A Study of the Effects of the Properties of Fuel, Compression Ratio and EGR on Diesel Exhaust Soot Physiochemical Characteristics

By

Edward Winward, MEng

Supervisors: Prof Rui Chen & Dr Graham Wigley

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Loughborough University

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Abstract

This research work characterises diesel engine soot physiochemical properties and engine performance and emissions for the combustion of two common mineral diesel fuels (low and medium sulphur) and a RME B100 biodiesel fuel at two geometric compression ratios (19.5:1 and 16.5:1) and a broad range of EGR (10 to 55%) for an otherwise unmodified VW 1.9TDI 130PS engine. The principal focus of the research is the physiochemical characterisation of soot sampled from the engine exhaust manifold and also a DPF in the exhaust and exploring how the fuel type, compression ratio and EGR influence the soot properties and how these properties then influence the evolution of the soot in the exhaust.

A broad set of soot physiochemical characteristics have been studied which include: surface elemental composition, bulk elemental composition, surface area, porosity, density, primary particle diameter, surface acidity, PAH profile and thermogravimetrical analysis. Together these physiochemical characterisations have revealed fundamental insights concerning the signature differences between conventional mineral diesel and biodiesel soots and how these differences can influence the evolution of the soots in the engine exhaust.

Key findings: The mineral diesel soots were largely similar apart from sulphur deposition and its associated effects for the medium sulphur fuel. In comparison, the RME B100 soot was observed to be morphologically quite different and to also have a 1.2 - 1.8x greater oxidation rate in the exhaust compared to the mineral fuel soots. Fuel sulphur was confirmed to be a primary factor for causing distinct changes in soot surface chemistry, bulk chemistry and affecting soot transformation in the exhaust system. A correlation of soot carboxylic surface acidity to soot surface O/C ratio revealed a linear relationship for most soots but there was observed to be a 'knee point' at an O/C ratio of ~0.07, below which carboxylic and total surface acidity went to zero very abruptly and this region of the O/C ratio was populated by the soots produced at high EGR. An overall 5% reduction in BMEP and increase in BSFC occurred with the engine compression ratio reduction and the particulate and gaseous emissions changes were found to be sensitive to manifold air temperature. The reduction in compression ratio also reduced the soot surface O/C ratio, reduced the medium sulphur fuel soot surface sulphur concentration 97% and increased lubricant consumption which increased the soot contamination from inorganics. Injector coking was 2-4 times higher for the B100 fuel and worse at the lower compression ratio whereas the mineral fuel coking sensitivity was unchanged.

Keywords: Diesel Engine, Soot, Physiochemical, Morphology, Diesel Fuel, Biodiesel, Sulphur, Compression Ratio, EGR

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Glossary

Nomenclature

Y	Gamma (Ratio of specific heats C_p/C_v)
\dot{m}_{air}	Mass flow rate of intake charge with EGR (kg/h)
\dot{m}_{egr}	Mass flow rate of EGR gas (kg/h)
\dot{m}_{zero}	Mass flow rate of intake charge without EGR (kg/h)
$\eta_{\scriptscriptstyle vol}$	Volumetric Efficiency (%)
P_{comp}	Compression Pressure (bar)
P ₀	Pressure in the cylinder at bottom dead centre (bar)
$ ho_{man}$	Charge density in intake manifold with EGR (kg/m ³)
$ ho_{\scriptscriptstyle zero}$	Charge density in intake manifold without EGR (kg/m ³)
Pzero	Intake manifold charge pressure without EGR (bar)
P _{man}	Intake manifold charge pressure with EGR (bar)
T _{man}	Intake manifold charge temperature with EGR (K)
T _{zero}	Intake manifold charge temperature without EGR (K)
V_{swept}	Swept volume (m ³)
d	Primary soot particle diameter
Ν	Engine revolutions per second
r	Primary soot particle radius
R	Characteristics Gas Constant
Vc	Clearance Volume
Vs	Swept Volume
H _c	Clearance Height
R _c	Compression Ratio

<u>Acronyms</u>

AAS	Atomic Absorption Spectroscopy
ACEA	European Automobile Manufacturers Association
AFR	Air Fuel Ratio
API	American Petroleum Institute
ASTM	ASTM International - formerly the American Society for
	Testing and Materials
ATDC	After Top Dead Centre
B30	30% Biodiesel Fuel and 70% Diesel
B100	100% Biodiesel Fuel
BDC	Bottom Dead Centre
BET	Brunsuer, Emmett and Teller Model
BMEP	Brake Mean Effective Pressure
BJH	Barrett-Joyner-Halenda Model
BSFC	Brake Specific Fuel Consumption
CAD	Crank Angle Degrees
CARB	California Air Resources Board
CAT	Catalyst
CEN	Committee European de Normalisation
CI	Compression Ignition
СО	Carbon Monoxide
CR	Common Rail
СТ	Ceramic Thimble
DCPS	Diffusion Charging Particle Sensor
DI	Direct Injection
DPF	Diesel Particulate Filter
ECU	Engine Control Unit
EDAX	Energy-Dispersive X-ray Spectroscopy
EIA	US Energy Information Administration
EGR	Exhaust Gas Recirculation
EPA	Environmental Protection Agency
ESCA	Electron Spectroscopy for Chemical Analysis
EU	European Union
EUDC	Extra Urban Driving Cycle
Eurol	European Emission Standard
EurolV	European Emission Standard IV
EuroV	European Emission Standard V

EuroVI	European Emission Standard VI
FMEP	Friction Mean Effective Pressure (bar)
FSF	Fuel Soot Fraction
GC-MS	Gas Chromatography Mass Spectroscopy
GM	General Motors
HC	Hydrocarbon
HD	Heavy Duty
HEI	Health Effects Institute
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
IDI	Indirect Injection
IMAT	Intake Manifold Air Temperature
IOF	Insoluble Organic Fraction
IMEP	Indicated Mean Effective Pressure (bar)
INJ	Injection
IR	Infrared-Spectroscopy
LD	Light Duty
LTC	Low Temperature Combustion
M11	Cummins M11 High Soot Test
MAF	Mass Air Flow
MD	Medium Duty
NIST	National Institute of Standards and Technology
NO _x	Nitrous Oxides
OEM	Original Equipment Manufacturer
PAH	Polycyclic Aromatic Hydrocarbon
PAS	Photoelectric Aerosol Sensor
PM	Particulate Matter
PM10	Particulate Matter (10 Micrometres or less)
PM2.5	Particulate Matter (2.5 Micrometres or less)
RME	Rape-Seed-Methyl Ester
SAE	Society of Automotive Engineers
SCR	Selective Catalytic Reduction
SCS	Sonex Combustion System
SEM	Scanning Electron Microscopy
SI	Spark Ignition
SOF	Soluble Organic Fraction
SMPS	Scanning Mobility Particle Sizing

SOI	Start of Injection
SRM	Standard Reference Material
TDC	Top Dead Centre
TDI	Turbocharged Direct
TEM	Transmission Electron Microscopy
TGA	Thermal Gravimetric Analysis
TPD-MS	Temperature Programmed Desorption Mass Spectroscopy
UHV	Ultra-High Vacuum
US	United States
WHO	World Health Organisation
VGT	Variable Geometry Turbocharger
VOF	Volatile Organic Fraction
VW	Volkswagen Group
XPS	X-Ray Photoelectron Spectroscopy
ZDDP	Diisopropyl Dithiophosphate
ZDP	Zinc Dithiophosphate
ZDTP	Zinc Dialkyl-dithiophosphate

Chapter 1

1 Introduction

The popularity of the diesel engine for use in light-duty automotive applications has steadily grown in Western Europe with the European Automobile Manufacturers Association (ACEA) stating growth from 30% market share in 1999 to over 60% present day [1]. This growth has been driven by the greater sensitivity of the motorist to fuel economy during this time as fuel prices and the cost of motoring have risen steadily. The improvement in the performance attributes off the diesel engine has also played a role in the engines' popularity and this has come about in parallel with the increasingly sophisticated technologies utilised for emissions reductions with the increased specific power of present day diesel engines' meeting or exceeding the performance of equivalent gasoline engines'.

