, et al reveals an increase in particulates with increasing load. It was noted that a significant decrease in HC emissions accompanied by an increase in exhaust gas temperature for increasing load would suggest a more efficient combustion and oxidation in the exhaust, so a lesser particulate production would be expected.

A possible explanation for the increase in particulate production was discussed by Maricq, et al: That particle levels rise instead, suggests that particle formation outstrips their removal. A plausible explanation is as follows: Increasing the load requires the injection of a larger mass of fuel into the cylinder. This reduces the intake temperature and, therefore, lowers the rate of fuel volatilization. Increasing engine speed leaves less time for the fuel droplets to evaporate. As a result, the residual fuel aerosol increases with speed and load, leading to higher PM emissions.

2.5. Effect of combustion processes on soot characteristics

By now it is a common understanding that the combustion process can also influence soot characteristics. The concentration and size distributions of particulate matter are affected by the dilution and cooling of exhaust, air/fuel ratio, and engine type [15]. Using a high temperature tube furnace, Vander Wal et al. [32] showed that the nanostructure of soot depends upon its formation conditions, such as residence time and temperature. Zhu et al. [15] found that the crystallite degree of soot increases with engine load and exhaust temperature. In addition, it is also found that soot particle size tends to
decrease when the exhaust temperature increases because of particle oxidation at high temperature. Nevertheless, Neer et al. [17] observed an increase in soot spherule and aggregate sizes with an increase of the engine load and exhaust temperature. This observation was explained by the impact of the change of the air/fuel ratio. Meanwhile, it is also observed that soot particles are smaller at higher engine speed because of the shorter residence time. Aside from these two studies, the spherule data in the literature are rather scarce and, if available, only for diesel engine conditions [33]. Far less studied are soots from SIDI engines [11].

2.6. Summary of Literature

Currently there is little information available about particulates in the exhaust of a SIDI engine, and how the particulates react to changing operating conditions is unknown. Measuring the number of particles is far more complicated than measuring the mass, since particles undergo processes such as deposition, mutation, particle-to-gas conversion, etc. during the exhaust process, which could then lead to a dramatic change in their total number. Various number-based particulate measurement instruments are commercially available as research tools. However, valid measurement requires in-depth knowledge of numerous experimental variables with the central objective being that the results should be representative of real exhaust particulate emission. It is also desirable to resolve the composition and the morphology of the particulate emission, which could enable researchers to model the formation of particulate matter and to understand the impact on health and environmental consequences.
Chapter 3

EXPERIMENTAL

3.1 Technical approach

The objectives undertaken in this study include the following: (1) To examine the impact of engine operating conditions in a Spark Ignited, direct injection engine with regards to physical and chemical measures; (2) Comparison of the diagnostic techniques used to accomplish objective 1; (3) Comparison of spark ignited, direct injection gasoline driven engine to a medium duty diesel engine of different size class, for similarities and differences. To achieve these objectives, soot samples were generated from different combustion systems under different conditions and analyzed by a variety of techniques. This section provides the experimental details.

All the experiments that involve SIDI engine were performed in the General Motors (GM) and University of Wisconsin Collaborative Research Laboratory (CRL) of the Engine Research Center (ERC) in room B131 of the Engineering Research Building, University of Wisconsin, Madison. This laboratory contains four different research engines; one of the four was used for these experiments mentioned in this document. The Diesel engine experiment, a PNNL-led field campaign was carried out at Michigan Technological University, Michigan.

With the first objective being to examine the impact of engine operating conditions in a SIDI engine. This involves examining the features, which could give clues
to particulate formation processes, features, which could effect filtration mechanics, and features, which may be relevant to oxidation kinetics and filter regeneration. Towards the first objective, soot samples were collected from a SIDI engine at different operating conditions. Microscopic and spectroscopic techniques were applied including high-resolution transmission electron microscopy (HRTEM) with subsequent image processing for morphology, size and nanostructure, X-ray photoelectron spectroscopy (XPS) for surface composition and chemical bonding, Fourier Transform Infrared Spectroscopy – Attenuated Total Reflectance (FTIR-ATR) for organic content. To determine the impact of engine operating conditions on soot properties such as soot reactivity, nanostructure, composition and surface functional groups, soot samples were collected under five diverse operating conditions. Towards the second objective, the above-mentioned characterization techniques were thoroughly compared.

Towards the third objective soot samples were collected from a medium duty diesel engine. The diesel engine itself was a Cummins 365 ISL engine, which has a horsepower about ten times greater than the gasoline driven engine used here. Nevertheless the comparison is more inclined towards the physical structure.

3.2 Particulate Sampling

The sampling manifold, which consisted a custom-made Swagelok Tee, provided for direct collection of soot upon a TEM grid for some samples at each operating condition and with respective fuels. The key advantage here is soot is directly collected from the aerosol phase. For the gasoline engine experiments, soot is directly collected on the TEM grid thereby bypassing filter collection and therein the need for re-dispersal
upon a TEM grid. Such processes are known to cause agglomeration of soot aggregates thereby obscuring individual aggregate recognition. For better HRTEM analysis, sampling was done on lacy carbon grid. Further details of the TEM grid holder and its insertion into the sampling probe exhaust stream have been documented and will be published elsewhere [34].

XPS and FTIR-ATR samples were collected using 400 mesh Au grids. Once sampling is complete, gold grids with sample deposited are directly analyzed by XPS and FTIR-ATR respectively. Gold grids are advantageous for such use as a) they are inert towards carbon (as opposed to an active transition metal), b) the Au core shell energies are well shifted from those of carbon and other light elements, thereby imposing no interference in the XPS scans and c) they are readily cleaned prior to use. For the diesel engine experiment, DPF cores were loaded with soot from each of the three fuels by connecting them to available ports before and after the diesel oxidation catalyst (DOC). These units were inline with, and downstream of the TEM sampling unit.

A valve upstream of the TEM sample holders permitted isolation of these units until the exhaust stream for the test condition of interest had cleared the line. By this user-defined, manual operation, samples were collected for a time somewhat shorter than the nominal test duration. Sample holders were periodically cleaned by a combination of wiping and swabbing with commercial grade rubbing alcohol. Multiple units allowed for pre-loading of TEM grids and gold coated screens for rapid insertion between test points as the engine was ramped up and down in power. With the primary emphasis being upon microscopy, partial or complete series sample sets as a function of engine operating
condition were obtained for EPA Tier II EEE fuel in the gasoline engine and for ULSD fuel in diesel engine experiment.

3.3 Gasoline Engine Experiment

3.3.1 Gasoline direct injected Ricardo Hydra single cylinder engine

The engine is a single-cylinder, four-stroke engine that is built into a Ricardo Hydra block with a machined cylinder liner and an aluminum cylinder head provided by GM. The head has a four-valve, pentroof design with ports for an in-cylinder fuel injector, a spark plug, and two in-line side-mounted ports within the clearance volume— one is used for the in-cylinder pressure transducer and the second is plugged but can be used for optical access. The spark plug is centered about the four valve ports, the pressure transducer is located on the side between the intake and exhaust valve ports, and the fuel injector is positioned between the intake valve ports. This can be seen in Figure 3.1

Figure 3.1 Top view of SIDI research engine used in this research
Engine technical specifications including dimensions and valve timing data are given in Table 3.1. More details of the engine mechanical systems can be found at [22].

<table>
<thead>
<tr>
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<td>Displacement [in³, cm³]</td>
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<td>Clearance Volume [in³, cm³]</td>
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<td>Connecting Rod Length [in, mm]</td>
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<tr>
<td>Exhaust Valve Lift [mm]</td>
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</tbody>
</table>

### 3.3.2 Experimental Setup

Figure 3.2 is the schematic of the experimental setup on site. During the campaign, the experiments were conducted on PM emissions as produced by a “gasoline direct injection Ricardo hydra single cylinder engine”. The sample probe rake at the exit of the engine and downstream manifold systems were connected by ¼” stainless steel tubing, each covered by insulating material to avoid water condensation.
The sampling manifold and associated custom holder provided for direct collection of soot upon a TEM grid for each engine operating condition. The soot sampling system was designed with four individual ports for simultaneous sampling on 4 different but separate grids. Each individual sampling port contains a modified Swagelok tee that held a TEM grid within a folded brass clip. For each test condition, samples were collected on all four grids, two being Lacy carbon and 2 bare gold mesh grids. These latter provided sample collection for later XPS analysis.

The PM sampling sequence and durations were dictated by a pre-planned sequence of engine operating conditions. The objective of the campaign was to sample PM from the SIDI engine for two days. Day 1 was dedicated for collecting samples at 5 different operating conditions that include Baseline, Rich, Lean, Late End-Of-Injection
(EOI) (-220°ATDC) and High load. Day 2 was dedicated for collecting PM at additional points along the EOI sweep and spark advance (MBT-15 degrees).

3.3.3 Engine operating conditions and fuel injection parameters

To determine the baseline injection timing, the engine was run at randomly chosen EOI timings to eliminate any hysteresis effects, i.e. the first run had an EOI time of 340 [°bTDC], then at 240 [°bTDC], 290 [°bTDC], etc. For this experiment, the AVL Smoke Meter was used, and data was recorded at each injection time. Since the smaller amounts of smoke indicate a more desirable baseline operating condition, it is determined that the baseline injection time should be set between EOI 270 and 300 [°bTDC]. From this, the baseline EOI time was chosen to be 280 [°bTDC], which was also suggested by GM.

Figure 3.3 Spray targeting diagram – EEE Injection timing
Shown in Figure 3.4 is the spray-targeting diagram, specifically the Injection timing for the standard EEE fuel is shown. Once the baseline operating condition was established, a number of other operating conditions were chosen as deviations from the baseline to investigate the sensitivity of particulate sizing, aggregate morphology, presence of organics to changes in engine operating conditions. As shown in Table 3.2, the defined operating conditions include variations in injection timing, fuel quantity, A/F, spark time, injection pressure, and temperature of coolant and oil to simulate a hot operation and a cold start operation. Each of these operational changes and their effects on emissions were discussed in Chapter 2.

Table 3.2 Validation matrix

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### 3.3.4 Test fuel

The current work was carried out using the standard EPA tier II EEE gasoline. The Tier 2 Vehicle and Gasoline Sulfur program is part of a series of major initiatives taken by the Environmental Protection Agency (EPA) that will reduce emissions from passenger vehicles, highway trucks and buses, and non-road diesel equipment. The
program grew out of a Clean Air Act requirement that EPA consider the need, feasibility, and cost-effectiveness of stronger tailpipe emission standards beginning in 2004. Table 3.3 lists the physical properties of the test fuel obtained from a U.S. refinery.

Table 3.3 Physical properties of tested fuel [35]

<table>
<thead>
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<th>Property</th>
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<td>Research Octane Number</td>
<td>97.2</td>
</tr>
<tr>
<td>Motor Octane Number</td>
<td>88.4</td>
</tr>
<tr>
<td>LHV [MJ/kg]</td>
<td>42.89</td>
</tr>
<tr>
<td>Density (293 K) [kg/L]</td>
<td>0.744</td>
</tr>
<tr>
<td>Boiling Point [K]</td>
<td>T10 = 326</td>
</tr>
<tr>
<td></td>
<td>T90 = 434</td>
</tr>
<tr>
<td>Heat of Vaporization (289 K) [kJ/kg]</td>
<td>~349</td>
</tr>
<tr>
<td>Reed Vapor Pressure (311K ) [kPa]</td>
<td>61.3</td>
</tr>
<tr>
<td>H/C [mol/mol]</td>
<td>1.88</td>
</tr>
<tr>
<td>O/C [mol/mol]</td>
<td>0</td>
</tr>
<tr>
<td>Stoich A/F</td>
<td>14.57</td>
</tr>
</tbody>
</table>

3.4 Diesel Engine Experiment

3.4.1 Cummins ISL Engine Soot

A Cummins ISL 365 bhp engine, 2100 rpm and 195 Nm, 6-cylinder diesel engine that was brought to steady state operating conditions was used. The test engine has a diesel particulate filter (DPF) fitted. The main engine characteristics are shown in Table
3.4. Powder PM after burning ULSD fuel was collected in original equipment from manufacturer (OEM) diesel particulate filter (DPF).

Table 3.4 ISL Cummins Engine characteristics

<table>
<thead>
<tr>
<th>Engine Parameter [units]</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Horse Power [HP]</td>
<td>365</td>
</tr>
<tr>
<td>Peak Torque [lb-ft]</td>
<td>1250</td>
</tr>
<tr>
<td>Governed Speed [RPM]</td>
<td>2100</td>
</tr>
<tr>
<td>Number of Cylinders [-]</td>
<td>6</td>
</tr>
<tr>
<td>Oil System Capacity [US Gallons]</td>
<td>7.3</td>
</tr>
<tr>
<td>Clutch Engagement Torque [lb-ft]</td>
<td>550</td>
</tr>
</tbody>
</table>

3.4.2 Experimental Setup

As mentioned earlier, the Diesel engine experiment, a PNNL-led field campaign was carried out at Michigan Technological University, Michigan. Thee samples were provided by them (PNNL) wherein I did all the analysis.

Figure 3.3 is the schematic of the DOC with available ports for collecting powder sample; it also displays the naming convention for sample ports used from which samples were collected. The raw exhaust emissions sampling is done at sampling ports P1, P2 and P3. After this the emissions pass through the DOC and are then sampled at ports P4, P5 and P6 after the DOC. DPF cores were loaded with soot from ULSD fuel by connecting them to available ports before and after the diesel oxidation catalyst (DOC).
Figure 3.4 Available ports before and after DOC

P1, P2, P3 refer to ports before the exhaust being passed through the DOC. P4, P5, P6 refer to ports that collect the sample which pass through the DOC and treatment process. TEM grids were used to collect small amounts of PM from each of the three fuels before and after the DOC. Table 3.5 show the summary of flow rates, temperature, and other test cell conditions.

Table 3.5 Summary of tested fuels, temperatures, flow rates and test cell conditions

<table>
<thead>
<tr>
<th>Test Fuel</th>
<th>Load Time</th>
<th>Inlet Temp ($^\circ$C)</th>
<th>Exhaust Flow Rate (LFE)</th>
<th>PM Conc.</th>
<th>Test Cell</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Minutes</td>
<td>DOC</td>
<td>CPF</td>
<td>Mass kg/min</td>
<td>Volumetric scm/s</td>
</tr>
<tr>
<td>ULSD</td>
<td>277.9</td>
<td>263</td>
<td>258</td>
<td>12.6</td>
<td>0.173</td>
</tr>
</tbody>
</table>
Appendix A summarizes the test emissions of the Cummins ISL engine for three different fuels ULSD, B10 and B20 respectively. Emissions are classified into four different categories: (1) Unburnt Hydrocarbons (UHC’s), (2) NOx, (3) NO and (4) NO2. Emissions were monitored before DOC, after DOC and at DPF and are tabulated in parts-per-million (ppm).

3.4.3 Test Fuel

Table 3 summarizes the composition by chemical class of the fuels tested in the Cummins ISL engine. The environmental Protection Agency (EPA) has established a comprehensive program to lower the combustion emissions from diesel engines [32], [36]. As a part of this federally mandated program, vehicles for highway use were required to use ULSD by June of 2006. ULSD is defined by the EPA as diesel fuel having a sulfur content that is equal to or less than 15 parts per million (ppm). Table 3.7 lists the physical and chemical properties of the ULSD fuel obtained from a U.S. refinery.

<table>
<thead>
<tr>
<th>Property</th>
<th>ASTM Method</th>
<th>ULSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cetane number</td>
<td>D 613</td>
<td>42</td>
</tr>
<tr>
<td>Aromatics, vol%</td>
<td>D 1319</td>
<td>25</td>
</tr>
<tr>
<td>Saturates, vol%</td>
<td>D 1319</td>
<td>74</td>
</tr>
<tr>
<td>Olefins, vol%</td>
<td>D 1319</td>
<td>2.0</td>
</tr>
<tr>
<td>Sulfur, ppm (wt.)</td>
<td>D 5453</td>
<td>1</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>D 4052</td>
<td>0.8</td>
</tr>
<tr>
<td>Flash Point, 0°C (min)</td>
<td>D 975</td>
<td>38-52</td>
</tr>
<tr>
<td>Kinematic Viscosity, 40 °C</td>
<td>D 445</td>
<td>2.5</td>
</tr>
</tbody>
</table>
The standards by which the fuel properties in Table 3.7 were measured are also included. Among the three different test fuels (ULSD, B10 and B20), ULSD was used as the reference fuel in this study.

3.5 Characterization method

3.5.1 Transmission electron microscopy (TEM)

To perform different levels of image analysis that include macro- (aggregate), micro- (primary particle) and nano-scale (nanostructure), a 200-kV field-emission TEM (JEOL EM-2010F) was used to take high-resolution bright field images. Some of the initial TEM images were taken using a Philips (FEI) EM420T (Tungsten Emitter) having a point-to-point resolution of 0.34 nm. The instrument was operated at 120 keV. Depending on the soot samples and the analysis, the applied magnifications varied between 40k and 500k. For every analyzed sample, images of soot aggregates at more than twenty locations were recorded.

Digital images that are acquired by the Gatan image software are subsequently processed using custom algorithms developed in-house by Dr. K. Yehliu, coded with Matlab software, a product of Math Works, Inc., Natick, MA [Ref – Kuen’s thesis]. Soot nanostructure (as characterized by the metrics of fringe length, tortuosity and separation space) was investigated in a comprehensive way by using the nanostructure analysis algorithms. For each sample, 3-5 grid openings were surveyed to verify reasonable uniformity of coverage. Periodic images at lower magnifications were collected as documentation of such but not for further analyses. In selected areas of each examined grid square 6-8 images of soot aggregates with clear configuration of graphene layers
were selected from all the recorded images for the above mentioned image analysis. For illustration purposes, representative images are shown. Analysis results were exported for subsequent plotting and statistical analyses to the program Kaleidagraph™, a product of Synergy software, Reading, PA. Histograms summarizing the distributions of primary particle size, fringe length, and fringe tortuosity were fitted to a lognormal density function with mean and standard deviation as the two adjustable parameters.

\[
f(x) = \frac{1}{x\sigma_y\sqrt{2\pi}} \exp \left[ -\frac{1}{2\sigma_y^2} (\ln x - \mu_y)^2 \right]
\]  

(3.1)

Where, \( \sigma_y = \) True mean \( \mu_y = \) Varience

### 3.5.2 X-ray Photoelectron Spectroscopy

The surface chemical compositions, chemical bonding and oxygen containing functional groups on the soot surface were investigated by X-ray Photoelectron Spectroscopy (XPS). The XPS spectra were recorded in an Axis Ultra from Kratos Analytical using a monochromatic Al-\( \text{K}\alpha \) (1486.6 eV) X-ray source operated at ultra high vacuum conditions (10\(^{-8}\) bar). The instrument is capable of detecting elements Li-U. The analyses area is roughly 1mm x 1.5 mm, and the sample surface was oriented normal to the analyzer entrance. The pass energy was set at 80 eV for survey scans, and 20 eV for high resolution scans. The instrument sampling depth varied between 0 – 10 nm with a sensitivity of 0.01 – 0.5% (atomic).

High-resolution multi-plex scans were run for carbon. The resultant high-resolution C1s peak was processed by commercial software CASA XPS. A Shirley background was subtracted from the high-resolution spectra. Then, the corrected spectra were curve fitted for possible elements (e.g., carbon 1s: 282-296 eV, oxygen 1s: 525.540
eV). Peak assignments are indicated in the individual spectra, allowing for shifts due to sample charging. Further details on the deconvolution procedure have been reported elsewhere [37], [38]. The software thereafter estimated the element percentages. In this study, the XPS spectra of all the PM samples mostly contain carbon and oxygen, and do not show any significant amounts of metal elements.

3.5.3 Fourier transform infrared spectroscopy – Attenuated total reflectance (FTIR-ATR)

Attenuated Total Reflectance (ATR) FTIR investigates the presence of functional groups throughout the particulate volume (as opposed to a surface measurement). The analyses were performed by a Hyperion 3000 FT-IR Microscope, which has the capability of analyzing very small (>10 µm) samples with diffraction limited spatial resolution. The 128 x 128 element focal plane array detector enables diffraction-limited mid-IR imaging of areas as large as 340 x 340 µm. For testing the soot samples a 20x Attenuated Total Reflectance objective, which has a Ge crystal with 80-µm diameter contact surface is used. The soot samples examined were those as directly collected upon the Au wire mesh.

ATR developed simultaneously and independently by Harrick and Fahrenfort, is a type of internal reflection spectroscopy in which the sample is placed in contact with an internal reflection element (IRE) of high refractive index. Infrared radiation is focused onto the edge of the IRE, reflected through the IRE, and then directed to a suitable detector (see Figure 3.5).
Figure 3.5 Schematic diagram of a horizontal ATR sampling accessory illustrating the parameters of significance to spectral acquisition (I = incident radiation; R = reflected radiation) [39]

Although complete internal reflection occurs at the sample/IRE interface, radiation (the evanescent wave) penetrates a short distance ($d_p$) into the sample (depending upon the wavelength, $\lambda$, of the incident light), where it can be absorbed. An absorption spectrum of the sample in contact with the IRE can thus be obtained, the spectrum being dependent upon a number of parameters including angle of incidence ($\theta$) and the refractive indices of the IRE material ($n_1$) and the sample ($n_2$), respectively (Eq. (3.2)). The penetration depth is defined as the distance required for the amplitude of the electric field to fall to e-1 of its value at the surface

$$d_p = \frac{\lambda}{2 \pi n_1 \sqrt{\sin^2 \theta - \left(\frac{n_2}{n_1}\right)^2}} \quad (3.2)$$

The incident infrared light passes through the optically denser IRE and reflects at the surface of the sample. The propagating light passing through the IRE (an optically thin, non-absorbing medium) then forms a standing wave perpendicular to the total reflecting surface. Thus, if the sample absorbs radiation, the propagating wave interacts with the sample and becomes attenuated.

The resultant spectrum was processed by OPUS 6.0 software. In this study, the FTIR results were qualitatively based on the band assignment of oxygen-containing functional groups summarized in Table 3.7.
### Table 3.7 Functional groups on soot and their corresponding FTIR band assignments

<table>
<thead>
<tr>
<th>Type of Vibration</th>
<th>Frequency cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO(_2)</td>
<td>From ambient lab environment</td>
</tr>
<tr>
<td>O - H</td>
<td>H(_2)O and carboxylic acid</td>
</tr>
<tr>
<td>C - H</td>
<td>Stretching mode in aromatic and aliphatic groups</td>
</tr>
<tr>
<td>C = O</td>
<td>Stretching mode in lactone, carboxylic and ketone groups</td>
</tr>
<tr>
<td>C = C</td>
<td>Stretching mode in aromatic group and quinones</td>
</tr>
<tr>
<td>C - H</td>
<td>Stretching mode in aliphatic group</td>
</tr>
<tr>
<td>C-O-H</td>
<td>C-O-H bending and stretching</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>Asymmetric stretching</td>
</tr>
</tbody>
</table>

### 3.5.4 Thermogravimetric analysis (TGA)

A thermogravimetric analyzer with recording software was used to estimate the degree of partial burnout. The TGA instrument itself was a TA instruments make. The system had a horizontal furnace and balance design with a dual beam balance. The maximum sample capacity of the instrument was 200 mg. The sample pans used here for the experiments are made from Alumina.

The TGA analyzer was used to oxidize the soot that is deposited on a Gold grid. The instrument was operated at a ramp rate of 10 °C/min until it reached 550 °C, once the desired temperature was reached; the system was set to cool down. The entire system was
under the air environment until the temperature reached 550 °C, once after the set point is reached Nitrogen was pumped as opposed to air to make it sure that there were no reactions occurring.
Chapter 4

SOOT CHARACTERIZATION METHOD

Four characterization techniques have been discussed in section 3.5: (1) Transmission electron microscopy (TEM), (2) X-ray photoelectron spectroscopy (XPS), and (3) Fourier transform infrared spectroscopy – Attenuated total reflectance (FTIR-ATR). Among the four techniques, the data from XPS was post-processed by commercial software, and the analytical methods are referred to those described in [37], [38]. Additionally, because the spectra of FTIR were merely interpreted in a qualitative manner, the FTIR data analysis is not explained further. Therein, this chapter describes the methods for analyzing TEM data in this study.

4.1. Transmission electron microscopy image analysis

In this study, in order to examine the physical and structural characteristics of the engine soots, analyses have been performed at different length scales. Physical measures of interest include (1) aggregate morphology, (2) primary particle size distribution, and (3) internal nanostructure.

The post-combustion significance of each of these physical measures is: (1) macrostructure gives information on soot aggregate morphology which is a record of primary particle density and the local concentration of growth species, (2) microstructure dictates the surface area available for heterogeneous chemistry followed by understanding coalescence relative to primary particle growth, and (3) nanostructure is convolved with soot chemistry and understanding the oxidation characteristics. The
image analysis at these length scales can be divided into three individual comprehensive matrices that include (1) macrostructure, (2) microstructure, and (3) nanostructure.

4.1.1. Macrostructure

As explained in the above section 4.1 macrostructure is a term that is used to describe or refer to soot morphology. It provides a record of primary particle coalescence. Aggregate morphologies can provide insight into primary particle density, which in turn depend upon initial local concentration of soot growth species. In this study, in order to examine the aggregate morphology we have compared various parameters that include roundness, aspect ratio, compactness, root form factor, and fractal dimension. The freeware/shareware software package ImageJ, a program developed by the National Institute of Health was used for the analysis. ImageJ was designed with an open architecture that provides for expansion via Java plugins and recordable macros via a built-in editor and compiler for image acquisition, analysis and processing.

Fractal dimension is one another way of generating information on aggregate morphology. Root form factor is descriptive of boundary irregularity, smaller numbers indicate more irregularity. The root form factor (RFF) [40] is a morphologically sensitive geometric measure, much more so than the nominal fractal dimension. Russ, introduced Root form factor in his book on “The image processing handbook, 1999”. Later on, Gary Chinga developed a plugin for ImageJ that can calculate shape descriptors that include root form factor. In real terms root form factor is the ratio of

\[ \text{Root form factor} = \sqrt{\frac{4\pi \cdot \text{Area}}{(\text{perimeter})^2}} \]
In this section, the steps for examining the root form factor using the shape descriptor plugin are discussed. Subsequently, the flowchart for calculating the shape descriptors (root form factor specifically) is given.

Figure 4.1 shows the structure of the shape descriptors algorithm. The algorithm steps consist of: (1) processing of the HRTEM images, setting the calibration, region of interest (ROI) selection, outlining the aggregate, thresholding for binarization, binarized image being further evaluated by the shape descriptors plugin in ImageJ, and finally generating shape descriptors (root form factor, aspect ratio, roundness, compactness) data into spreadsheet.

Figure 4.2 is more intuitive with the screen shots of images at various stages as explained above. The same method is repeated for multiple images, to demonstrate consistency of results and validate the statistics.
Figure 4.1 Flow chart of the shape descriptors plugin used to examine root form factor
Figure 4.2 Illustration of image enhancement and processing steps
The root form factor calculated from the above image processing steps is evaluated as a measure of the irregularity of the soot aggregate. Another measure, the Fractal Dimension (Df) is also examined as a different measure of morphological irregularity. It serves as a benchmark by which to gauge the RFF as an alternative metric. As results will show, the RFF provides a more sensitive geometric measure of morphology than the traditional fractal dimension.

4.1.2. Microstructure

Soot microstructure pertains to the surface area available for heterogeneous chemistry. In the combustion process general aerosol dynamics control the coalescence timescale relative to primary particle growth: (1) Early coalescence followed by growth leads to virtually unrecognizable primary particles, and (2) Late coalescence relative to primary growth leads to distinct primary particles. Therein the degree of particle fusion or merging between primary particles provides a clock of growth relative to coalescence times. With regards to post-combustion oxidation, primary particle size is of interest as it can provide an estimate of available surface area for oxidation.