However, the increase in popularity has slowed in recent years as diesel powered vehicles have come to have an associated cost premium [2] due to the needs of engine manufacturers to implement expensive technologies both in the engine and the exhaust to meet the ever tightening Particulate Matter (PM) and Nitrous Oxide (NO_x) legislation. This has been coupled with a disparity in fuel prices with diesel now generally more expensive than gasoline since 2004 which is explained by the US Energy Information Administration (EIA) to be due to the increased diesel demand and the costs refineries have faced in upgrading to meet low sulphur diesel fuel legislation [3]. Consequently, it is now estimated the average motorist needs to own a diesel vehicle for at least 14 years to recoup these additional costs through the diesel engines renowned increased efficiency [2]. This cost of ownership equation could continue to balance further against the diesel engine and therefore innovation is needed to mitigate this by more cost effectively meeting legislative emissions requirements through research.

This growth in the popularity of the light duty diesel engine and its continued dominance of the medium and heavy-duty on-road and off-road markets has only been possible by the revolutionary developments in the engine fuel injection system, the air management system, the aftertreatment system and the engine control system. Between Euro II and Euro IV it was largely the combination of

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Aims and Objectives

fuel direct injection at increasingly higher pressures and more sophisticated control combined with turbocharging (multi-stage), Exhaust Gas Recirculation (EGR) and lower compression ratio which provided the performance and exhaust smoke improvements required. From Euro IV onwards in larger engines this combination of technologies was no longer sufficient and thus the then maturing Diesel Particulate Filter (DPF) technology which had come from over 20 years of development started to become increasingly common.

The 80% reduction in NO_x demanded for the transition from Euro V to Euro VI is now forcing engine manufacturers to use much higher levels of EGR on smaller engines and the deployment of selective catalytic reduction with urea based fuel additives and catalysed DPF traps on larger engines. In combination with all these fundamental engine technology changes there has also been a significant shift in the diesel fuel market with the use of biodiesel increasing through legislative measures both in Europe and in the US in particular [4].

The increasing dependence on the use of DPF technology and the growth in proportion of alternative fuels have placed great emphasis in recent years on an improved understanding of diesel engine PM emissions, especially the physiochemical surface and bulk characteristics of the dry carbonaceous part of diesel PM which is often referred to as soot. This is because the regeneration performance of DPF systems, whether they are catalysed or non-catalysed, has proven to be sensitive to soot properties [5]. In turn, the soot properties are sensitive to fuel, engine operating condition, EGR etc. and can evolve in the exhaust system as the soot trapped in the exhaust gas is subject to the combined processes of oxidation and condensation of volatile exhaust products [6].

1.1 Aims and Objectives

The *primary aim* of this work is to identify elemental and physical changes in soot surface, bulk chemistry and morphology that result from: 1) the use of mineral diesel (low and medium sulphur) and biodiesel fuels 2) changes to the pressures and temperatures in-cylinder during combustion (achieved through engine geometric compression ratio change) and 3) the effect of high levels of EGR (>50%).

A secondary aim of this work is to identify how changes to soot physiochemical and morphological characteristics influence the subsequent evolution of the soot as it is conveyed from the exhaust manifold to a DPF in the exhaust system.

1

Background and Motivation

This work therefore seeks to extend the present understanding of the influences of mineral/biodiesel fuel, geometric compression ratio and EGR on the soot trapped in a DPF to provide information to help in the development and optimisation of exhaust filtration systems.

1.2 Background and Motivation

1.2.1 Brief Synopsis of the Diesel Engine, Soot and Relevant Trends and Legislation

One of the primary concerns with diesel combustion is the production of PM. This consists largely of carbon (soot) but also other organic and inorganic products of fuel pyrolysis and combustion. The primary particle diameter of these soots is typically 15-30 nm upon exit from the cylinder but they then grow into aggregate structures of several hundred nanometres as they move down the exhaust and later mix with the ambient air resulting in a broad size distribution. Diesel engine exhaust PM therefore has a complex physiochemicalmorphological description which derives from the fuel and conditions/composition during combustion and the conditions/composition of the exhaust gas.

Studies on the toxicology and multiagency of diesel engine PM have grown in number in recent years and show that beyond the short term impairment of breathing in some people there are also longer-term risks of permanent lung damage and even cancer. Recent studies have also shown that the latest diesel engine technology can cause increased emission of smaller nano-sized particulates which are known to be more dangerous as they can penetrate deeper into the alveoli of the lung. The importance of this escalated very recently with the World Health Organisation (WHO) officially elevating diesel engine PM from a potential to a known carcinogen which was announced 12th June 2012 [7]. This was because of an increasing weight of evidence of a negative impact from PM on human health and increasing problems in major cities with high concentrations of aerosols from an ever larger population of diesel vehicles.

As part of the Euro V-Euro VI legislation the European Union has begun the introduction of particulate number based restrictions for engine emissions [8] to ensure that the reduced mass of particulate matter from modern engines is not causing a higher proportion of the more dangerous smaller nano-particles. This is likely to encourage the more widespread adoption of DPF technology on newer engines and the retrofitting of older vehicles with the technology. There is

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Background and Motivation

therefore continued pressure to better optimise and improve the design of these particulate filter systems. This highlights the relevancy and importance in engine research for improving the knowledge and understanding of diesel engine soot physiochemical properties.

The question of the importance of the fuel in regard to diesel engine soot has reduced on the one hand with the widespread introduction of low sulphur fuels which help to reduce the total PM and are also necessary for Selective Catalytic Reduction (SCR) systems to avoid catalyst poisoning. However, on the other hand there has been growth in the use of biodiesel and biodiesel fuel blends in the last decade which has been encouraged by legislation in Europe {EU Renewable Energy Directive 2003/30/EC} [9] and America {Environmental Protection Agency, Renewable Fuel Standard} [10]. In the UK, the government have set a target for 5% {Renewable Energy Directive} [11] of fuel to come from renewable resources by 2013/2014 which follows from the EU directive mandating a target of 10% by 2020. In America the EPA mandates the blending of 3.1 billion litres of biodiesel into the petroleum fuel, which is less than 2% of the annual consumption [12, 13].

There have been increases in food prices which have been partly attributed to the reallocation of agricultural land and there is growing evidence for less than expected real-world lifecycle reductions in net CO_2 emissions. Together these are highly likely to result in freezing of policy nearer to the current EU average of 4.5% biofuels (78% share of which is biodiesel) with recent news reports indicating an impending EU policy update [14]. The UK government commissioned independent Gallagher Review (indirect effects of biofuels production) [15] is a good example of the raised concerns about the sustainability of biofuel targets above 5% with first generation biodiesel fuels. However, as things stand, biodiesel is already a part of the transport fuel system and it is thus an important factor in diesel engine soot research. In Europe rape seed is the most significant biodiesel fuel feedstock in use whereas elsewhere soybean, palm oil and canola oil are popular. Several references in literature agree that in addition to the widely reported reduction in PM mass when combusting biodiesel, the soots have also been observed to have a much higher rate of oxidation in the exhaust which has been observed to correlate to a different physical mode of oxidation Song et al. [16] though the fundamental reasons for this are not completely understood Song et al. [17].

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As the nucleation and growth process for particulates is complex and dependent upon a broad array of inter-related variables such as fuel, lubricating oil, injection system, combustion chamber geometry, air motion etc. it is necessary to research into the effects each of these individual variables in order to understand the overall collective effect. Two important parameters are the cylinder pressure and temperature which influence the formation process of soot. For example, Wal et al. [18] detail that pressure/temperature affect the soot nanostructure which then leads to different oxidation properties of the soot.

EGR has become ubiquitous on diesel engines as a technique for reducing exhaust NO_x but it also increases the amount of PM and has been shown to influence the primary particle diameter Zhu et al. [19]. The further 80% reductions in NO_x emissions between Euro V and Euro VI will likely see increased use of EGR and even cooled EGR and some of alternative diesel combustion modes being actively developed today such as Low Temperature Combustion (LTC) use very high rates of EGR [20] and thus the use of very high EGR is an important research area when considering diesel engine soot.