This study involves measuring primary particle sizes of a diesel and gasoline engine for both purposes. Given the new engines and fuels, unknown was the sensitivity of particulate number distribution to changes in engine operating conditions and fuel type. ImageJ was applied to evaluate the primary particle sizes. Figure 4.3 shows the structure of the primary particle distribution flowchart. The flowchart consists of two major subroutines: (1) processing of the TEM images with ImageJ, setting the calibration, measure the diameter of primary particles from each TEM image with the measure tool,
generating statistics, saving the data into a spreadsheet file; and (2) exporting the data into Kaleidagraph\textsuperscript{TM}, binning the data, plotting the histograms, applying log-normal curve fitting, and saving the data.
For primary particle distribution analysis, more than 15 images from different locations in the grid are selected for analysis. Each image is individually analyzed and the
data is saved. Finally all the data is brought up together into one individual spreadsheet file, followed by binning the data, plotting and applying lognormal distribution.

4.1.3. Nanostructure

Nanostructure is convolved with soot formation chemistry and can be used to understand the oxidation characteristics. As a concept it refers to the detailed arrangement of carbon lamella within carbons, here specifically engine produced soot. An analytical method was implemented for quantitatively analyzing the TEM images of soot particles. The details of the method can be found in [41–43]. The method is composed of two major parts: digital image processing and lattice fringe characterization. In order to examine the nanostructure, the fringe analysis code developed by Dr. Kuen Yehliu using MATLAB (a product of The Math Works Inc., Natick, MA) was applied [67]. The code involves two major parts (1) Digital image processing composed of following operations: negative transformation, region of interest (ROI) selection, contrast enhancement, Gaussian low pass filter, top-hat transformation, thresholding to obtain a binary image, morphological modification, clearing fringes on the ROI border, skeletonization, and removing short fringes that lack physical meaning; and (2) Fringe characterization generates statistics on fringe length, fringe tortuosity, and fringe separation based on the skeletons of the graphene layers. Fringe tortuosity and fringe length are obtained automatically from the features of the skeletons, while fringe separation permits the user to manually select fringe pairs. Further details have been published elsewhere [42].
Figures 4.4 and 4.5 shows the detail step-by-step process for examining the nanostructure involving fringe analysis. Figure 4.4 shows the flowchart of TEM image processing by MATLAB software. The output of image processing is a binarized image, which can be further processed for fringe characterization.

(1) Main TEM image processing, MATLAB

Figure 4.4 TEM Image processing, MATLAB
Figure 4.5 Fringe characterizations, (a) Fringe length and tortuosity analysis, (b) Fringe separation analysis, and (c) Histogram generation and data output, Kaleidagraph™
Figure 4.5 illustrates three individual subroutines for fringe characterization. (a) fringe length and tortuosity analysis, by loading the binarized image, followed by obtaining the statistics and plotting them; (b) fringe separation by loading the binarized image, manually selecting fringe pairs with further data processing and plotting; and (c) loading all the data into Kaleidagraph™ for fitting and presentation.
Chapter 5

RESULTS AND DISCUSSION

5.1. Impact of operating conditions on the size, morphology and nanostructure of particulates emitted from a gasoline engine

5.1.1. Impact of operating conditions on the size

The gasoline particulates that were collected using a sampling manifold and associated custom holder provided for direct collection of soot upon a TEM grid for each operating condition were thoroughly analyzed by a TEM. As explained previously this bypasses filter collection and therein the need for re-dispersal upon a TEM grid. Sampling has been done at five different operating conditions and the results are presented for the same.

Typical TEM images emitted from a SIDI engine are shown in the figures 5.1 to 5.5. The sampling was done at 100% load (2100 rpm). For rational comparison, all the images were taken at a magnification of 40,000x, while the sampling times were identical. Three essential features of gasoline engine soot emissions can be noticed from the TEM images, which are similar to TEM observation [5], [11], [22] in other gasoline engines. First, there is a large variation in overall aggregate primary particle sizes. Second, aggregates had different shapes with compact, clustered structures. Third, more particles deposited onto a grid as the fuel loading increased. The higher grid loading was due to the injection of more fuel into the combustion cylinder at the same engine load
which, in turn, enhanced the rate of soot formation and therefore particle production. Higher fuel to air ratio also results in the acceleration of the agglomeration process.

![Figure 5.1 TEM images of gasoline particulates sampled at Late End of Injection (220°bTDC) (magnification of 40,000x)](image)

The images in Figure 5.1 have mostly clearly defined primary particles with an open, branched and chain-like structure. There is certainly aggregate – aggregate agglomeration. This operating condition showed the lowest primary particle size which was estimated to be 16.2 nm.
Figure 5.2 TEM images of gasoline particulates sampled at Rich (A/F-13) (magnification 40,000x)

The images in Figure 5.2 look highly compact. Under rich conditions the aggregates are much more compact, presenting a denser cluster. Governing the compactness are 2 factors: a) spatial particle or seed nuclei density and b) rate of concurrent/subsequent surface mass growth upon particles. Both factors will be higher under fuel-rich conditions. The average primary particle size (diameter) was estimated to be 18.6 nm.
To the extent that growth occurred following nucleation and particle coalescence, a high degree of fusion is observed between primary particles as evident in Figure 5.3. The average primary particle size (diameter) was estimated to be 20.9 nm.
The TEM images in Figure 5.4 show better visualization of primary particle size variation. The images have more clearly defined primary particles than observed before. The average primary particle size was estimated to be 23.4 nm.
Figure 5.5 TEM images of gasoline particles sampled at High Load (fuel quantity - 21 mg/cycle) (magnification of 40,000x)

Perhaps the largest variation of primary particle size, certainly within an aggregate is shown by the images in Figure 5.5 for the High Load operating condition. For high load, being fuel-rich, this would be not typical of diesel engine particulate, either in terms of aggregate morphology or variation of primary particle size range. The average particle size is estimated to be 24.6 nm.
Figure 5.6 Primary particle size distributions that are lognormally fitted at different operating conditions (a) Late EOI (16.2 nm), (b) Rich (18.6 nm), (c) Baseline (20.9 nm), (d) Lean (23.4 nm), and (e) High Load (24.6 nm)
The images in Figures 5.1 to 5.5 identify the detailed structure of a typical gasoline particulate. The images indicate soot aggregation under different operating conditions in a SIDI engine, show more variation in primary particle size than is typical for diesel PM [16],[19]. As can be seen, many spherical primary particales collected to form clusters (aggregates) of fractal like geometries. Primary particles have nearly uniform diameters, in contrast to aggregates, which appears to have a broad size distribution.

Figure 5.6 illustrates the primary particle distributions of the gasoline particulate matter collected at different operating conditions which include Late EOI, Rich, Baseline, Lean and High Load. Primary particles with unclear boundries due to overlapping at the aggregate cores were omitted to minimize experimental error and estimation. As mentioned in the chapter 4, all the images are processed using ImageJ and the saved data is further analyzed using Kaleidagraph™ for statistical analysis. Data is binned, particle size (nm) is plotted against relative frequency (of 100-200 primary particles) yielding a histogram. Uncertainties in primary particle size measurements were largely due to problems with identifying particle borders.

Standard deviations of primary particle diameters, $\sigma_p$, were 15-30% of the mean values, exhibiting no specific trend with respect to engine condition. By long-standing precedence, a Lognormal pdf was applied for representing primary particle size distributions. This is illustrated for all operating conditions in Figure 5.6. Although there the distributions differed somewhat from lognormal, this can be due to the limited number of primary particles considered for each condition.
The arithmetic mean $\bar{x}$ is easy to compute. Furthermore, it is a statistically unbiased estimator of $\mu$ no matter what the underlying distribution may be (normal, lognormal, Weibull, etc.). If the underlying distribution is normal, it is also the Minimum Variance Unbiased (MVU) estimator of $\mu$. Unfortunately, $\bar{x}$ does not have this MVU property when the underlying distribution is lognormal. Also, $\bar{x}$ is highly sensitive to the presence of one or more large data values. Nevertheless, even when the underlying distribution is lognormal, $\bar{x}$ is probably the preferred estimator if the coefficient of variation $\eta$ is believed to be less than 1.2 (a rule suggested by Koch and Link, 1980). The goodness-of-the-fit was examined by the D’Agostino’s test, which is illustrated in Appendix B.

A T-test is performed to check if the mean primary particle sizes across the range of conditions is significantly different or not. From the two distributions (as shown in the Appendix C) for the two different test conditions – the distributions are seemingly similar but somewhat different distributions. Are they statistically different or not? The calculated $t$ was extreme thereby rejecting the null hypothesis suggests that there is a significant difference for the means calculated across the range of conditions.

At each engine operating condition, the measured distribution was averaged to calculate mean primary particle diameter, within an experimental uncertainty of less than 10%. The number averaged primary particle diameter ($d_p$) ranged from 16.1 nm and 24.6 nm across all engine conditions, the same can be inferred from Table 5.1. This is the first direct measurement of primary particle sizes for a spark ignited –direct injection particulates, comparative literature data on primary particle size appears unreported but for one [11]. Hence reference is mostly made to far better know diesel engine produced
soots. The diameters appeared to be smaller than those typically reported for diesel engine particulates (28 – 35 nm) [1], [15–17], [44].

Figure 5.7 Comparison plots showing consistent average particle diameter on Y1-axis and operating condition on X-axis, which are compared to (a) Fuel Quantity, (b) Spark Advance, (c) Air / Fuel ratio, and (d) Exhaust Temperature on the Y2-axis.

The effect of engine operating condition on the average primary particle diameter at the exhaust of the present gasoline engine was investigated. Although the combustion flow, and particulate processes within the engine cylinders are quite complex, general emission trends were realized when operating condition and averaged particle diameter
(nm) were plotted as a function of fuel quantity (mg/cycle), spark advance (\(^\text{0}^\circ\text{bTDC}\)), and A/F ratio in Figure 5.7.

With but two exceptions, mean primary particle diameters increased with engine load. Many correlations were tested with fuel quantity, spark advance and A/F ratio. Table 5.1 gives a comprehensive data for the same. For various operating conditions, primary particle size increased with increase in fuel quantity and decreased with spark advance before piston top-dead-center. There was no trend observed for changes to A/F ratio.

Table 5.1 Engine operating conditions and particulate measurement data

<table>
<thead>
<tr>
<th>Operating Condition</th>
<th>Average particle diameter (nm)</th>
<th>Fuel Quantity (mg/cyc)</th>
<th>Spark Advance (0(^{\circ})TDC)</th>
<th>A/F ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Late EOI</td>
<td>16.17</td>
<td>11</td>
<td>25</td>
<td>15</td>
</tr>
<tr>
<td>Rich</td>
<td>18.58</td>
<td>11</td>
<td>25</td>
<td>13</td>
</tr>
<tr>
<td>Baseline</td>
<td>20.87</td>
<td>11</td>
<td>25</td>
<td>15</td>
</tr>
<tr>
<td>Lean</td>
<td>23.37</td>
<td>11</td>
<td>25</td>
<td>17</td>
</tr>
<tr>
<td>High Load</td>
<td>24.6</td>
<td>21</td>
<td>18</td>
<td>15</td>
</tr>
</tbody>
</table>

It was expected that the higher load case would produce more soot and emissions due to the increased amount of fuel injected per cycle, based on the study from Maricq, et al [45], [46]. The results of the primary particle size distribution are shown in Figure 5.6 (e). The high load engine operating conditions do, in fact, produce larger primary particulates in comparison to the baseline. High load condition may show some of the most variation in primary particle size. Smaller particles seem more common at the
periphery of aggregates – may indicate different trajectories. Smaller particles may have undergone partial oxidation. Some instances of apparently fully-formed aggregates of smaller particles.

Next, the A/F was changed from the baseline operation. For the rich and lean cases, the fueling rate remained constant, 11 [mg/cyc], while the air flow rate changed. The rich condition was run with an A/F of 13 and the lean case was run with an A/F at 17, the baseline operation was performed at an A/F of 15. The spark timing was maintained at 25 [°bTDC], and other operating parameters are shown in Table 5.1 and more detailed is shown in Table 3.2. Previous research on the identical SIDI engine [22] revealed that it was expected that the rich operation would yield a higher number of particulates, while the lean operation would result in a lower number of particulates relative to the baseline operation. Contradicting this statement, from the particulate size distribution plots for the A/F changes that are shown in Figure 5.6 ((b), (d)) respectively, the rich condition produced lower primary particle sizes, while the lean operation condition resulted in higher particle size relative to the baseline operation. The hypothesized conclusions did not hold true for the lean and rich operation. Based on the data of this experiment combined with Farron et al work [22], a lean engine operation will cut down on the number of particles produced, and a rich engine could increase the number of particles to 10 times that of the baseline, but at the same time having an increase in particle size for lean and decrease in particle size for rich condition.

In summary the final properties of particulates emitted from an engine mainly depend on the relative contributions of carbon nucleation, growth, oxidation, and aggregation processes within the cylinders. In addition to gas phase species, residence
times, and flow characteristics, temperature is another key factor that affects soot formation mechanisms, because it is related to the competition between surface growth and oxidation rates.

5.1.2. Impact of operating conditions on aggregate morphology

As explained in Chapter 2, sub-micron particles produced by combustion processes evidently have a significant impact on health by penetrating through the human respiratory system and on environment by accelerating global climate change. Existing emission standards impose restrictions on the total mass of emitted particulate matter larger than 2.5 µm (PM2.5). While particulates below this size threshold provide only a small contribution to the overall mass, changing regulations from a mass basis to a size basis is being advocated due to the health consequences of smaller particles. Particulate size and morphology are directly related to their transport, toxic, optical, chemical, and deposition properties. These characteristics govern the particulate inhalation, settling time, radiation balance and visibility levels, and participation in the atmospheric chemistry.

Carbonaceous particulates formed during the combustion of hydrocarbon fuels exhibit common morphological characteristics, reflecting general aerosol processes. As will be shown in figures 5.9 to 5.13, aggregate particles appeared to have a variety of different shapes and sizes. Each aggregate particle consisted of tens to hundreds of near-spherical primary particles agglomerated together. These particles may contain significant amount of soluble organic fraction and/or absorbed hydrocarbons [33], which have not completely reacted during the combustion process. The chemical compounds
absorbed on these particles evaporate at a lower temperature and oxidize at a higher rate than the soot particles.

Figures 5.8 shows that, many spherical primary particles collected to form aggregates of fractal – like geometry. Two different shape descriptors are examined for the images collected at each of the operating condition, namely root form factor (RFF) and fractal dimension (Df). The root form factor (RFF) is a morphologically sensitive measure, much more so than the nominal fractal dimension.

Mathematical morphology provides a powerful tool for TEM image processing. As a parameter for assessing the compactness of the image, the root form factor (RFF) which is sensitive to boundary irregularity can be expressed as

$$ RFF = \frac{4\pi \cdot \text{Area}}{\text{(perimeter)}^2} $$  \hspace{1cm} (5.1)

RFF value equal to 1 corresponds to a filled-in disk while elongation and it is closer to 0 the more indented and disconnected it is.

Since aggregates are considered as fractal-like structures it is acceptable to quantify their irregularity with the fractal dimension, Df, as originally proposed by Mandelbrot, and it is also accepted that, in case of being composed by a sufficient number primary particles, they can be characterised by means of the power-law relationship

$$ n_{po} = K_f \left( \frac{d_g}{d_{po}} \right)^{D_f} $$ \hspace{1cm} (5.2)

where \( n_{po} \) is the number of primary particles (whose diameter is \( d_{po} \)), \( K_f \) is a dimensionless prefactor and \( d_g \) is the diameter of gyration of the aggregate.
The prefactor in Equation 5.2 is a key parameter for the morphological characterisation of aggregates. It has been associated with the lacunarity and with the porosity of the aggregate [47]. Additionally the moment of inertia and radius of gyration can be related to each other. The moment of inertia of a spherical primary particle of radius $r_{po}$ with respect to its own centre of gravity is:

$$ I_G = \frac{4 \pi r_{po}^5 \rho}{5} $$  \hspace{1cm} (5.3)

Analogously the radius of gyration of the aggregate, $r_g$, is the radius of a ring with the same mass and moment of inertia as the aggregate. Therefore, the diameter of gyration can be calculated from:

$$ d_g = 2 \sqrt{\frac{I_G}{m}} $$  \hspace{1cm} (5.4)

Figure 5.8 TEM image of a gasoline aggregate
This section presents comparison of aggregates at different engine operating conditions. Representative aggregates are presented here for comparison of morphology. The Root form factor was calculated using the shape descriptors plugin as explained in section 4.1.2. Fractal dimension and gyration diameter are calculated by a MATLAB program that was coded by Dr. Magnin Lapuerta et al [47]. For interpretation purposes the aggregates that are morphologically analyzed are highlighted on their edges as shown in Figure 5.9 to 5.13.
Figure 5.9 TEM Images of gasoline aggregates sampled at Late End of Injection condition

The images in Figure 5.9 have well defined primary particles but more branching in a 2-dimensional image. Further aggregate morphology tests showed that the mean root form factor is 0.33 and fractal dimension being 2.20. Table 5.2 lists the individual root form factor and fractal dimension for each aggregate shown in Figure 5.9.

Table 5.2 Geometric analysis of aggregate morphology at Late End of Injection condition

<table>
<thead>
<tr>
<th>Particulate</th>
<th>Root Form Factor</th>
<th>Fractal Dimension</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.36</td>
<td>2.09</td>
</tr>
<tr>
<td>2</td>
<td>0.28</td>
<td>2.20</td>
</tr>
<tr>
<td>3</td>
<td>0.33</td>
<td>2.32</td>
</tr>
<tr>
<td>Mean</td>
<td>0.33</td>
<td>2.20</td>
</tr>
</tbody>
</table>
The images in Figure 5.10 show that the aggregates from rich condition seem to be denser and more compact. We can also see highly fused primary particles. The possible reason for this might be rich operating condition refers to having a lower A/F ratio, less air (143 mg/cycle) is supplied than required for burning the full quantity of fuel. The incomplete combustion, results in higher un-burnt hydrocarbons and PM. Further geometric analysis of aggregate morphology tests showed that the mean root form factor is 0.29 and fractal dimension being 2.37. Table 5.3 lists the individual root form factor and fractal dimension for each aggregate shown in Figure 5.10.

Table 5.3 Geometric analysis of aggregate morphology at Rich condition

<table>
<thead>
<tr>
<th>Particulate</th>
<th>Root Form Factor</th>
<th>Fractal Dimension</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.26</td>
<td>2.46</td>
</tr>
<tr>
<td>2</td>
<td>0.32</td>
<td>2.21</td>
</tr>
<tr>
<td>3</td>
<td>0.30</td>
<td>2.45</td>
</tr>
<tr>
<td>Mean</td>
<td>0.29</td>
<td>2.37</td>
</tr>
</tbody>
</table>
The images in Figure 5.11 have nearly a linear structure. Under Baseline operating condition there is stoichiometrically equivalent air for burning the total fuel. This is the ideal condition at which the engine should operate. Further geometric analysis of aggregate morphology tests showed that the mean root form factor is 0.32 and fractal dimension being 1.69. Table 5.4 lists the individual root form factor and fractal dimension for each aggregate shown in Figure 5.11. Both the Baseline and Late end of injection images have a similar value for the root form factor but they differ largely in terms of fractal dimension value.

Table 5.4 Geometric analysis of aggregate morphology at Baseline condition

<table>
<thead>
<tr>
<th>Particulate</th>
<th>Root Form Factor</th>
<th>Fractal Dimension</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.28</td>
<td>1.54</td>
</tr>
<tr>
<td>2</td>
<td>0.35</td>
<td>1.67</td>
</tr>
<tr>
<td>3</td>
<td>0.32</td>
<td>1.85</td>
</tr>
<tr>
<td>Mean</td>
<td>0.32</td>
<td>1.69</td>
</tr>
</tbody>
</table>
The images in Figure 5.12 have generally distinct primary particles with open and chain like structure. Under Lean operating condition there is more air than required stoichiometrically. At this condition, the A/F ratio was set to 17. Stoichiometrically for burning 11mg/cycle of fuel, 165 mg/cycle of air is required. But in this case 187 mg/cycle of air is supplied. Excess air provides more complete combustion and lower PM emission but at the penalty of reduced engine efficiency. Further geometric analysis of aggregate morphology tests showed that the mean root form factor is 0.29 and fractal dimension being 1.86. Table 5.5 lists the individual root form factor and fractal dimension for each aggregate shown in Figure 5.12.

Table 5.5 Geometric analysis of aggregate morphology at Lean condition

<table>
<thead>
<tr>
<th>Particulate</th>
<th>Root Form Factor</th>
<th>Fractal Dimension</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.26</td>
<td>2.10</td>
</tr>
<tr>
<td>2</td>
<td>0.32</td>
<td>1.81</td>
</tr>
<tr>
<td>3</td>
<td>0.30</td>
<td>1.66</td>
</tr>
<tr>
<td>Mean</td>
<td>0.29</td>
<td>1.86</td>
</tr>
</tbody>
</table>
The images in Figure 5.13 show that the aggregates from high load condition show the most variation in primary particle size. Smaller particles seem more common at the periphery of aggregates which may indicate different growth trajectories in space and time. Smaller particles may also have undergone partial oxidation. One reason for this special aggregation might be the amount of fuel quantity that is injected into the combustion chamber. Under High Load condition 21 mg/cycle of fuel is injected compared to 11 mg/cycle for other conditions. Geometric analysis of aggregate morphology tests showed that the mean root form factor is 0.31 and fractal dimension being 2.06. Table 5.6 lists the individual root form factor and fractal dimension for each aggregate shown in Figure 5.13.

Table 5.6 Geometric analysis of aggregate morphology at High Load condition

<table>
<thead>
<tr>
<th>Particulate</th>
<th>Root Form Factor</th>
<th>Fractal Dimension</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.36</td>
<td>2.33</td>
</tr>
<tr>
<td>2</td>
<td>0.22</td>
<td>1.71</td>
</tr>
<tr>
<td>3</td>
<td>0.33</td>
<td>2.13</td>
</tr>
<tr>
<td>Mean</td>
<td>0.31</td>
<td>2.06</td>
</tr>
</tbody>
</table>
The root form factor is a parameter for assessing the compactness of the image, which is most sensitive to the boundary irregularity. Both metrics were self-consistent as to changes with respect to aggregate morphology value. We can infer from the Figure 5.14 that for the five engine operating conditions, the root form factor was measured in a range of 0.29 – 0.33. Thus the above values suggest that the aggregates were more open branched and chain-like structures.

Table 5.7 summarizes the results of aggregate morphology that include the Root Form Factor (RFF), and Fractal Dimension (D_f). The diameter of gyration (d_g) of aggregate particles were measured in a range of 205 – 285 nm for all experimental conditions. Aggregates became slightly larger with increasing in fuel quantity. A fractal dimension close to 1.8 also supports that the diffusion–limited cluster–cluster collisions are mainly responsible for the aggregate growth in diesel engines.
Table 5.7 Engine operating conditions and geometric analysis of aggregate morphology

<table>
<thead>
<tr>
<th>Operating Condition</th>
<th>Fuel Quantity (mg/cyc)</th>
<th>Spark Advance (0bTDC)</th>
<th>A/F ratio</th>
<th>Particle Diameter (nm)</th>
<th>Gyration Diameter (nm)</th>
<th>Root Form Factor</th>
<th>Fractal Dimension</th>
</tr>
</thead>
<tbody>
<tr>
<td>Late EOI</td>
<td>11</td>
<td>25</td>
<td>15</td>
<td>16.17</td>
<td>209.32</td>
<td>0.33</td>
<td>2.20</td>
</tr>
<tr>
<td>Baseline</td>
<td>11</td>
<td>25</td>
<td>15</td>
<td>20.87</td>
<td>205.86</td>
<td>0.32</td>
<td>1.69</td>
</tr>
<tr>
<td>High Load</td>
<td>21</td>
<td>18</td>
<td>15</td>
<td>24.6</td>
<td>261.68</td>
<td>0.31</td>
<td>2.06</td>
</tr>
<tr>
<td>Lean</td>
<td>11</td>
<td>25</td>
<td>17</td>
<td>23.37</td>
<td>256.87</td>
<td>0.29</td>
<td>1.86</td>
</tr>
<tr>
<td>Rich</td>
<td>11</td>
<td>25</td>
<td>13</td>
<td>18.58</td>
<td>285.08</td>
<td>0.29</td>
<td>2.37</td>
</tr>
</tbody>
</table>

The physical sizes of the majority of collected gasoline particulates were distributed near the lower limit of the EPA size standard of PM1.0, which are rather close to the sizes of PM0.1 particles. None of the particles were found in the size ranges of EPA standards PM2.5 or PM10 from the gasoline direct injection engine. This result suggests that the EPA standards for gasoline PM sizes need to be more accurately refined.

Figure 5.15 shows the overall trend of the aggregate morphologies (that include fractal dimension and also root form factor) across the range of conditions. In summary Root form factor exhibited no change for the change in conditions and the value being < 0.5 suggests that the aggregates were more open, branched. Whereas the fractal dimension being > 2.0 suggest that if fuel-air mixture is more homogeneous, then particle formation may be more diffusion-limited rather than reaction-limited.
Figure 5.15 Overall comparison of geometrical morphology measures
5.1.3. Impact of operating conditions on the nanostructure

As reported elsewhere [32], [48], we have observed soot produced under different conditions of temperature and time possess different structures ought not be surprising. Variations in these features are likely to affect the soot’s reactivity toward oxidation among other physical properties dependent upon the dimensions and relative orientations of the graphene segments. Such a design would have significant implications for design of practical combustion devices and their emission requirements.

High-resolution TEM images (Figure 5.17 to 5.21) were used to examine the nanostructure of primary particles. Image processing algorithms as described in section 3.5.1 and 4.1.3 were used to quantify the extent of order observed in the graphene sheets, which make up the solid particle matrix. A range of nanostructures was observed, even within some samples. Figure 5.16 is an illustration of the nanostructure evolution with change of operating condition. Nanostructures were generally more amorphous (less graphitic) than is typical for diesel soot. In general the lamella is neither well ordered nor highly stacked but are clearly evident. And also it makes complete sense that the most ideal condition has clear fringes. However the fact that internal nanostructure is recognizable is strong evidence for continued change in gas-phase chemistry during particle growth relative to the Rich condition. At the ideal engine operating condition (Baseline) graphitic ribbons within particles were common. Yet the overall nanostructure of the primary particle is not uniform but radially irregular, suggesting growth conditions of temperature and species with time.
From an early survey of samples across different engine operating conditions, a subset was selected for image analysis. Consistent with the aforedescribed visual representations, there is a change in nanostructure with change in operating condition. Quantification of the HRTEM images can provide several statistical metrics describing the nanostructural order. These changes are quantified by the lattice fringe analyses for fringe (lamella) length and for fringe (lamella) tortuosity. Starting from Figure 5.17 to 5.21, each figure shows two representative HRTEM images of the specific operating condition, and corresponding binarized image after processing with the fringe analysis algorithm.
Figure 5.17 Lattice fringe analysis for Late EOI: (a)-(b) HRTEM images, and (c)-(d) Binarized images

Upon initial inspection of the HRTEM images (Figure 5.17 (a) and (b)), the nanostructure appears more varied and less graphitic than those derived from engines using diesel fuel [49]. Nevertheless, varied gas-phase chemistry along with partial oxidation as well might be contributing for growth species.
The HRTEM images (Figure 5.18 (a) and (b)) show the nanostructure of soot formed during Rich operating condition. As we have seen in the earlier section 5.1.2, that the aggregates under Rich condition were much more compact and denser, spatially suggesting long continued mass growth after particle coalescence. The image (a) has more disorganized nanostructure organization among lamellae. Image (b) looks more nearly amorphous.
The HRTEM images (Figure 5.19 (a) and (b)) show that there is more evidence of nanostructure, i.e. recognizable lamella with order. So there clearly is a range of nanostructural content. We can also discern other information from the images; to the extent the rate-limited growth occurred following nucleation and particle coalescence, a high degree of fusion is observed between primary particles.
The HRTEM images (Figure 5.20 (a) and (b)) are more chaotic, but certainly with disorganized nanostructure. The images clearly show a similar range of nanostructure as for the baseline condition with largely partial graphitic and disorganized structure. The term chaotic reflects growth of varied species. The lamella appears less tortuous than the images from baseline condition as will be shown by the image analysis algorithm.
Figure 5.21 Lattice fringe analysis for High Load: (a)-(b) HRTEM images, and (c)-(d) Binarized images

The HRTEM images (Figure 5.21 (a) and (b)) show once again a highly disorganized nanostructure. The fuel rich condition resulted in high soot collection on the grid leading to agglomeration. Evidence of aggregate-aggregate agglomeration was discussed in the section 5.1.2 for the high load condition.