1.2.2 Important Research Topics

By combining the practical diesel engine engineering challenges faced today with available knowledge, it is possible to identify the key topics which need addressing in diesel engine research in relation to the understanding of soot physicochemical properties:

- Medium/low Sulphur Mineral Fuel (US and European) of Different Origin – What are the differences in soot physiochemical characteristics arising from two mineral fuels from different feedstock and with different sulphur content such as those typically used in Western Europe and the United States?
- 2. Rape Seed Methyl Ester (RME) B100 Soot Oxidation Research indicates that biodiesel soot has a higher oxidative reactivity and thus lower DPF break even temperature (temperature at which a catalysed DPF's regeneration rate matches the soot deposition rate) [17]. Thus, what are the distinguishing physiochemical-morphological characteristics of mineral and biodiesel soot which impact on soot oxidation rate in the exhaust?
- Cylinder Pressure-Temperature During Combustion Research shows that the conditions during the pyrolysis and combustion of diesel

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Contributions of This Work

fuel (such as local temperature and pressure) affect the physiochemicalmorphological characteristics of the soot [21]. Thus, how has the compression ratio reduction trend of the last decade potentially affected soot physiochemical-morphological characteristics?

4. Very high rates of EGR – The last decade has seen extensive research of alternative diesel engine combustion modes such as LTC which utilises high rates of EGR (>50%) as a way to achieve smoke-less, NO_x-less combustion [20]. In what ways do such a high levels of EGR influence soot physiochemical-morphological properties for mineral and biodiesel fuels, does the soot produced by these two fuels respond the same to high EGR?

1.3 Contributions of This Work

This thesis has the following contributions to knowledge:

- A positive linear correlation has been identified between soot surface carboxylic acid concentration and soot surface O/C ratio between an O/C ratio of (~ 0.07 to 0.12); this applies to mineral and biodiesel soot with surface sulphur concentrations (< 0.3%) weight with the following exceptions:
 - Surface sulphur concentrations (>0.3%) weight lead to substantially higher carboxylic surface acidity than is described by the O/C ratio correlation of contribution 1.
 - b. At high rates of EGR (~55%) both mineral and biodiesel soot was observed to have no surface acidity and this correlated with a soot surface O/C ratio (<0.07), this produces a 'knee' in the linear correlation of contribution 1.
- The reduction in compression ratio reduced the medium sulphur (497 ppm) mineral fuel soot surface sulphur concentration by 97%. This surface sulphur reduction influenced the surface acidity as outlined in contribution (1a).
- At high rates of EGR (~55%) the *low exhaust O₂ concentration (1.93-3.09%) and low NO_x concentration (23-24ppm) suppressed the oxidation based soot surface O/C ratio increase* in the exhaust system and is thought to be the causative effect of contribution (1b).
- The B100 soot exhaust evolution through oxidation was distinct from that of the mineral fuel soot in that it *typically increased in surface O/C ratio by a*

1 1.3 Contributions of This Work

> factor of 1.2 to 1.8 relative to the mineral fuel soots and had associated large changes in surface area, porosity and density.

5. When PAH were detected, the PAH molar mass profile analysis showed a preference for the PAH molar mass 178 g/mol (Phenanthrene,

Anthracence) for all mineral and biodiesel fuels, speed/load, compression ratio, exhaust sample location and EGR condition.

2 Literature Review

2.1 Introduction

This chapter presents a literature review of diesel engine particulate matter with the emphasis on the carbonaceous soot part. First the human health and environmental impact of soot is considered which highlights the importance of improving understanding of soot physiochemical properties. This is then followed by a factual and quantitative review of the physiochemical characteristics of soot reported in literature with the emphasis on the properties investigated in the research work reported herein.

2.2 Definition of Particulate Matter and Soot

Soot is not a clearly and consistently defined substance in literature [22] and it is therefore important to outline several definitions utilised throughout this work.

2.2.1 Particulate Matter

In this work particulate matter (PM) is used to describe the combined solid and liquid-phase materials that are collected when engine exhaust gas is filtered as occurs in an emissions homologation test. The morphology of this PM at the exhaust exit can be summarised as a highly agglomerated solid carbonaceous material with condensed soluble fraction which is formed into aggregate structures of multiple primary particles [23, 24].

2.2.2 Soot

The *solid-phase material* of PM is referred to in this work as *soot* and is sometimes called the solid organic fraction. This carbonaceous soot forms in locally fuel rich regions [24] and constitutes a variable fraction of the total particulate matter of usually 50% or more [22]. This is the cause of the traditional black smoke emissions from diesel engines. Diesel engine soot at the exhaust manifold physically is composed of nanometre sized particles of broad size distribution from the 10 nm scale (nucleus formed from several primary 1-2 nm

Definition of Particulate Matter and Soot

nuclei with a defined outer shell) to over 30 nm (coagulation of multiple primary 1-2 nm nuclei surrounded by ordered graphene planes which form an outer shell).

The composition of diesel engine soot is dominated by carbon as it originates from unburned fuel during combustion of hydrocarbon fuel and this carbon dominated composition changes as the soot ages from the first inception in fuel-rich regions and subsequent oxidation. Newly formed soot can have an initial H/C ratio as low as 1 and then as the soot matures this ratio can increase to over 8 [22, 25]. The solid-phase soot when filtered from the exhaust also has inorganic components entrained and these include wear metals from the engine and sulphur, calcium, phosphorous and zinc from the burned/partially burned fuel and lubricant [26, 27]. The inorganic metallic contaminates are usually grouped together and are referred to as 'ash' [24] which is the remaining residue when soot has been heated to over 700°C.

This work focusses on characterising this solid-phase soot component of diesel engine PM and in this work **soot** is used throughout to describe this.

2.2.3 Soluble Organic Fraction

The soluble-phase material of PM is referred to in this work as the *Soluble Organic Fraction (SOF)* [23] but is also sometimes called the Volatile Organic Fraction (VOF). SOF is composed of hydrocarbons or other molecules which are the unburned fraction of the fuel and atomized and evaporated lubricant and in some cases hydrocarbons from the engine and exhaust wall deposits [24, 28]. These can either condense onto the soot surface or can nucleate to form fine drops in the dilute exhaust [24] or both depending upon the surrounding conditions in the exhaust such as temperature [6] and saturation ratio [24]. SOF is comprised of Polycyclic Aromatic Hydrocarbon (PAH) compounds, nitrogen and sulphur [24]. The SOF fraction of PM can range from less than 10% to more than 90% by mass and is a function of engine operating condition, being highest at light engine loads when exhaust temperatures are relatively low [24].

2.2.4 Sulphates

Sulphates in PM have traditionally come from the organic sulphur compounds in the fuel [29] when sulphur concentrations in the fuel were (>50 ppm) but with the widespread adoption of Ultra-Low-Sulphur Diesel fuel (ULSD) with (<10ppm) sulphur, the sulphate component has been reduced significantly. The sulphur is typically oxidised to SO₂ with a smaller fraction (approximately 2% [30]) being

 SO_3 that quickly reacts with water to produce sulphuric acid droplets {boiling point 330°C [31]} and sulphate aerosol [24].

2.3 Soot: Health and Environmental Considerations

PM are distributed throughout the atmosphere and have many sources both natural and anthropogenic, some of these sources include: skin tissue, plant materials, and wildfires, dust from space, construction sites, process wear, and combustion processes [29].

When carbonaceous soot is released into the atmosphere from the exhaust of an engine it becomes an aerosol and as a result of its physical size, size distribution, composition and colour etc. it can have consequences for human health, atmospheric weather and also when it leaves the atmosphere it can pollute the soil [29, 32]. Consequently, engine PM emissions are tightly regulated with low emitted mass limits (g/kWh) and also newly introduced particulate number emissions limits as part of Euro V and VI in the European Union. The introduction of particulate number legislation follows reports which state that the technologies introduced to reduce PM mass are leading to increases in the number of nanoparticles [33] and that there is a possibility the number of particles and the characteristics of them (size, composition) have a higher impact on health [29]. For example, particulate traps have become increasingly common as a result of the tightening PM legislation and these can achieve a really dramatic reduction in particulate emissions (typically > 99% for solid particles) [6]. However, there are reports that whilst particulate traps reduce the mass of soot emissions, they may also shift the size distribution to smaller particles [33, 34].

2.3.1 PM and Health Concerns

Diesel engine exhaust is composed of many components of potential health concern including: PM, NO_x, Carbon Monoxide (CO), and a number of air toxics {e.g., aldehydes, volatile organic compounds, PAH} [35, 36].