Figure 5.22 summarizes the fringe length histograms from the HRTEM image analysis of figures 5.17 to 5.21 respectively.
Figure 5.22 Fringe length histograms and corresponding log-normal fit overlaid and \( \bar{x} \) values derived from the extracted fringes; (a) Late EOI (\( \bar{x} - 0.74 \)nm), (b) Rich (\( \bar{x} - 0.72 \)nm) (c) Baseline (\( \bar{x} - 0.82 \)nm), (d) Lean (\( \bar{x} - 0.8 \)nm), and (e) Heavy Load (\( \bar{x} - 0.8 \)nm)
Mean fringe lengths for the conditions Baseline, Lean and High load were found to be in similar range of 0.8 – 0.82 nm as compared to mean fringe lengths for the conditions Rich and Late EOI had only 0.72-0.74 nm. But standard deviations of mean fringe length, $\sigma_{FL}$, were between 39 – 43% of the mean values, which suggests that the mean is not a meaningful measure.

But the differences are visually clearly evident from the lognormal distributions. As seen in Figure 5.22, the fringe length histogram for the Late EOI and Rich condition soot extends to smaller fringe length, indicating a smaller graphene layer dimension whereas the fringe length histogram for the Baseline, Lean and Heavy Load condition soot extends to much longer fringe length, indicating a larger graphene layer dimensions. Relative to the fringe length histogram for the Late EOI and Rich condition soot with 77% of the lamella smaller than 1 nm in length, only 65% of the fringe length histogram for Baseline, Lean and High Load soot is less than 1 nm. Alternatively only 2.5% -3.1% of the Late EOI and Rich condition soot fringe length histogram is greater than 2 nm while 6.3%-4.5% of the lamella in the Baseline, Lean and High Load condition is greater than 2 nm. The mean of the fringe length histograms shows an order of Baseline (0.82nm) > Lean (0.802 nm) > High Load (0.80nm) > Late EOI (0.74 nm) > Rich (0.72nm).

Figure 5.23 summarizes the fringe tortuosity histograms from the HRTEM image analysis of figures 5.17 to 5.21 respectively. Progressing from amorphous at the high fuel condition, lamella become increasingly distinct and organized in stacks in Baseline condition.
Figure 5.23 Fringe tortuosity histograms and mean values derived from the extracted fringes in figures 5.2 to 5.6: (a) Late EOI ($\bar{x} = 1.19$), (b) Rich ($\bar{x} = 1.21$), (c) Baseline ($\bar{x} = 1.17$), (d) Lean ($\bar{x} = 1.17$) and (e) Heavy Load Load ($\bar{x} = 1.19$)
Mean fringe tortuosity for the conditions Late EOI, Rich, Baseline, Lean and High load were found to be in similar range of 1.17 – 1.21 nm. The standard deviations of mean fringe tortuosity, \( \sigma_T \), were between 20 – 25% of the mean values, which suggests that the mean is not a meaningful measure.

Visual comparison of the histograms indicates that Late EOI and Rich has fringes that contain a wide range of tortuosity, implying high degree of curvature among the lamella of the soot [43] when compared to the other three operating conditions. Relative to the distribution of the Baseline, Lean and Heavy Load soot with 62%, 67% and 59% of the lamella smaller than 1.2 in tortuosity ratio, only 53% and 48% of the fringe tortuosity of Late EOI and Rich soot fringe tortuosity histogram is smaller than 1.2. Table 5.8 lists a summary of the mean fringe length, mean fringe tortuosity and their range.

<table>
<thead>
<tr>
<th>Operating Condition</th>
<th>Fringe Length</th>
<th>Fringe Tortuosity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean &lt; 1 nm</td>
<td>&gt; 2 nm</td>
</tr>
<tr>
<td>Baseline</td>
<td>0.824 65%</td>
<td>6%</td>
</tr>
<tr>
<td>Lean</td>
<td>0.802 67%</td>
<td>6.3%</td>
</tr>
<tr>
<td>High Load</td>
<td>0.8 68%</td>
<td>4.4%</td>
</tr>
<tr>
<td>Late EOI</td>
<td>0.74 76%</td>
<td>3.1%</td>
</tr>
<tr>
<td>Rich</td>
<td>0.72 78%</td>
<td>2.7%</td>
</tr>
</tbody>
</table>
There is already a great amount of literature showing how the gas phase chemistry effects the soot formation by way of some intermediates [50–52]. The length distributions are rather similar across the range of conditions. Surprisingly however the tortuosity distributions divide into two subgroups. The first is the late EOI and fuel-rich condition. The second group is composed of the high load, baseline reference and lean condition.

It is speculated that there are fuel-rich regions or pockets produced by the interaction of the mixing induced turbulence and the diffusion flame. That the lean case corresponds well with the baseline reference suggests that the mixing for the set of conditions at hand is about as good as can be and that lowering the fuel concentration does not significantly change these indicates that the remaining soot producing regions are relatively unaffected by the spray injection. Based upon numerical models of diesel sprays and combustion it seems reasonable to locate such regions as being at the central core of the jet.

For the other group of conditions their commonality is that the fuel concentration is higher in the soot producing regions, but for two very different regions. In the late EOI case this would be due to late end of injection that is purposefully used in other instances to produce a stratified charge and at the very least allows less time (CAD) for mixing to occur. In the rich case, the fuel injection timing is the same as the reference case but a higher fuel amount is injected.

So it would seem that the soot producing regions in these two cases are more fuel-rich, i.e. having a higher fuel concentration. So why do they exhibit a higher level of tortuosity as evidenced by the broader distribution?
For any case the working construct suggested here is that there will be an ensemble of fuel-rich regions or pockets with varied equivalence ratio. Alternatively these may be thought of as isopleths of varied fuel concentration but highly broken up by turbulence. For the late EOI or rich conditions the high degree of partial mixing promotes oxidation of benzene, which lies at the crossing point to aromatic formation towards soot nucleation. If significant oxygen is present, fuel pyrolysis processes will be accelerated, resulting in production of odd-numbered carbon species. Oxidation process such as upon benzene will be concurrent. This later step yields the phenoxy radical that undergoes unimolecular decomposition by loss of CO to produce C5, the cyclopentadiene species. These are integral to producing curvature in the carbon lamella comprising the soot. These regions contribute to the soot from the (unchanging) very fuel rich regions to extend the tortuosity distribution by virtue of their different nanostructure.

For any injection case turbulent mixing will create varied levels of fuel-to-air concentration. If producing soot these will necessarily be above a critical threshold for soot production. For the late EOI or fuel-rich conditions regions or pockets with a high degree of mixing will yet persist, given the lesser time for mixing to occur prior to ignition. At longer times (dwell before ignition) as in the reference case timing, these
same regions “wash out” as more mixing yet further lowers the fuel concentration sufficiently to the point where they do not produce soot or at least a much lower amount.

For similar injection pressure, rpm, cylinder pressure, etc., it seems reasonable to interpret the different tortuosity distributions as reflecting soots from different spatial regions, with these regions being preserved or existing across the range of conditions but with only their fuel/air ratio changing in response to conditions, as an initial approximation.

This implies that soots from different regions all have very different tortuosity distributions. If so, then the above is valid. If however all aggregates appear to have the same tortuosity distribution, this would argue against different regions with different fuel/air ratios, as suggested above!

If the soots “look” similar or have equivalent tortuosity distributions, then this would suggest that the above “multiple-region” postulate is not valid, at least not supported by the data. In this case the only argument that can be made is that the mixing in these two cases is sufficiently different than that of the other group of conditions and sufficiently similar to each other that the tortuosity distributions mirror each other. That said, the only way to increase tortuosity is by the increased concentration of C5. So the present conundrum is that conditions with nominally lesser mixing by virtue of timing or higher fuel (injected) quantity lead somehow to regions that are more premixed to support the oxidation-induced formation of C5.

Regardless of the A/F ratio or which condition the engine is operated at or even the local stoichiometry of the fuel rich packets, there tend to be differences in nanostructure. Which suggests that as the soot is forming from the gas phase species, the
gas phase species should be different at different conditions. The conditions of nucleation and growth (supersaturation, temperature) in the carbon-forming volume of the source will determine the abundance of well-ordered particles versus the irregular objects seen in HRTEM. It is observed that the soot morphology is changing with different settings of the test SIDI engine.
5.2. Comparison of soot reactivity at initial rate and 50% partial burn-off

As we have seen earlier in section 5.1.3, the HRTEM images (Figure 5.18 (a) and (b)) of soot formed during Rich operating condition. The image (a) had more disorganized nanostructure organization among lamellae. Image (b) looked more near to amorphous. The fringe analysis showed it had poor graphitic structure.

With improvised testing methodology to estimate the degree of burnout, TGA partial oxidation runs were conducted with intermediate study by HRTEM. The TGA analyzer was used to oxidize the soot that is deposited on a Gold grid. The TGA analyzer was operated at a ramp rate of 10 °C/min until it reached 550 °C, once the desired temperature was reached; the system was set to cool down. The entire system was under the air environment until the temperature reached 550 °C, once after the set point is reached Nitrogen was pumped as opposed to air to make it sure that were no reactions occurring.

The Gold grids are removed from the TGA and are further analyzed under a High resolution TEM. Some of the resultant images are shown below in Figure 5.24. High-resolution images of the partially oxidized Rich soot reveal very fine agglomerates. Spherical particles appear not larger than 5 nm and seldom observed. The graphene segments are strongly bent forming single- or double-layered fulleroid-like structures, coagulated to long chain-like agglomerates.
Figure 5.24 High-resolution TEM images of the Rich sample, which is further partially oxidized at 550°C
The change in nanostructure [53] is motivation for further TEM image analysis. Figure 5.25 puts the images of (a) SIDI Rich condition, and (b) SIDI Rich – partially oxidized~50%, condition, for visual comparison. Readily observed that the partially oxidized soot had a substantial nanostructural change. Partial oxidation transformed the soot nanostructure, which initially was amorphous, disorganized to a more graphitic form.

Figure 5.25 Representative (a, b) HRTEM images (c, d) Binarized images, of initial and partially oxidized soot
Figure 5.26 Fringe length and Fringe tortuosity histograms and mean values derived from the extracted fringes in figures 5.27 (a) Rich (mean = 0.2nm), (b) Rich – Partially oxidized (mean = 0.83nm), (c) Rich (mean = 1.217), and (d) Rich – Partially oxidized (mean = 1.17)

Visual comparison of the histograms indicates that the partially oxidized Rich soot extends to much longer fringe length, indicating a larger graphene layer dimensions. Whereas the nascent Rich soot has fringes that contain a wide range of tortuosity, implying high degree of curvature among the lamella of the soot [43]. Figure 5.26 (a) and (b) shows the histograms of fringe length for nascent Rich soot and partially oxidized
Rich soot (at 50% burn-off). Relative to the fringe length histogram for the Rich condition soot with 78% of the lamella smaller than 1 nm in length, only 65% of the fringe length histogram of partially oxidized Rich soot is less than 1 nm. Alternatively only 2.7% of the nascent Rich soot fringe length histogram is greater than 2 nm while 7% of the lamella in the partially oxidized Rich soot is greater than 2 nm.

5.26 (c) and (d) shows the histograms of fringe tortuosity for nascent Rich soot and partially oxidized Rich soot (at 50% burn-off). Relative to the fringe tortuosity distribution for the Rich condition soot at initial state with 48% less than 1.2 in tortuosity ratio, around 62% of the partial oxidized rich soot fringe tortuosity ratio is less than 1.2. Alternatively the Rich condition soot at initial state has 15% of the measured fringes having a tortuosity ratio of greater than 1.5, while only 8% of the fringe tortuosity ratio of partially oxidized rich soot is greater than 1.5.

(a) Fringe length difference plot  
(b) Fringe tortuosity difference plot
Figure 5.27 Fringe Length and Tortuosity difference between nascent and partially oxidized soot

Figure 5.27 (a) and (b) shows the difference plots for the fringe length and fringe tortuosity between the nascent (initial) and partially (550 0C) oxidized soot. The summation of the net histogram for fringe length yields a value 0.0005 and that of fringe tortuosity is 0.857. These values suggest the accuracy of the image analysis algorithm. Figures 5.27 (c) and (d) shows the percentile of nascent Rich and partially oxidized soot with respect to length scales. The Y-axis scales are different.

In summary the lack of nanostructure and high organic content predispose the soot to oxidation induced structural changes. However, for this degree of burnout, estimated to be ~ 50%, the soot particles followed a shrinking sphere model, but undoubtedly the rate varies as graphitization occurs.

5.2.1. Discussion

The soot formed during the Rich condition can be argued as the most reactive soot. The reason is the very defective structure, which is observed in the TEM
micrographs. The material consists of fine subunits not larger than 5 nm building up agglomerates with a high surface area. Strongly bent graphenes lead to localised double bonds resulting in an olefinic structure [54].

Figure 5.28 Simplified oxidation progression model for Rich condition soot (a) nascent sample (b) partial oxidation (at 550 °C)
Theoretical investigations of nanocarbons predict the influence of geometric changes on chemical properties (increasing reactivity upon increasing curvature) [54]. The graphenes in this soot are small as seen in Figure 5.25 (a). This increases the ratio of carbon atoms on graphene edge sites to carbons in the centre of the graphene sheet. A high ratio between border carbon and graphene carbon is equivalent to high reactivity. Carbon atoms in edge sites can form bonds with chemisorbed oxygen and hydrogen due to the availability of unpaired sp2 electrons, while carbon atoms in basal planes are more aromatic having only shared $\pi$-electrons to form chemical bonds. To further validate this finding, spectroscopy techniques should be able to identify the organic species, functional groups that are present inside the solid soot sample.
5.3. Impact of engine operating conditions on the chemical composition and presence of functional groups

SPLAT II mass spectra (tests conducted by PNNL) indicated that the SIDI particulates contained significant organic content, up to 40% of the particulate mass. The first round of cooperative experiments at the ERC examined two VPR methods, a thermodenuder and an evaporative chamber. Under most of the conditions studied, neither of these treatments significantly altered the particle size distributions or compositions. The very unusual soots, based on morphology and nanostructure motivated the detailed interrogation via complimentary spectroscopy techniques. Samples are tested by XPS which is a surface measurement technique. XPS results should give a clear idea as to the surface absorbed stuff. Following XPS, samples are then analyzed under an FTIR-ATR instrument, which is a volumetric averaged (less surface area relative to mass is tested) technique. The results are presented in the following sections.
5.3.1. Impact of operating conditions on the surface chemical composition as analyzed by XPS

As reported elsewhere [38], [55], XPS can provide a wealth of chemical information regarding both heteroatom content in addition to bonding configurations. The samples examined were on the Au TEM grids. Substantial organic content was observed in all the conditions. Figure 5.29 to 5.33 show the XPS data for all the five engine-operating conditions. As explained in chapter 4, the deconvolution of C1s peak was performed using commercially available software, CASA XPS. Deconvolution demonstrates that the C 1s (at 284.6 eV) spectrum of soot produced from a gasoline engine can be quantitatively differentiated into five different carbon components, sp2 hybridized carbon atoms (at 284.4 eV) of the graphitic structure, sp3 hybridized carbon atoms (at 285.2 eV), the alcohol group (C-O)(at 286.6 eV), the carbonyl group (C=O)(at 288.0 eV), the carboxylic acid group (O-C=O) (at 289.2 eV), and the π – π* signal (plasmon) (at 290.5 eV).

Figure 5.29 shows the deconvolution of high resolution C 1s peak which reveals the soot surface chemistry for SIDI engine produced soot for the Late EOI operating condition. The ratio of sp2/sp3 can be considered as the ratio of organic to elemental carbon [37]. For this condition, consistent with the graphitic physical nanostructure revealed by HRTEM, the physical bonding mainly consists of C-C sp3, characteristic of disordered, amorphous carbon. Notably the surface oxygen content is significantly higher relative to the other operating conditions. Figure 5.30 shows the deconvolution of high resolution C 1s peak that reveals the soot surface chemistry for SIDI engine produced soot for the Rich operating condition. In this case also the physical bonding mainly
consists of C-C sp3 consistent with the HRTEM results. The organic content is observed to be slightly more than that is found in the Late EOI condition. This might be mainly because of global A/F ratio, which is less relatively for the Rich condition, leading to the formation of fuel-rich pockets consisting mainly unburnt hydrocarbons. HRTEM micrographs revealed very poor structure, which suggests the soot is very reactive.

Figure 5.29 High resolution XPS spectrum over the C1s Region of soot generated from SIDI engine at Late EOI operating condition
Figure 5.30 High resolution XPS spectrum over the C1s Region of soot generated from SIDI engine at Rich operating condition

Figure 5.31 High resolution XPS spectrum over the C1s Region of soot generated from SIDI engine at Baseline operating condition
Figure 5.32 High resolution XPS spectrum over the C1s Region of soot generated from SIDI engine at Lean operating condition

Figure 5.33 High resolution XPS spectrum over the C1s Region of soot generated from SIDI engine at High Load operating condition
Figures 5.31 to 5.33 shows the deconvolution of C 1s peak for the operating conditions Baseline, Lean and Heavy Load respectively. All the three scans suggest that the physical bonding mainly consists of C-C sp2, which is a characteristic of graphitic carbon. These results well agree with the HRTEM image analysis.

![Graph showing sp2/sp3 ratio as a function of engine operating condition](image)

**Figure 5.34** Summary of C-C sp2/sp3 ratio as function of engine operating condition

The surface bonding and functional group content which include carbon sp2, sp3 components, oxygen functional groups, phenolic, carbonyl and carboxylic are summarized in Table 5.9. More details on the curve fitting and its related parameters can be found in Appendix D.
Table 5.9 Summary data of high resolution scan over C 1s region for soot collected at different engine operating conditions

<table>
<thead>
<tr>
<th>Operating Condition</th>
<th>sp2 (atom %)</th>
<th>sp3 (atom %)</th>
<th>Phenol (atom %)</th>
<th>Carbonyl (atom %)</th>
<th>Carboxylic (atom %)</th>
<th>Plasmon (atom %)</th>
<th>Carbon sp2/sp3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Late EOI</td>
<td>53.15</td>
<td>26.26</td>
<td>8.09</td>
<td>7.04</td>
<td>0.5</td>
<td>4.93</td>
<td>2.02</td>
</tr>
<tr>
<td>Rich</td>
<td>59.63</td>
<td>30.50</td>
<td>4.67</td>
<td>3.65</td>
<td>1.52</td>
<td>-</td>
<td>1.95</td>
</tr>
<tr>
<td>Baseline</td>
<td>59.91</td>
<td>26.61</td>
<td>8.73</td>
<td>3.17</td>
<td>1.55</td>
<td>-</td>
<td>2.25</td>
</tr>
<tr>
<td>Lean</td>
<td>56.23</td>
<td>23.66</td>
<td>11.56</td>
<td>5.16</td>
<td>3.38</td>
<td>-</td>
<td>2.37</td>
</tr>
<tr>
<td>High Load</td>
<td>59.13</td>
<td>28.03</td>
<td>6.67</td>
<td>4.58</td>
<td>1.56</td>
<td>-</td>
<td>2.10</td>
</tr>
</tbody>
</table>

The elemental content on the surface of the soot samples is summarized in Table 5.10 and their individual survey scans are shown in the Figure 5.35. Each operating condition shows a significant amount of oxygen (14.7% - 21.9%) on the surface of the soot.

Table 5.10 Summary of the elemental content of the survey scans for soot collected at five different operating conditions

<table>
<thead>
<tr>
<th>Operating Condition</th>
<th>C 1s (atom %)</th>
<th>O 1s (atom %)</th>
<th>Au 4f (atom %)</th>
<th>Si 2p (atom %)</th>
<th>Zn 2p (atom %)</th>
<th>Cu 2p (atom %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Late EOI</td>
<td>63.21</td>
<td>19.91</td>
<td>11.11</td>
<td>5.45</td>
<td>0.15</td>
<td>0.14</td>
</tr>
<tr>
<td>Rich</td>
<td>77.97</td>
<td>17.17</td>
<td>4.48</td>
<td>-</td>
<td>0.36</td>
<td>-</td>
</tr>
<tr>
<td>Baseline</td>
<td>79.08</td>
<td>18.4</td>
<td>0.27</td>
<td>2.11</td>
<td>0.06</td>
<td>-</td>
</tr>
<tr>
<td>Lean</td>
<td>63.29</td>
<td>21.9</td>
<td>1.29</td>
<td>12.98</td>
<td>0.36</td>
<td>0.08</td>
</tr>
<tr>
<td>High Load</td>
<td>56.22</td>
<td>14.7</td>
<td>7.32</td>
<td>21.11</td>
<td>0.30</td>
<td>0.316</td>
</tr>
</tbody>
</table>
Figure 5.35 Survey scans of the soot samples collected at different operating conditions
In summary significant organic content was observed by XPS especially for the Late EOI and Rich conditions. Significant differences in composition between conditions were observed. The quantitative XPS measurements nevertheless showed a large proportion of inorganic carbon on the particle surfaces, adding more evidence that organic content is integrated into the solid matrix throughout the bulk of the primary particles. This is consistent both with the TEM observations of particle nanostructure and with the difficulty in removing by VPR organics observed in SPLAT II mass spectra. This serves as additional evidence of tightly integrated organic content within the elemental carbon matrix.
5.3.2. Impact of operating conditions on the functional groups throughout the particulate volume analysis by FTIR-ATR

In order to further characterize the chemical structures of the particles collected from the engine exhaust, FTIR – Attenuated Total Reflectance was performed on the soot samples. Attenuated Total Reflectance (ATR) FTIR measures the absorbance of functional groups throughout the particulate volume as opposed to surface concentration measurements that XPS performs. The samples that were collected on Au TEM grids were analyzed. Significant differences in composition were observed between the five different operating conditions. The spectra were collected using the custom software Opus 6.0, with the data then exported into Kaleidagraph™ for plotting purposes. Various published research papers were referred to FTIR-ATR spectral interpretation [39], [56].

Figures 5.36 to 5.37 show the FTIR – attenuated total reflectance spectra for four of the five engine operating conditions studied in the SIDI engine. In general the FTIR spectrum is collected over the wavenumber range of 500 to 4000 cm$^{-1}$. Aliphatic groups (2860–2950 cm$^{-1}$, 1450 cm$^{-1}$), aromatic groups (1500–1540 cm$^{-1}$), and oxygen-containing functional groups are present. For better pictorial representation two plots are included for each conditions; the first one is the total scan and the second one focused on the range 2000 to 1000 cm$^{-1}$.

The FTIR spectra show several sharp peaks suggesting molecular character of the investigated structures. Three consecutive peaks are noted in the spectrum at 2960, 2925 and 2850 cm$^{-1}$, of which the absorption is found to be the maximum for the middle wavelength. A sharp peak is observed in the spectrum at 1720 cm$^{-1}$, while several major
peaks are also noted in the wavenumber range of 1450 and 1380 cm\(^{-1}\) and also between 1300 and 1000 cm\(^{-1}\). The information revealed from the FTIR spectrum show several similarities in the bond chemistries or functional groups of soot particles from the gasoline engine exhaust and hydrocarbon flames.

The peaks at 2960, 2925 and 2850 cm\(^{-1}\) in the FTIR spectrum are assigned to aliphatic C-H symmetric and asymmetric stretches in the soot structures at engine exhaust [56]. The presence of aliphatic groups is further suggested by the peaks in the range of 1380 and 1450 cm\(^{-1}\) found in the spectrum, which are attributed to the in-plane deformation of aliphatic C-H bonds [57].

Aromatic C-H stretch has been reported from FTIR study in the PAH samples by Ciajolo et al. [58] and McKinnon et al [59] through a peak at 3050 cm\(^{-1}\). The FTIR spectrum recorded in the present work fails to detect any significant peak around 3050 cm\(^{-1}\), as expected for aromatic structures. However, signals have been observed between 1000 and 1300 cm\(^{-1}\) representing the in-plane deformation of aromatic groups [57]. The sharpest peak in this range at 1280 cm\(^{-1}\) is more likely due to the ether C-O-C structure as also reported by Cain et al. [56] through a peak at 1260 cm\(^{-1}\) in the nascent soot sample collected from flame. Rusciano et al. however assigned the peak at 1260 cm\(^{-1}\) observed in their transmission signal to aliphatic C-C stretching vibration.

The sharp peak observed in the present FTIR spectrum at 1720 cm\(^{-1}\) is attributed to the carbonyl C=O stretch. Such oxygen related functionality has been reported in the soot precursor species and polyaromatic hydrocarbon generated from flames [60], [61].
The exact origin of oxygen in the soot precursor is not well understood and yet today some doubt has been raised as to whether the oxygen is added in a post-flame reaction. The significant presence of carbonyl structures may lend hydrophilic character to the particles.

Figure 5.36 FTIR-ATR spectra of the soot collected from the SIDI engine exhaust at Rich condition, (a) full wavenumber range, and (b) selected peak with substantial profiles 2000-1000 cm\(^{-1}\)
Figure 5.37 FTIR-ATR spectra of the soot collected from the SIDI engine exhaust at full wavenumber range and selected peak with substantial profiles 2000-1000 cm$^{-1}$ for (a)-(b) baseline, (c)–(d) Lean, and (e)-(f) High Load
5.3.2.1. Discussion

Fuel rich conditions lead to a significant amount of organics in the form of paraffins and aromatics. It is likely that there is a significant amount of alkyl-substituted aromatics, as suggested by flame measurements of soot formation in premixed (rich) systems. All spectra were measured as direct absorbance, using attenuated total internal reflection (ATR) mode. Significantly FTIR provides a volumetric measure of the chemical composition as manifested by the functional groups. Of interest is that the particulate contained sufficient organic content as to directly measurable via absorbance, rather than by diffuse reflectance, as is commonly done due to the few functional groups upon/within a near perfect absorber of far greater proportion.

Carbon atoms in edge sites can form bonds with chemisorbed oxygen and hydrogen due to the availability of unpaired sp2 electrons, while carbon atoms in basal planes are more aromatic having only shared p-electrons to form chemical bonds [62]TEM results, especially the tortuosity results are in perfect agreement. Additionally, oxygen containing functional groups attached to non-six-membered rings may occur as very reactive sites. The defective non-six-membered rings may produce highly localized olefinic electronic structures prone to the addition of molecular oxidants.

The significance of such compositional differences is that the soot produced under fuel rich conditions has significant organic content and hence its oxidation rate should be similarly different, with lower activation energy and threshold temperature. Burning mode, to be determined.
5.4. Comparison of the physical and chemical diagnostic measures

5.4.1. FTIR results in agreement with SPLAT II results

An initial round of cooperative experiments at the ERC generated a very large set of SIDI particulate data over a wide range of engine operating parameters with standard gasoline. Vacuum aerodynamic diameter and composition data were collected using the SPLAT II (second-generation Single Particle Laser Ablation Time-of-Flight mass spectrometer) instrument developed at PNNL, which obtains size and complete mass spectra for up to 100 individual particles per second. SPLAT II mass spectra indicate that the SIDI particulates contained significant organic content, up to 40% of the particulate mass, which is also shown in the Figure 5.38.