Carbon based PM in the atmosphere is grouped into two categories; *black carbon* and *organic carbon*. Black carbon is defined optically by measuring the change in light transmittance, reflection or absorption caused by particles [37]. Carbon particles collected on a filter usually attenuate light more than suspended particles [38-40] and most studies that characterise carbon particulates measure the elemental carbon rather than black carbon [37]. This black carbon has a relatively short residence time in the atmosphere compared to other

anthropogenic pollutants of concern, being estimated to remain in the atmosphere for about a week [41-43]. Organic Carbon is a term used most commonly in climate research to distinguish the carbon fraction of PM which is not black [37] and can describe 1000's of different organic compounds.

2.3.1.1 Anthropogenic PM Emissions

The black carbon of PM global emissions enters the atmosphere from burning of both biomass (wood, agricultural wastes, etc.) and fossil fuels and regulations in most developed countries have forced down the amount emitted by these counties. However, rapidly growing economies in China and India have been emitting large amounts of black carbon into the atmosphere [44] in recent years.

Total global annual emissions estimates for black carbon and organic carbon in literature have a large spread. Lamarque et al. calculate that 5.02 Tg/year of black carbon is going into the atmosphere and that the rate is increasing, additionally, around 12 Tg/year of organic carbon is emitted and this is also increasing [45]. Bond et al. suggest that 8.0 Tg/year for black carbon and 33.9 Tg/year for organic carbon are emitted [37]. This work also estimates the relative contributions of fossil fuel, biofuel, and open burning are as 38%, 20%, and 42%, respectively for black carbon. These percentages are 7%, 19%, and 74% respectively for organic carbon. Chughtai et al. estimate that 8Tg/year of soot is emitted globally and accounts for about 5% of the total mass of anthropogenically produced aerosol [46]. Thus, in literature there is a consensus of 5-8 Tg/year of total anthropogenic black carbon emissions currently.

In the case of PM emissions from internal combustion engines; Diesel engines generate up to 100 times more PM than equivalent sized gasoline engines [47, 48, 49]. Thus, research has traditionally focussed on diesel engine PM emissions.

2.3.1.2 PM Size and Atmospheric Concentration

The human body has the capability to protect against particulate matter but for particles below 10 μ m (10,000 nm) the measures the body uses are less effective and this group of particles have been defined as PM10 and describe the *respirable* PM fraction [24, 47]. Indeed, the particle size is the most relevant factor for the respirability of soot [34]. It is estimated 70-80% of particles with diameters between 1 and 7 μ m are deposited in the nose and throat and never reach the lung.

As the particle size gets smaller, the respirability increases and thus a second PM size designation exists PM2.5 which describes PM of less than 2.5 µm (2500 nm) in diameter. It is believed that this class of PM are responsible for much of the health effects attributable to PM10 as the much smaller size of the particles means they can penetrate much deeper into the lungs and do more harm [50-52] Tsolakis et al. report that PM2.5 appear to have considerably enhanced toxicity per unit mass as compared to coarser particles between PM2.5 and PM10 [53]. PM2.5 particles can also remain suspended in the atmosphere for longer periods than larger particulate matter and can be transported by winds over long distances. In the atmosphere the concentrations of PM10 are seasonal, varying from low in the summer to high in the winter months.

The concentration of diesel engine PM is variable with population density with differences of more than 35% between rural and the higher concentrations in urban areas. For example in the United States the average concentration is estimated to be 2 mg/m^3 but concentrations can approach $20 - 25 \text{ mg/m}^3$ when measured local to the source such as at the side of the road [54-57]. Close to a busy road, particle numbers are increased by a factor far greater than their mass [58].

2.3.1.3 Diesel Exhaust - An Official Carcinogen

Diesel exhaust had long been considered as simply dirty, smelly and generally unpleasant with diesel particulate regarded as a nuisance dust but then in the 1970s the first evidence of potential negative health effects were demonstrated [59]. In 1988 with an increasing weight of evidence the World Health Organisation (WHO) first classified diesel engine particulate as a *potential carcinogen*. This designation then persisted for over 20 years but as the body of evidence linking diesel exhaust to human respiratory system impairment continued to grow, the WHO declared 12th June 2012 that *diesel engine exhaust is carcinogenic* to humans [7]. Although the official designation occurred in 2012, legislators had been implementing PM emissions limits for much of the period since the WHO's first clarification with ever more restrictive mass-based limits.

2.3.1.4 Associated Health Effects

The susceptibility of humans to ambient ultrafine particles is known to vary amongst individuals [60-62] with a period of only brief exposure observed to cause acute short-term symptoms such as irritation of the eyes and nose and throat, breathing difficulty, wheezing, dizziness, nausea and headache.

Persistent exposure to diesel exhaust over longer periods, such as experienced by mine workers, construction, and road workers has been associated with more serious health problems such as lung cancer, cardiovascular and cardiopulmonary disease [63-65]. Indeed, many studies have shown that exposure to increased levels of respirable particulate is associated with increases in mortality and morbidity from cardiovascular and respiratory causes [66-70].

Rissler et al. have found when studying how diesel engine soot gets lodged in the lungs that in some cases more than half of the exhaust soot inhaled by healthy volunteers can remain in the body [60]. This is of great concern as cancer studies in experimental animals have shown that carcinogenicity appears to be due to the particulate component of the exhaust, because the filtered vapour phase of exhaust does not cause lung tumours [71].

Human trials have shown that exposure to diesel exhaust of both healthy and asthmatic individuals can cause airway inflammation though the evidence is contradictory as to whether asthmatics suffer more from exposure [47, 54]. The biological pro-inflammatory response to diesel exhaust exposure is reported to have an associated threshold exposure level which is 300 mg/m³ and which is likely dependent upon the gaseous/particulate composition [54]. Somers et al. even indicate that particles can induce inheritable mutations [72].

Though there is significant literature reporting on the links of PM to human health; the development of accepted and therefore established biological mechanisms to explain the underlying effects has remained elusive [34, 47, 63].

2.3.1.5 Mortality Rates

The WHO estimates that there are more than half a million excess premature deaths a year caused by PM globally [47]. Individual countries official statements suggest quite wide ranging estimates for diesel soot mortality rates. In the UK the most recently reported government advice is that there are 35,000 excess deaths per year from air pollution which is equivalent to a reduction of between 7-8 months on everyone's life [73]. In Germany it has been estimated that in 2001 there was at least 14,400 deaths from diesel soot exposure out of the German population of 82 million [74]. In the United States it is estimated that there are 22,000-52,000 deaths per year caused by PM pollution [75].

2.3.1.6 Physiochemical Characteristics and Associated Concerns

Diesel engine PM as described earlier has diverse physiochemical characteristics and consequently the severity of the concern associated with PM is a function of these physiochemical characteristics [76]. The smaller the particle the greater the penetration into the lung and also the greater the surface area for the same overall particle mass respired, thus the higher the potential activity of the particles in the lung [24]. The toxicity of the particles is also a function of the particle bulk composition, morphology and surface composition [24, 35].

With the expanding research into the health impact of diesel exhaust PM, there has been a growing recognition that other particle characteristics may have a more significant impact on health than total particulate mass [24]. This is because over 90 % of diesel particles are below 0.1 μ m (100 nm) in diameter and constitute between 1-20 % of the mass [24]. Consequentially, Setten et al. advocate the incorporation into legislation of a measure of diesel PM toxicity [29].

The physiochemical properties of soot produced in diesel engines are a function of the fuel, engine, combustion conditions etc. and thus the reported measured parameters in literature for diesel soot are often broad. This is discussed in more detail in Section 2.4.

2.3.1.6.1 Engine, Fuel and Operating Conditions

Su et al. state that for the same mass concentration, soot particles produced under low-emission conditions exhibit a much higher toxic and inflammatory potential than particles from an old diesel engine operating under black smoke conditions [77]. This was ascribed to the surface structure of the soot from a Euro IV diesel engine being more active, thus a soot mass restriction for such an engine may fail to reduce the overall toxicity to humans.

Rissler et al. found that the deposited number of particles in the lungs of volunteers was much higher when exposed to diesel engine exhaust gas from an idling engine than during transient driving conditions [60]. This was isolated to the presence of a nucleation mode for which the probability of deposition was high [60]. Sehlstedt et al. also investigated the effects of diesel exhaust for a vehicle running the European Transient Cycle on 15 healthy subjects and determined there were was different sensitivity to different particles from different engine operating conditions and these differences were identified to relate to differences in the exhaust composition [78].
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Bagley et al. report that the reduction in fuel sulphur content resulting from legislation change, whilst giving a benefit of 90% reduction in particle numbers, may have resulted in increases in the mutagenicity of the particle phase due to resultant fuel compositional changes [79].