![Figure 5.38 Mass spectra from SPLAT II showing the presence of Elemental carbon, Organics and Polycyclic aromatic hydrocarbons](image)

European particle number emissions standards include an elaborate sampling and dilution specification, including volatile particle removal (VPR) methods, which strip away volatile components from diesel aerosols before counting, typically altering the particle size distribution as well as particle composition. The first round of cooperative
experiments at the ERC examined two VPR methods, a thermodenuder and an evaporative chamber. Figure 5.39 shows the vacuum aerodynamic diameter for high load and medium load conditions without using any of the VPR method and also using a Thermodenuder or an evaporative chamber. Under most of the conditions studied, neither of these treatments significantly altered the particle size distributions or compositions. The only exception was a set of conditions intended to mimic a cold start.

Figure 5.39 Vacuum aerodynamic diameter for high load and medium load conditions
Figure 5.40 Mass spectra from SPLAT II showing the presence of Organics and Polycyclic aromatic hydrocarbons even after passing the exhaust through Thermodenuder /evaporative chamber; (green) raw exhaust without VPR, (yellow) Thermodenuder, and (red) evaporative chamber.

The fact that the significant organic content observed under other engine operating conditions was so difficult to remove suggests that organics were not present as separate droplets or as coatings on the surfaces of solid soot particles, as is often observed in raw diesel exhaust. Significant organic content was observed by both XPS and FTIR-ATR techniques. The quantitative XPS measurements nevertheless showed a large proportion of inorganic carbon on the particle surfaces, adding more evidence that organic content is integrated into the solid matrix throughout the bulk of the primary particles. Attenuated Total Reflectance (ATR), which detects the presence of functional groups throughout the particulate volume suggested fuel rich conditions lead to a significant amount of organics in the form of paraffins and aromatics. Taken with FTIR/ATR measurements, strong evidence for matrix-distributed organic content. This is consistent both with the TEM observations of particle nanostructure and with the difficulty in removing by VPR organics observed in SPLAT II mass spectra.
5.4.2. **Comparison of XPS and HRTEM analysis results**

In the previous two sections, we have seen the results of XPS and HRTEM analysis for the particulates generated from a SIDI engine. The sp2/sp3 ratio derived from high-resolution C 1s XPS spectrum and the mean fringe lengths derived from high resolution TEM images were compared directly. Figure 5.41 shows mean fringe length, sp2/sp3 ratio versus individual operating condition. Figure 5.41 indicates a qualitative agreement between the results from XPS and HRTEM analysis.

![Figure 5.41 Comparison of mean fringe length, sp2/sp3 ratio versus engine operating condition](image-url)
From figure 5.41, the fringe tortuosity percentile (< 1.2) of soot generated at Rich and late EOI operating condition is consistent with the smallest sp2/sp3 ratio from high resolution XPS. Tortuosity measures the undulation of carbon lamella, arising from 5 and 7-membered ring structures within the aromatic framework. Therein, high tortuosity in soot nanostructure prevents development of stacked layers [53], [63].

In the previous section 5.1.3, a range of nanostructures were observed, even within some samples: amorphous, disorganized, and partial graphitic. Nanostructures tended to be much more amorphous (less graphitic) than is typical for diesel soot. Lack of order is thought to be indicative of integrated organic compounds that tend to interrupt growth of the graphene layers. Heterogeneity of species incorporated into particles implies a non-uniform growth environment with respect to time, temperature, and gas-phase chemistry. Degree of order will affect reactivity and burning mode of soot, less nanostructure is more reactive.
5.4.3. **Comparison of XPS and FTIR-ATR analysis results**

As discussed in section 5.2.2, fuel rich conditions lead to a significant amount of organics in the form of paraffins and aromatics. It is likely that there is a significant amount of alkyl substituted aromatics, as suggested by flame measurements of soot formation in premixed (rich) systems. Of interest is that the particulate contained sufficient organic content as to directly measureable via absorbance, rather than by diffuse reflectance, as is commonly done due to the few functional groups upon/within a near perfect absorber of far greater proportion.

The spectrums of FTIR were merely interpreted in a qualitative manner, but we observed significant differences in composition between the four operating conditions examined. The significance of such compositional differences is that the soot produced under rich conditions has significant organic content and hence its oxidation rate should be similarly different, with lower activation energy and threshold temperature. Burning mode shall be determined.

XPS interpreted that there are significant differences in composition between five different engine-operating conditions. High resolution spectrums over the C 1s regions showed that the soot particulates surface mostly consisted elemental carbon with some surface bound organics. Proportions suggest that organics observed by FTIR-ATR are not concentrated in a surface film. Taken with FTIR-ATR measurements, this serves as strong evidence for matrix distributed organic content. The degree of oxygen functionality was also found to be consistent with FTIR.
5.5. Comparison of SIDI gasoline engine to a medium duty diesel engine of different size class, for similarities and differences

Technologies such as SIDI offer the possibility of dramatically increasing the fuel efficiency of engines, which run on gasoline and similar hydrocarbons. Development of this technology and application to a range of fuel blends will blur the lines that have traditionally existed between gasoline and diesel engines. Although some similarities are expected between diesel soot and particulates generated by lean-burn engines designed to use other fuels, significant differences could require adaptation of existing aftertreatment technologies. Initial data indicates that SIDI particles are smaller than diesel particles, and particle production can vary widely between engine operating conditions. Regulation of engine particulate emissions in Europe is moving from mass-based standards toward number-based standards, and it is likely that North American regulators will move in the same direction. This will place more emphasis on the reliable removal of smaller particles, which make up the vast majority of the particulates generated on a number basis.

Reliable and efficient regeneration of particulate filters is a significant issue on diesel vehicles. Soot accumulated in filters must be removed by oxidation to maintain acceptable back-pressures, often necessitating complicated estimation and control schemes. Many strategies for removing the soot require the use of additional fuel to raise exhaust temperatures. Gasoline engines typically run significantly hotter than diesel engines, raising the possibility that soot may be continuously oxidized without burning additional fuel, especially if the filter can be close-coupled to the engine. Filtration
efficiency could be a major issue if there is little accumulation of soot in the filter, since a soot cake performs much of the filtration over the operating cycle of a typical diesel particulate filter (DPF). This is particularly true for meeting number-based particulate emissions standards.

In this section comparison is made between a spark ignited, direct injection gasoline driven engine to a medium duty diesel engine. This comparison is purely inclined towards checking the similarities and differences. The medium duty diesel engine used here is a Cummins ISL 365 hp engine that is almost ten times more powerful than the SIDI engine that was discussed earlier.

Typical low magnification TEM images of the soot emitted from the diesel engine are shown in figures 5.42. The fuel used in the diesel engine is the US standard Ultra low sulfur diesel (ULSD). The sampling was done at 100% load (2100 rpm). For rational comparison, images of the same length scales are compared individually.
Figure 5.42 TEM images of diesel engine particles sampled at 100% load in a medium duty engine: (a) – (d) length scales of 20 nm, and (e) – (f) length scales of 100 nm
The diesel engine soot aggregates that are shown above in Figure 5.42 convey that the soot aggregates are more compact. The primary particles lacked definition or individuality. The primary particle size analysis of the above soot aggregates revealed that the average particle size (diameter) is 19.76 nm. The primary particle size distribution that are fitted to a lognormal distribution is shown in the below figure 5.43.

![Graph showing particle size distribution](image)

**Figure 5.43** Primary particle distributions that are fitted to a lognormal distribution

Further geometric analysis of aggregate morphology analysis showed that the mean root form factor is 0.62 and fractal dimension being 2.39. The fractal dimension is well within the range that was published in the literature earlier [47]. Table 5.11 lists the individual root form factor and fractal dimension for three of the particulates shown in Figure 5.40. Similar to the results shown for the gasoline drive engine, each measure
shows high self-consistency, indicative of the similarity of the aggregate morphology for the ULSD soot.

Table 5.11 Geometric analysis of aggregate morphology for a medium duty diesel engine tested with ULSD as the fuel

<table>
<thead>
<tr>
<th>Particulate</th>
<th>Root Form Factor</th>
<th>Fractal Dimension</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.60</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0.70</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>0.55</td>
<td>2.39</td>
</tr>
<tr>
<td>Mean</td>
<td>0.62</td>
<td>2.39</td>
</tr>
</tbody>
</table>

When the fractal dimension and root form factor values of diesel engine soot are compared with the SIDI engine values (which are reported in earlier sections 5.1.1 and 5.1.2), we see a stark contrast between the values. The diesel soot was more like a “compacted assembly” as compared to “open and chain-like” aggregates as shown for gasoline soot in the earlier section.

Table 5.12 compares the aggregate morphology measures for both the diesel (ULSD) engine and gasoline (mean value of five operating conditions) engine. Both Root form factor and Fractal dimension exhibited higher values for diesel soot and lower values for gasoline soot.

Table 5.12 Comparison of aggregate morphology measures

<table>
<thead>
<tr>
<th>Type</th>
<th>Root Form factor</th>
<th>Fractal Dimension</th>
</tr>
</thead>
<tbody>
<tr>
<td>ULSD – Diesel Engine</td>
<td>0.62</td>
<td>2.39</td>
</tr>
<tr>
<td>EEE – Gasoline Engine</td>
<td>0.30</td>
<td>2.03</td>
</tr>
</tbody>
</table>
Figure 5.44 shows the key point of the comparison, namely that the RFF exhibits a much greater dynamic range for the same range of particulate morphologies than the fractal dimension. Given this as a shape descriptor it has far greater potential for distinguishing such differences. We can understand from the below figure that there is far less variation in the fractal dimension than in the RFF metric, particularly when considering that traditional confidence intervals are +/- 5 – 10%.

Upon initial inspection of the HRTEM images Figure 5.45 (a), the nanostructure of the ULSD fueled diesel engine appears to be more graphitic than those derived from engines using gasoline fuel, which we observed are more amorphous, disorganized and chaotic.
Figure 5.45 representative (a) HRTEM Image and (b) Binary image, (c) fringe length distribution (mean – 0.95nm), and (d) fringe tortuosity distribution (mean - 1.3)

As seen in Figure 5.45 (c) and (d), the fringe length histogram for the diesel soot extends to much longer fringe length, indicating a larger graphene layer dimensions. relative to the fringe length histogram for the gasoline soot with 71% (average of five operating conditions) of the lamella is smaller than 1 nm in length, only 56% of the fringe length histogram of diesel soot is less than 1 nm. Alternatively only 4.5% of the gasoline
soot fringe length histogram is greater than 2 nm while 13% of the lamella in diesel soot is greater than 2 nm.

We compare these few measures not to find or demonstrate a statistically significant difference after-all, a real production Cummins ISB 365 hp medium duty diesel engine vs. a single-cylinder test standard engine, but to identify real values indicative of differences observed by TEM. Not that aerosol instruments are rather insensitive to such variations by measuring only equivalent spherule size. These initial observations suggest that there are significant differences resolvable that could and should be better quantified.
CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

6.1. Summary and conclusions

This study focuses on the impacts of engine operating conditions in a spark ignited, direct injection (SIDI) gasoline (EPA tier II EEE) driven engine. The impact of engine operating conditions are examined by both physical and chemical measures to check the effects on size, morphology, nanostructure, surface chemical composition and functional groups. Next to this the study also involved comparing between the diagnostic measures and then comparing the results with a medium duty diesel (ULSD) engine to check the similarities and differences.

6.1.1. Observations on aggregate structure

Spark ignited, direct injection (SIDI) samples exhibited a distinctly different aggregate morphology. Aggregates were highly open, branched structure compared to compacted clusters as characteristic of normal diesel engine aggregates. SIDI engine generated particulates had largely recognizable primary particles, much more so than for the medium duty diesel engine soots. Partly this reflects the first statement. TEM measurements of primary particle size variation at various end of injections agree remarkably well with estimates previously made using aerosol analysis methods.

Primary particle size distributions were observed to be somewhat broader than those in diesel soot. The full range of variation was found within a single aggregate more
often heterogeneity in size was largely dictated by engine operating conditions. Primary particle size similar to diesel for baseline operating conditions, but can be smaller or much larger.

Possibly there might be two size classes of aggregates - several smaller, stunted aggregates observed. Some aggregates may be partially oxidized, but they do not look like diesel soot samples that have been partially oxidized by $O_2$ at atmospheric pressure. Under some conditions, primary particle sizes do not fit a log-normal distribution, suggesting different growth processes than in diesel engines.

Significant differences in aggregate morphology were observed when soot from SIDI engine and Diesel engine are compared. Both Root form factor and Fractal dimension exhibited higher values for diesel soot and lower values for gasoline soot. These initial observations suggest that there are significant differences resolvable that could and should be better quantified.

6.1.2. Observations on nanostructure

A range of nanostructures were observed, even within some samples: amorphous, disorganized, and partial graphitic. Nanostructures tended to be much more amorphous (less graphitic) than is typical for diesel soot. Less ordered structure could imply incorporation of organic compounds during particle formation (also suggested by VPR experiments at the ERC) that tend to interrupt growth of the graphene layers. Higher organic content as well as higher proportions of edge sites and curved lamella suggest that SIDI soot will be more reactive than diesel soot.
The results from fringe analysis algorithm suggested that out of the five engine operating conditions, Progressing from amorphous at the Late EOI and Rich condition, lamella become increasingly distinct and organized in stacks in Baseline, Lean and Heavy Load condition. Visual comparison of the fringe tortuosity histograms indicates that Late EOI and Rich has fringes that contain a wide range of tortuosity, implying high degree of curvature among the lamella of the soot. The only way to increase tortuosity is by the increased concentration of C5. Therefore the conditions with nominally lesser mixing by virtue of timing or higher fuel (injected) quantity lead somehow to regions that are more premixed to support the oxidation-induced formation of C5.