2.3.1.6.2 Particle Number and Particle Size

There is evidence in literature that soot particle number is more important than the mass concentration in respect to human biological response [80, 81]. Schraml et al. support this by stating that there is a strong indication the diesel soot particle size distribution is just as important, if not more so, than the mass concentration in terms of the health hazard [34].

Rissler et al. comment that differences in soot particle size, morphology, volatile vs. core mass fraction, etc. may explain differences and similarities in cardio-respiratory responses [60]. Salvi et al. state a similar opinion that soot particle size may have distinct effects on the airways [47].

Some studies have shown that the smaller the particle, the greater inflammatory response in the alveolar space and which is thought to be related to the larger surface area of the smaller particles [6, 34, 82, 83, 86]. Furthermore, Donaldson et al. consider smaller particles to have a higher respirability and are easily deposited in the respiratory tract and in the alveolar region by diffusion and are thus more likely to cause respiratory diseases, inflammation, and damage to the lungs [84]. Research by Oberdörster et al. indicates that the smaller soot particles can potentially penetrate the cell membranes and enter into the blood and even reach the brain [85].

2.3.1.6.3 Particle Surface Composition and Area

Results in literature suggest that there is a good correlation between inflammatory responses and soot surface area measured using the surface area measurement method utilised in this work [6, 85, 86], see Section 3.6.4.1.

The surface chemical composition of the particle is reported to be important in determining the pulmonary oxidative stress [6] and a recent study has found that soot oxygen surface chemistry can have significant negative health consequences [77].

When soot leaves the engine exhaust and becomes an aerosol in the atmosphere, further changes occur particularly to the soot surface which can include the addition of material and oxidation. These can change the

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hydrophilic/hydrophobic properties of soot and increase the probability of soot acting as cloud condensation nuclei.

2.3.1.6.4 Particle Bulk Composition

There are several components in diesel engine exhaust soot which are of toxicological concern and include: elemental carbon, organic carbon, PAH, nitro-PAHs, dioxins/furans and metals [35]. The transition and rare earth elements in soot may be released in aqueous, buffered environments as found in lung and epithelial tissue of the intratracheal pathway [63]. It is proposed that the deposition of these metals on the lower airway may lead to the generation of hydroxyl radicals which in turn would cause both acute and chronic lung injuries [87, 88].

2.3.1.6.5 Polycyclic Aromatic Hydrocarbons (PAH)

Diesel engine exhaust soot has long been known to contain PAH and several such as benzo[a]pyrene are known mutagens and/or carcinogens [89] and thus both the PAH concentration and PAH profile of diesel exhaust is important [63, 90].

PAH are mainly deposited at the surface of carbonaceous soot particles and thus smaller particles which have a higher surface area may be of greater concern as they have the potential for exposing lung tissue to higher levels of PAH [34, 91].

2.3.1.6.6 Hydrophilic/Hydrophobic Characteristics

Soot particles emitted into the atmosphere are either hydrophilic or hydrophobic and if hydrophilic the primary particles can grow in size in an aqueous environment while hydrophobic soot particles cannot [46, 92]. The hydration of soot derived from a variety of fuel types is generally increased by aging, surface oxidation, and O_2 physisorption. In high relative humidity environments (>83%) measurements have shown that the soot surface area determines the adsorption capacity of the soot. In lower humidity environments the hydration is determined by surface functionalities. It is reported that for these reasons in atmospheric studies carbon blacks are not acceptable substitutes for soot [46]. Smith et al. investigated soot with ozone for soot derived from JP-8 aviation fuel and found that the ozone created additional surface carboxylic groups which in turn increased the hydration of these particles [93].

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2.3.2 Soot Environmental Concerns

Evidence has been accumulating that the global mobilization of black carbon from natural and anthropogenic sources is responsible for significant chemical and physical effects in the atmosphere [46]. These effects include participation in tropospheric chemistry, light scattering/absorption (thus affecting earth's radiation balance), in addition to the aforementioned human pulmonary health impacts.

2.3.2.1 Radiative Forcing

Black carbon is considered to influence the earth's radiation balance through radiative forcing microphysical indirect effects. The processes by which it affects the atmosphere are quite different to those for greenhouse gases which primarily trap heat that rises from the Earth's surface. It has been proposed that reductions of light-absorbing particles may assist in slowing the rate of global warming [37, 94]. While particles of any composition reflect light back to space, only a few can absorb light. These include black carbon, soot and desert dust [95], and some organic carbon species [96]. Of these, black carbon is thought to dominate light absorption by aerosols in many regions [97], and it is the most efficient at absorbing visible light.

Firstly, black carbon is highly efficient at absorbing solar radiation [98, 99] in the atmosphere and also light reflecting from the Earth's surface. This is especially so when it is present in the air above snow or ice as sunlight can interact with the carbon both on the way to the surface and also when reflected from it [100].

Secondly, soot can influence clouds and precipitation as soot present in the cloud can affect light bouncing around the clouds and within cloud drops which in turn can affect the quantities of energy absorbed by the cloud, so influencing temperature and cloud lifetime and reflectivity [98, 101]. Soot can also dissolve in the cloud drops which can influence their surface tension [102]. Atmospheric aerosols can also act as cloud nuclei [32].

Thirdly, soot can deposit onto ice surfaces reducing albedo which can increase the energy absorbed into these surfaces and hence potentially accelerate a phase change in the ice [103].

Numerical models for these processes have to consider the particle residence time and optical properties which are both affected by the soot particle size and <u>___</u>

Soot Physiochemical Characteristics Review

morphology [104]. Such properties are therefore important for the study of soot from diesel engine exhaust [32].

Diesel exhaust can also have an opposing effect by cooling the atmosphere primarily by sulphates [37, 105]. Current estimates of sulphate forcing are approximately 0.4 W/m², and are uncertain by about a factor of 2 [37].

2.3.2.2 Soot Atmospheric Lifetime

The residence time of soot in the atmosphere is around one week as precipitation acts to remove the particles [106] so the radioactive forcing effect is not persistent like observed for CO_2 .

2.3.2.3 Soot Physiochemical Considerations

Soot from diesel engine exhausts can possess large pore volumes (Section 2.4.2.2) and these can act as adsorption surfaces for harmful pollutants like PAH [107, 108]. Concerns also exist that diesel combustion derived nano-particles can impact on crops and the food chain through deposition of the particles upon plants and in the soil and can be subsequently absorbed by the plant and impair its growth [108, 109].

2.3.3 Concluding Remarks

The review of soot and its health and environmental impacts in this section has highlighted the general importance of diesel engine exhaust soot but more importantly *that the magnitude of impact of soot is fundamentally linked to individual physiochemical properties of soot particles which vary widely* as is illustrated in the following section.

2.4 Soot Physiochemical Characteristics Review

The complex processes of soot formation and oxidation when coupled with variation in fuels, diesel engine design and engine operating conditions all lead to both fundamental and some highly variable soot physiochemical characteristics. These differences in soot physiochemical characteristics can subsequently result in quite different soot oxidation behaviour [110-113] which is a very important consideration in the design of efficient aftertreatment systems [110]. For example, soot oxidation rate is one of the important factors which govern the temperature at which DPF soot deposition rate matches the soot oxidation rate i.e. the break even temperature [113].

Physical soot properties of specific interest include; the structure of the primary particles, the tortuosity within the nucleus (crystalline/amorphous), the crystalline structure and thickness of the outer shell, the primary particle diameter, the surface area and the porosity of the surface [113]. These properties are usually termed the 'soot nanostructure'.

Chemical soot properties of interest include the H/C and O/C ratios, the sulphur contamination in the bulk and the surface, the type and concentration of inorganic elements in the soot, the surface functional groups and the PAH profile and concentration. The surface properties such as O/C ratio and functional groups are important in how reactive soot is to oxidation [18, 113, 114].

The present section summarises these principal soot physiochemical characteristics reported across a broad collection of diesel engine exhaust soot and also carbon black literature and provides a datum for the soot physiochemical results reported later in this work (Chapter 5 to Chapter 9).

2.4.1 Soot Elemental Composition

The elemental composition of the soot is considered in two sections, the first discusses the surface composition and the second reviews the bulk elemental composition of soot and carbonaceous particles.