Regardless of the A/F ratio or which condition the engine is operated at or even the local stoichiometry of the fuel rich packets, there tend to be differences in nanostructure. Which suggests that as the soot is forming from the gas phase species, the gas phase species should be different at different conditions.

With improvised testing methodology to estimate the degree of burnout, TGA partial oxidation runs were conducted with intermediate study by HRTEM. The lack of nanostructure and high organic content predispose the soot to oxidation induced structural changes. However, for this degree of burnout, estimated to be ~ 50%, the soot particles followed a shrinking sphere model, but undoubtedly the rate varies as graphitization occurred.

6.1.3. Observations on Chemical composition and functional groups

The quantitative XPS measurements nevertheless showed a large proportion of inorganic carbon on the particle surfaces, adding more evidence that organic content is
integrated into the solid matrix throughout the bulk of the primary particles. This is consistent both with the TEM observations of particle nanostructure and with the difficulty in removing by VPR organics observed in SPLAT II mass spectra. This served as additional evidence of tightly integrated organic content within the elemental carbon matrix.

Attenuated total reflectance Fourier transform infrared spectroscopy analysis indicates significant matrix-distributed organic content. Previous results from SPLAT II suggested particles contained elemental carbon, polycyclic aromatic hydrocarbons, and inorganics, all tightly bound together within the same fractal structures.

6.2. Recommendations for future work

6.2.1. Additional diagnostic techniques that might be applicable

Optical emission spectroscopy (OES) based on a plasma excitation source is a useful detection method due to its linearity, sensitivity and because of the possibility of element-specific detection [64]. By its operation the plasma generates reactive ions, metastables and energetic electrons that maintain its operation free of contamination, permitting long-term use by providing device stability. The development of a permanent and steady glow discharge depends in greater part on the quality of the metalized disc elements. Demonstrating versatility for chemistry analysis, the plasma detector could distinguish carbonaceous aerosols with different C/H ratios.

Surface enhanced Raman spectroscopy (SERS) can provide positive identification of an analyte or an analyte mixture with high sensitivity and selectivity [65], [66]. The highlights of the technique include analysis of a molecule in situ, standoff detection,
well-established instrumentation, and little or no sample preparation with very high levels of sensitivity. In many papers, theory is dealt with by describing two mechanisms of SERS enhancement, electromagnetic enhancement and charge-transfer or chemical enhancement. Historically, these two mechanisms were thought to be quite different. In both, the analyte must be adsorbed on a SERS active substrate and the substrate irradiated by monochromatic radiation usually from a laser, and the resultant scattering analyzed using a Raman spectrometer. It is generally acknowledged that the electromagnetic effect is larger than the charge-transfer effect. The enhancement arises from one mechanism that is essentially the one described in the electromagnetic approach but with some elements of the charge-transfer approach. The main steps are as follows: (1) an analyte is adsorbed on a surface patterned or roughened so that the chosen excitation frequency will excite a plasmon and create scattering. (2) Energy from the plasmon is transferred to the adsorbed molecules and the Raman process occurs on the molecule. (3) Energy is transferred back to the plasmon less the amount transferred to the nuclei and scattered from the surface as wavelength shifted light.

6.2.2. Revised/Improved sampling procedures and setup

Different TEM grids are best for different analyses and are not interchangeable. Need to decide which analyses will be desired for each condition.

Cu grid with carbon film captures a lot of particles, including small aggregates. The film interferes with HRTEM and chemical analysis. The grid is good for primary particle size and aggregate morphology (when lightly loaded)
Lacey carbon grids are good for aggregate analysis especially if the aggregates are larger. Besides this the carbon thin film grid is only good for primary particle size and aggregation analysis purposes. In a high magnification image, the carbon thin film on grid will show up in the image too, both carbon thin film structure and soot structure will be seen in the image. Usually, the thin film structure will overlap soot nanostructure, so carbon thin film will be clearer than soot nanostructure. Therefore, for high resolution TEM images (soot nanostructure analysis), Lacey carbon grid will be best option.

For a better TEM image, a flat TEM grid sample is also important, because electron beam is coming from top of grid. Therefore, if the grid is bent, it will increase the difficulty to focus the soot particles under high Mag. Therefore, paying extra caution is important while inserting and taking out the grid from the clip holder.

A Gold grid allows chemical analysis by XPS. If there are enough grid clip holders, it will be a best option to leave bare/gold grid inside the clip holder after sampling (this will not only help and reduce operation time for XPS analysis but also acquire optimum XPS analysis result). Moreover, marking the soot deposited side is also recommended (exhaust air flow direction). If there are not enough holders, it will be also good if soot deposited side of grid can be marked or recorded. Then there is no extra effort for distinguishing soot deposited side and backside, and this will also help reduce chances for sample contamination.
Bibliography


Appendix A

Test emissions of the Cummins ISL 365 engine

During the three days of testing, the ISL 365 (medium duty diesel engine) was brought to steady state operating conditions of 2100 rpm and 195 Nm. Tables show flow, temperature, and emissions data collected for the three fuels.

<table>
<thead>
<tr>
<th>Load Time</th>
<th>Average DOC Inlet Temperature</th>
<th>Average CPF Inlet Temperature</th>
<th>Average CPF Temperature</th>
<th>Exhaust Mass Flow Rate (LFE)</th>
<th>Exhaust Volumetric Flow Rate (LFE)</th>
<th>Engine out PM Conc.</th>
<th>Test Cell Temperature</th>
<th>Test Cell Relative Humidity</th>
<th>Test Cell B.P.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minutes</td>
<td>°C</td>
<td>°C</td>
<td>°C</td>
<td>kg/min</td>
<td>scm/s</td>
<td>mg/scm</td>
<td>°C</td>
<td>%</td>
<td>in. Hg</td>
</tr>
<tr>
<td>Day One ULSD</td>
<td>277.9</td>
<td>263</td>
<td>258</td>
<td>259</td>
<td>12.6</td>
<td>0.173</td>
<td>16.0</td>
<td>28.3</td>
<td>13.7</td>
</tr>
<tr>
<td>Day Two B10</td>
<td>270.6</td>
<td>266</td>
<td>260</td>
<td>260</td>
<td>12.9</td>
<td>0.177</td>
<td>15.0</td>
<td>29.1</td>
<td>14.1</td>
</tr>
<tr>
<td>Day Three B20</td>
<td>415.9</td>
<td>267</td>
<td>263</td>
<td>262</td>
<td>12.9</td>
<td>0.178</td>
<td>13.8</td>
<td>29.0</td>
<td>16.6</td>
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<table>
<thead>
<tr>
<th></th>
<th>HC (ppm)</th>
<th>NOx (ppm)</th>
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<tbody>
<tr>
<td>UDOC</td>
<td>91</td>
<td>89</td>
</tr>
<tr>
<td>DDOC</td>
<td>89</td>
<td>86</td>
</tr>
<tr>
<td>DCPF</td>
<td>2</td>
<td>84</td>
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</table>

<table>
<thead>
<tr>
<th></th>
<th>NO (ppm)</th>
<th>NO2 (ppm)</th>
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<tbody>
<tr>
<td>UDOC</td>
<td>57</td>
<td>32</td>
</tr>
<tr>
<td>DDOC</td>
<td>62</td>
<td>27</td>
</tr>
<tr>
<td>DCPF</td>
<td>33</td>
<td>52</td>
</tr>
</tbody>
</table>

| ULSD | B10 | B20 |
Appendix B

Using D’Agostino’s test to check the goodness-of-fit of the lognormal distribution

D statistic is used to test the null hypothesis of normality or lognormality when \( n \geq 50 \). In this case the test is performed to check if the below data follows a lognormal distribution or not.

Assuming the significance level \( \alpha = 0.05 \) for \( n = 72 \) soot particle diameters which have been drawn at random from the target population. The null hypothesis to be tested is

\[
H_0: \text{The distribution is lognormal}
\]

versus

\[
H_A: \text{The distribution is not lognormal}
\]

<p>| | | | | | |</p>
<table>
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</thead>
<tbody>
<tr>
<td>8.703</td>
<td>12.697</td>
<td>15.054</td>
<td>16.931</td>
<td>20.467</td>
<td>26.82</td>
</tr>
<tr>
<td>9.928</td>
<td>13.159</td>
<td>15.926</td>
<td>17.41</td>
<td>20.672</td>
<td>28.166</td>
</tr>
<tr>
<td>10.809</td>
<td>13.42</td>
<td>15.952</td>
<td>17.5</td>
<td>22.16</td>
<td>31.232</td>
</tr>
<tr>
<td>10.879</td>
<td>13.76</td>
<td>15.963</td>
<td>17.905</td>
<td>22.384</td>
<td>31.974</td>
</tr>
<tr>
<td>10.949</td>
<td>13.772</td>
<td>15.987</td>
<td>17.927</td>
<td>23.988</td>
<td>32.871</td>
</tr>
</tbody>
</table>

1. Draw a random sample \( y_1, y_2, \ldots, y_{72} \) of size \( n = 72 \) from the population
2. Order the 72 data points from smallest to largest to obtain the sample order statistics
\[ y_{[1]} \leq y_{[2]} \leq \ldots \leq y_{[72]} \].

3. Compute the statistic
\[
D = \frac{\sum_{i=1}^{n} \left[ i - \frac{1}{2} (n+1) \right] y_{[i]}}{n^2 s}
\]
Where
\[
s = \left[ \frac{1}{n} \sum_{i=1}^{n} (y_i - \bar{y})^2 \right]^{1/2}
\]

Using spreadsheet the above parameters are calculated and the values obtained are
\[ s = 0.366534 \]
\[ D = 0.282328205 \]

4. Transform \( D \) to the statistic \( Y \) by using
\[
Y = \frac{D - 0.28209479}{0.02998598/\sqrt{n}}
\]

\[ Y = 0.06605 \]

5. Table A8 (Gilbert 1987) contains no quantiles of the \( Y \) statistic for \( n=72 \), Hence interpolating is done
   a. If \( n = 70 \), the \( \alpha/2 = 0.05/2 = 0.025 \) quantile is -2.652, and the 1-0.025 = 0.975 quantile is 1.176.
   b. If \( n = 80 \), Table A8 (Gilbert 1987) gives -2.613 and 1.226 for these quantiles.
   c. Linear interpolation between the 0.025 quantiles for \( n = 70 \) and 80 gives -2.6325 as the approximate 0.025 quantile for \( n = 72 \).
   d. The 0.975 quantile when \( n = 72 \) is similarly approximated to be 1.201.
6. Since $Y = 0.06605$ is neither less than $-2.6325$ nor greater than $1.201$, the null hypothesis of a lognormal distribution cannot be rejected. Hence we accept the hypothesis for the above data and the distribution is lognormal.
Appendix C

T-test for independent samples

This is the test of the mean between two distributions, are they different or not

- From the two distributions (as shown in the earlier slide) for the two different test conditions – the distributions are seemingly similar but somewhat different distributions

- Are they statistically different or not?

We can re-write these hypotheses as follows:

H₀: \( \mu_1 - \mu_2 = 0 \)

Hₐ: \( \mu_1 - \mu_2 \neq 0 \)

To test the null hypothesis, we’ll again compute a t statistic and look it up in the t table.

Steps for Calculating a Test Statistic (Independent Samples)

1. Calculate \( X_1 - X_2 \)
2. Calculate pooled variance
3. Calculate standard error
4. Calculate T and d.f.
5. Use Table A 2 (Gilbert)
STEP 1: Get mean difference

\[ \bar{X}_1 - \bar{X}_2 = 7.2 \]

STEP 2: Compute Pooled Variance

\[
s_p^2 = \frac{SS_1 + SS_2}{df_1 + df_2} = \frac{41 + 15.6}{(129 - 1) + (93 - 1)} = \frac{56.6}{220} = 0.257
\]
STEP 3: Compute Standard Error

\[ SE = \sqrt{\frac{s_p^2}{n_1} + \frac{s_p^2}{n_2}} = \sqrt{\frac{0.257}{129} + \frac{0.257}{93}} = 0.06 \]

STEP 4: Compute T statistic and df

\[ t = \frac{(\bar{X}_1 - \bar{X}_2) - (\mu_1 - \mu_2)}{s_{\bar{X}_1-\bar{X}_2}} = \frac{(23.37 - 16.17) - 0}{0.06} = 104.3 \]

\[ d.f. = (n_1 - 1) + (n_2 - 1) = (129 - 1) + (93 - 1) = 220 \]

STEP 5: Use table A2

\[ t = 104 \text{ with 220 degrees of freedom} \]

For alpha = .01, critical value of \( t \) is 2.57

Our \( t \) is more extreme, so we reject the null hypothesis

There is a significant difference between the means calculated for two test conditions
Appendix D

Deconvolution of C 1s high-resolution XPS scan

In this section, the raw spectra (before exporting to Kaleidagraphtm) as seen in CASA XPS software is shown for all the five different engine operating conditions. The idea is to show the residual fit and residual standard deviation.

Figure B.1 High resolution XPS spectrum over the C1s Region of soot generated from SIDI engine at Late EOI operating condition (residual STD – 3.4)
Figure B.2 High resolution XPS spectrum over the C1s Region of soot generated from SIDI engine at Rich operating condition (residual STD – 4.7)

Figure B.3 High resolution XPS spectrum over the C1s Region of soot generated from SIDI engine at Baseline operating condition (residual STD – 1.2)
Figure B.4 High resolution XPS spectrum over the C1s Region of soot generated from SIDI engine at Lean operating condition (residual STD – 2.6)

Figure B.5 High resolution XPS spectrum over the C1s Region of soot generated from SIDI engine at High Load operating condition (residual STD – 1.2)
VITA

Chethan K. Gaddam

Education

Ph.D., Energy and Mineral Engineering 01/2012 – Present
The Pennsylvania State University, University Park, PA
Specialization: Fuel Science

The Pennsylvania State University, University Park, PA
Specialization: Fuel Science

Chaitanya Bharati Institute of Technology (OU), Hyderabad, India