2.4.1.1 Surface Elemental

In literature the surface of soot is reported to be largely dominated by the elements: carbon, oxygen, hydrogen, nitrogen and sulphur. The relative concentrations of these elements are highly sensitive to the conditions in which soot forms and persists [115] with many factors of potential significance including: engine, fuel, lubricant, conditions during combustion, exhaust temperature, free oxygen in the exhaust, sampling method and sample location and surface elemental analysis method. Muckenhuber et al. states that the surface properties of soot vary considerably due to soot being sampled from different sources and aged under different conditions [116].

The dominant element of the surface of soot is carbon which as stated earlier develops from an initially balanced H/C ratio when soot first forms to a ratio in excess of 8 [22, 25] as the soot matures. During this process oxygen is chemisorbed onto the surface and the other elements also become components of the surface including sulphur (if present in the fuel and lubricant) and some nitrogen. The ratio of O/C is reported by Bardasz et al. to be dependent on the

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Soot Physiochemical Characteristics Review

engine speed and load with high engine speed observed to produce a higher O/C and hence more oxidised surface with a lower O/C ratio observed at high load conditions [117].

Many properties of soot such as wetting and adsorption behaviour are strongly influenced by chemisorbed oxygen [118]. The oxygen in the surface oxides of soot may be bound in in the form of a multitude of functional groups [118] and these include carboxylic acids, lactones or carboxylic anhydrides [116]. Bardasz et al. report that high resolution X-ray photoelectron spectroscopy shows that oxygen is attached to the carbon by a single or double bond [117, 119]. These reactive surface sites on soot are already formed a short time after nucleation when the virgin soot reacts with principally oxygen and NO_x [116]. The functional groups are distributed over the inner and outer surface of the soot and are located at the edges of graphite platelets or within the sections of amorphous carbon [120].

Surface oxides decompose to CO₂ and CO when the soot is exposed to high temperatures and some highly reactive sites remain and are believed to have a free-radical characteristic [121, 122]. Subsequent cooling in the presence of oxygen or water vapour can encourage the formation of new surface oxides, a process which is typically characterised by a very rapid initial chemisorption of oxygen which then plateaus [118].

Unlike oxygen which is strongly bonded to the carbon, sulphur is usually found as compounds that are adsorbed onto the surface as sulphates and appears to derive from the fuel and lubricant and is therefore sensitive to the concentration in both [123].

One of the most frequently used surface composition analysis techniques is X-Ray Photoelectron Spectroscopy (XPS) though this is unable to detect surface hydrogen. The technique can involve both low and high resolution surface surveys to detail the elements present and also the binding energy which can be used to understand the nature of the carbon and oxygen bonds [119, 124]. Alternative techniques include: selective neutralization, Infrared-Spectroscopy (IR) and Temperature-Programmed-Desorption-Mass-Spectroscopy (TPD-MS) [116].

Following a review of literature, a selection of reported soot and carbon black surface elemental composition results have been collated and this information is summarised in Table 2.1 (this is not an exhaustive list). The mean value

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Soot Physiochemical Characteristics Review

percentage weight concentrations for this data confirm that carbon is the dominant surface element followed by oxygen, hydrogen and sulphur and finally nitrogen. The percentage of carbon is typically above 80% but there are some examples where it has been observed as low as 43% [233] although it is not clear what the other elements are in these carbon samples.

Table 2.1 shows that the variation in carbon and oxygen is much more significant than that observed for sulphur, nitrogen and hydrogen with the latter two in particular always observed in low concentrations (<3% typically). The concentration of sulphur in one case is high at over 5% [233] but is typically less than 1.5%.

There are a number of publications which look at carbon black soot substitutes and also reference samples from the National Institute of Standards and Technology (NIST) which have defined properties supported with test certificates; there are several examples of these included in Table 2.1. With the many varied sources for the soots detailed in Table 2.1, it is not surprising to see such a wide variation in reported properties.

As described previously, the oxygen concentration is one of the most important characteristics of the soot surface and thus the O/C ratio has been calculated for the results in Table 2.1 where possible and this data is presented in Figure 2.1. The average O/C ratio appears to be just below 0.1 though as shown in Figure 2.1 this is somewhat influenced by the relatively high O/C ratios reported by Nguyen at al. [124] and the majority of results are in the range of 0.04 to 0.12.





Table 2.1: Summary of Soot/Carbon Particulate Surface Elemental Composition Reported In Literature

					wt%			a (a
	Reference	Information	С	0	S	Ν	н	0/0
1	Lamharess_2011 [112]	XPS, DPF ULSD, 1500rpm 5 bar BMEP	91.80	7.20	<0.10	<0.05	0.53	0.0784
2		XPS, DPF B30, 1500rpm 5 bar BMEP	89.30	8.90	<0.10	<0.05	0.58	0.0997
3	Stanmore_1999 [139]	Idle	79.40	-	1.20	1.40	3.10	-
4		Medium RPM	66.00	-	1.00	0.60	1.30	-
5		High RPM	85.90	-	1.70	0.80	0.90	-
6	Nguyen_2006 [124]	SRM 2975	-	-	-	-	-	0.2000
7		SRM 1650b	-	-	-	-	-	0.1800
8		Hexane	-	-	-	-	-	0.1000
9		Oxidised Hexane	-	-	-	-	-	0.2000
10	Setiabudi_2004 [262]	Common Rail Diesel - Idle	70.80	-	0.48	-	-	-
11		Common Rail Diesel - Full Load	68.95	-	0.63	-	-	-
12	Clague_1999 [233]	XPS, 6-cyinder Mack Engine Soot	80.80	15.50	1.50	2.10	-	0.1918
13		6-cyinder Mack Engine Soot	91.40	4.10	0.70	0.40	2.90	0.0449
14		6-cyinder Mack Engine Soot	94.10	3.40	0.60	0.30	1.70	0.0361
15		6-cyinder Mack Exhaust Soot	43.40	-	5.10	0.30	0.70	-
16		6-cyinder Mack Exhaust Soot	51.40	-	5.00	0.30	0.70	-
17	Bardasz_1995 [117]	XPS GM6.2L High Torque	-	-	-	-	-	0.0380
18		XPS GM6.2L High Speed	-	-	-	-	-	0.0700
19		EM6-285 High Torque	-	-	-	-	-	0.0500
20		EM6-285 High Speed	-	-	-	-	-	0.0870
21	Bardasz_1996 [119]	XPS, GM 6.5I Engine, Diff Lube, CT Exh Man	96	3.7	0 to 0.11	-	-	0.0390
22		XPS, GM 6.5I Engine, Diff Lube, CT Exh Man	96	4.4	0 to 0.11	-	-	0.0460
23	Bardasz_1997 [115]	XPS, Mack T8, Diff Lube, CT Exh Man	89	9.5	0.4	-	-	0.1067
24		XPS, Mack T8, Diff Lube, CT Exh Man	90	9.8	0.7	-	-	0.1089
25		XPS, Mack T8, Diff Lube, CT Exh Man	93	6.8	0.6	-	-	0.0731
26		XPS, Mack T8, Diff Lube, CT Exh Man	93	6.4	0.3	-	-	0.0688
27	Bardasz_1997_2 [211]	XPS, GM 6.5I Engine, Diff Lube, CT Exh Man	96	4.1	-	-	-	0.0427
28		XPS, GM 6.5I Engine, Diff Lube, CT Exh Man	95.3	4.6	-	-	-	0.0483
		Mean	83.1	6.8	1.4	0.8	1.4	0.0909

2.4.1.2 Bulk Elemental

The PM from diesel engine exhaust is dominated by elemental carbon which forms 50-70% of the exhaust particulate mass depending upon the engine, fuel and operating conditions [54]. The other components are organics (19-43% though much higher at low load in some engines), sulphates, nitrates and metals. In the dry soot fraction, the elemental carbon is an even greater percentage and is typically 80-99% of the total bulk soot mass with the remainder being largely metals. The solid carbon is formed during combustion in locally fuel rich regions [24].

Although trace metals make up a small fraction of the soot (<1%) [35], they are important as elements such as lead, manganese, arsenic and chromium have been reported in literature and these have associated toxic potential [35]. In DPF equipped engines, there may be increased concentrations of catalyst metals such as vanadium, copper, and iron [35]. However, Liu et al. report a 93% reduction in total metals emissions with a DPF [125]. The concentration of metals in the soot is somewhat linked to the engine and engine technologies with Khalek et al. reporting an average reduction of 98% for metals and elements when comparing 2007 to 2004 engines [126].

Some of the metallic elements emitted from a diesel engine which are bound to soot include silicon, copper, calcium, zinc, lead, manganese, barium, nickel and chromium [87]. Organo-metallic additives in lubricant such as Zinc Dithiophosphate (ZDP) can contribute calcium, phosphorous and zinc to soot due to consumption of lubricant during combustion [87]. At least one study reports that calcium was the dominant metallic element [87] though this is not a universal result.

Iron, chromium, nickel and aluminium are usually present in the soot and derive from the engine cylinder, piston and cylinder head metallurgy and corrosion of the exhaust manifold [29, 127]. Depending upon where the soot is sampled from, e.g. close to the cylinder or at the end of the tailpipe, the metallurgy of the exhaust manifold and exhaust pipe is important [29].

Wang at al. found that the majority of the metal in the exhaust particulates was explained by the metal contaminates in the fuel [220]. It was also found that the emissions of crust elements (aluminium, calcium, iron, magnesium, silicon) were higher generally than anthropogenic elements.

Wang et al. importantly observed that there was a coupling between the concentration of PM in the exhaust and the concentration of metals, such that as the PM concentration reduced with operating conditions, the percentage weight of metallic elements increased [220]. This suggests that the metals which are thought to derive mostly from the fuel and lubricant consumption are observed in higher concentrations in the soot when the engine operating condition is such that the fraction of carbonaceous matter is reduced.

Sulphur is largely dependent on the concentration of sulphur in the fuel as was detailed for the soot surface composition in Section 2.4.1.1.

A sample of the reported PM bulk elemental results from literature is presented in Table 2.2; note that this table is not exhaustive. Each row of Table 2.2 represents one sample result set and each column (apart from C/O ratio) defines an element detected in the PM. As a consequence of the different sample analysis methods used and level of detail in reporting, there is a very broad range of elements that have been detected in PM and reported in literature. These issues thus make it difficult to analyse quantitatively what the general observations are regarding individual element concentration but the mean percentage weight has been calculated and this is presented in Figure 2.2.

							Rep	orted	n Litera	ature																
											Bull	Elemen	ts (Wt%	_												
Reference	Information	сно	I S	c/0	AI Ca	Fe	Mg S	Şi Zn	٩	cu Cr	8	Co	Рb	Mn	Mo	Na	Ni	B A	8	a Sb	Sr	F	>	¥	zr	-
Clague_1999 [233]	6-cyinder Mack Engine Soot	94.1 2.9 4.1 0.	4 0.7	23.0	- 0.5	,		- 0.1	0.1		1	1	,					ļ		1	1	1			,	
	6-cyinder Mack Engine Soot	92.6 2.6 3.3 0.	4 0.6	28.1	- 0.2			- 0.2	0.1			•								1	•	•				
	6-cyinder Mack Exhaust Soot	43.4 0.7 - 0.	3 5.1		- 1.9	5.2		- 0.8			1	1								1	1	•	•			
	6-cyinder Mack Exhaust Soot	51.4 0.7 - 0.	ω. Ω		0.2 2	7.8		1.2 0.9	1.2		•	•	1							1	•	•	•		•	
Bardasz_1997_2 [211	1 XPS, GM 6.5I Engine, Diff Lube, CT Exh Man	96.6 <0.5 1.5 <0	15 0.2 I	64.4	•	,		' 	,		'	1	,			,				'	'	1	,	,	,	
	XPS, GM 6.5I Engine, Diff Lube, CT Exh Man	96.6 <0.5 1.5 <0	15 0.2	64.4	1	•	-	<u>.</u>		1	1	•						Ì		1	1	•	ł			
Agarwal_2010 [87]	ICP-OS, Small Single Cylinder Diesel, tail pipe, diluted, low load	•		· ·	- 3.5	2.8	1.8	- 0.6		- 25	'	1	0.31	,	,	8.5	0.13			'	'	'	,	,	,	
	ICP-OS, Small Single Cylinder Diesel, tail pipe, diluted, 80% load	•		'	- 2	1.4	. 0.9	- 0.35	- ~	- 20:	1	1	0.1		,	ŝ	0.08	ļ		1	1	1	1		,	
Gangwar_2011 [266]	1 CR DI Diesel Engine, No Load, 1800 rpm, Diesel			 '	- 0.62t	1.244	0.193 0.6	- 625	0	264 0.04	4 -	•	0.655	0.027		2.98	- 0.	434 -		1	•	•	•			
	CR DI Diesel Engine, No Load, 1800 rpm, B20		1	 '	- 1.164	0.885	0.085 0.2	208	0	185 0.00	' 6	1	0.235	0.06		3.5		335 -		1	1	1	,	,	,	
	CR DI Diesel Engine, No Load, 2400 rpm, Diesel			· · ·	- 2.445	0.966	0.178 0.2	244 -	0	217 0.01	י ק	1	0.261	0.0061		5.159	0	036 -		1	1	1	,	,	,	
	CR DI Diesel Engine, No Load, 2400 rpm, B20		1	'	- 3.174	0.831	0.227 0.0	- 200	0	211 0.01		1	0.515	0.031		2.029	'	- 110		'	1	1	,	,	,	
	CR DI Diesel Engine, Full Load, 1800 rpm, Diesel		1	· · ·	- 0.184	0.086	0.156 0.1	105 -	0	193 0	1	1	0.065	0.003		0.554	0	041 -		1	1	1	,	,	,	
	CR DI Diesel Engine, Full Load, 1800 rpm, B20		1	'	- 0.231	0.33	0.061 0.0	- 880	0	197 0.00	י 8	1	0.104	0.021		1.14	'	154 -		'	1	1	,	,	,	
	CR DI Diesel Engine, Full Load, 2400 rpm, Diesel		'	· · ·	- 0.045	0.078	0.031 0.0	- 118	0	035 0.00	' 8	,	0.037	0.005	,	0.195	0	018 -		1	1	1	,	,	,	
	CR DI Diesel Engine, Full Load, 2400 rpm, B20		1	· ·	- 0.026	0.036	0.008 0.0	- 80C	0	013 0.00	י פ	,	0.065	0.003	,	0.141	, 0	003		1	1	1	,	,	,	
Wang_2003 [220]	Diesel Engine Exhaust, Full Load, 100% rpm	•	1	- 2	74 2.84	3.84	0.616 2	01 0.37	4 - 0	327 0.86	9 0.058	3 0.145	0.0931	0.327	1		0.604	- 0.0	365 0.07	739 0.14	4 0.296	0.137	0.0784			
	Diesel Engine Exhaust, Full Load, 100% rpm	•	1	- 5	14 2	3.13	0.497 1.	66 0.33	5 - 0	332 0.58	5 0.042	7 0.122	0.0715	0.123	0.741	,	0.38	- 0.0	0.0 0.0	81 0.11	5 0.173	0.151	0.0883	,	,	
	Diesel Engine Exhaust. Full Load. 100% rom		,		94 1.86	2.92	0.475 1.	52 0.35-	4	346 0.5	9 0.051	1 0.126	0.0919	0.149	0.57	,	.351	- 0.0	557 0.09	927 0.14	4 0.174	0.147	0.0778	,	,	
Rockne 1999 [227]	Bus Diesel	20.5 1.6	,		- 1.5	31		- 0.82		0.0	, 5	•		0	0.04	,	0		0.0		0	•		0	0.012	
	Marine Diesel	718 83 -	,	 '	- 0.85	0.24		0.11		0.0		,		C	c	,	c				0000	, 6	,	0.16	c	
	Dorderane	912 11 -		· · · · ·	-			0.01	, , ,	m1 01		,	,			,		,		,	-	,	,	-		
		1.1 1.1				050		10.0							0000						2000			0000	1000	
		7.7 7C			76.0 -	60.0		-			י הר				1000						nn-n	. c		6000	1700.0	
0 11 0000 11 0	Wood Stove	38.4 3.3		- - -	- 0.0	0.83		7.0		0.0	'			0.023	STU:		50.0		0.0	- /1	0000	י ת		5	0.0032	
Collura_2004 [134]	Virgin Soot A	87.9 0.9 10.8 0.	4 0.2	8.1							'						,									
	Virgin Soot B	85 1.2 13.3 0.	0.2 0.2	6.4																1						
	Extracted Soot A	87.9 0.6 10.4 0.	4 40.2	8.5							'									1						
	Extracted Soot B	90.1 0.6 10.7 0.	4 <0.2	8.4		•	-	<u>.</u>		1	'	•						Ì		1	'	•	•			
Covitch_1988 [138]	Mack T-7 Engine Test, ceramic Thimble Exh Manifold	•	1.56		- 0.090			- 0.36	- 0		'	1			,		,			'	'	'	•	,		
	Mack T-7 Engine Test, ceramic Thimble Exh Manifold	•	0.84	,	- 0.140			- 0.49	0		'	•					,			1	'	•	•			
	Mack T-7 Engine Test, ceramic Thimble Exh Manifold	•	1.39		- 0.24			- 0.47	- 2		'	1			,	,	,			'	'	'	,	,		
	Mack T-7 Engine Test, ceramic Thimble Exh Manifold	•	1.37		- 0.080			- 0.31	- 0		1	1			,		,	ļ		1	'	'	·	,		
	Mack T-7 Engine Test, ceramic Thimble Exh Manifold		1.22	'	- 0.140			- 0.39	- 0		'	1			,	,	,			'	'	'	,	,		
	Mack T-7 Engine Test, ceramic Thimble Exh Manifold		0.99		- 0.090		-	- 0.07	- 0	-	•	•									•	•				
Ripple_1990 [165]	Mack T-6 Engine Test, ceramic Thimble Exh Manifold, Lube A	6:11	0.15		- 0.560	-		- 0.09	- 0		'	1	,			,		ļ		'	'	'	·	,	,	
	Mack T-6 Engine Test, ceramic Thimble Exh Manifold, Lube A repeat		0.13	 '	- 0.970	-		- 0.38	-		'	1	,			,		ļ		'	'	'	,	,	,	
	Mack T-6 Engine Test, ceramic Thimble Exh Manifold, Lube B	84.4	0.26		- 0.020		,	- 0.04	- 0	1	'	1			,	,	,			'	'	'	,	,		
	Mack T-6 Engine Test, ceramic Thimble Exh Manifold, Lube B repeat	86.2	0.26	'	- 0.040			- 0.05	- 0	-	1	1	•							1	1	1	•			
Ripple_1990 [165]	Mack T-7 Engine Test, ceramic Thimble Exh Manifold, Lube A, reg Diesel		0.4	 -	- 0.000			- 0.10	- 0		1	•	•							1	•	•	•			
	Mack T-7 Engine Test, ceramic Thimble Exh Manifold, Lube A, LSD Diesel		0		- 0.000			- 0.70	· 0		'	1	,		,		,			'	'	'	,	,		
	Mack T-7 Engine Test, ceramic Thimble Exh Manifold, Lube B, reg Diesel		0.7	· · ·	- 0.000			- 0.10	- 0		1	1	,	,						1	1	1	,	,	,	
	Mack T-7 Engine Test, ceramic Thimble Exh Manifold, Lube B, LSD Diesel		0	· · ·	- 0.000			- 0.60	- 0		1	1	,	,						1	1	1	,	,	,	
Bardasz_1996 [115]	XPS, GM 6.5I Engine, Diff Lube, CT Exh Man, sample 8	97.63 <0.5 1.58 <0	5 <0.12	61.8	•			•			1	•								1	1	•				
1	XPS, GM 6.5I Engine, Diff Lube, CT Exh Man, sample 13	96.31 <0.5 2.36 <0	.5 0.06	40.8	1	,			,		1	'	,		,	,	,			'	'	'	,		,	
	XPS, GM 6.5I Engine, Diff Lube, CT Exh Man, sample 10	97.56 <0.5 1.21 <0	5 <0.4	80.6		,			,			,	,	,						'	'				,	
	Mean Wt%:	78.13 2.05 5.52 0.4	14 0.97	35.86 1	76 0.86	3.22	0.40 0.	58 0.34	1 0.60 0	.15 0.1	5 0.05	0.13	0.26	0.05	0.30	2.92	0.16 0	13 0.0	0.0	3 0.1	3 0.08	0.15	0.08	0.04	0.00	
	All Mean Wt%	38.2 0.6 1.4 0.	1 0.5	8.8	1.2 0.7	1.4	0.1	12 0.2	0.1	0.1	0.0	0.0	0.1	0.0	0.1	0.6	0.0	0.	0	0.0	0.0	0.0	0.0	0.0	0.0	

2 2.4

Table 2.2: Summary of Soot/Carbon Particulate Bulk Elemental Percentage Weight

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Working through Table 2.2 and Figure 2.2 and referring also to the elements found in the soot surface (Section 2.4.1.1), it is clear that the two main elements from which soot is composed are carbon and oxygen with some hydrogen and quite low concentrations of nitrogen and sulphur and thus the surface and bulk elemental compositions are quite similar.

The crust elements aluminium, calcium iron, magnesium and silicon are generally observed to be present in many soot samples and have thus been grouped in Table 2.2 and Figure 2.2 to highlight this. Iron and sodium are present in fairly high concentrations in some samples with the iron being the principal element in the metallurgy of many engines and the sodium likely to derive mainly from the fuel.

2.4.2 Soot Morphology

The most important morphological related properties of soot from a review of literature are: surface area, porosity, density and primary particle diameter and in this section each of these is summarised in turn.

2.4.2.1 Surface Area

The surface area of soot is a function of the size of the primary particle, the porosity of the surface [25] and the extent and form of the aggregation of the soot particles. Surface area is an important parameter when characterising soot morphology because the greater the surface area, the greater the surface on which the volatile organic matter and other components can condense [24, 128].

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Soot Physiochemical Characteristics Review

Since surface area is inversely proportional to primary particle diameter, the smaller the soot particles, the greater the surface area. Thus, the very small soot nanoparticles identified in Section 2.3.1.2 as being of greatest concern for human health due to their higher respirability; can also carry more PAH into the lung and thus be more toxic in addition to being able to penetrate deep into the lung. The greater toxicity is because PAH have been found to be mostly deposited on the surface of soot [34, 89].

One potential issue with modern diesel engines that has been highlighted by Kittelson et al. is that the reduction in carbonaceous soot mass following improved technological measures has resulted in the reduction in the surface area available for the volatile organic matter to condense onto. This has increased the saturation ratio which has been observed to cause a nucleation mode where the volatile organic matter condenses out to form high numbers of nanoparticles in the exhaust and especially at the exhaust exit [24]. i.e. the amount of material adsorbed onto the carbonaceous soot is dependent on the particulate surface area available as well as the saturation ratio [24].

One of the popular methods used to quantify the surface area of nanoparticles is referred to as the Brunsuer, Emmett and Teller (BET) approach (see Section 3.6.4.1) which Darmstadt et al. notes provides very useful information on soot surface defects [129]. For example, using this soot analysis method, they and also Ahlstrom et al. [130] observed that the surface area of diesel soot increased from 35 to 270 m²/g simply by heating the soot to 600°C in the presence of nitrogen. A very similar finding has also been reported by Ishiguru et al. [131]. These observations indicate that the surface area of the soot increases with the removal of the condensed volatile organics (SOF) [123] and thus there is an underlying porous surface. This is supported by Smith at al. [132] where it is reported that a 6 fold increase in surface area was observed during oxidation due to porosity development and similar observations by Bonnefoy et al [133].

Chughtai et al. considered hydration for a variety of black carbons produced from a variety of fuel types and found it to generally increase with aging which was from surface oxidation and chemisorption of O_2 . It was observed that this effect increased with greater soot surface area especially for high relative humidity (83%) [46]. At lower humidity, it was the surface functionalities which determined hydration.

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Presented across Table 2.3 (Part 1) and Table 2.4 (Part 2) is a summary from literature of reported soot and soot analogue surface area determined with different test methods and for soots from different origins. This data is summarised in Figure 2.3.

Table	2.3: Summary of Soot/Carbon	Particulate	Surface Area	a Reported Ir	Literature
(Part	1)				

Reference	Information	Surface Area (m^2/g)
1 Lamharess_2011 [112]	DPF ULSD, 1500rpm 5 bar BMEP	414
2	DPF B30, 1500rpm 5 bar BMEP	448
3 Ishiguro_1991 [131]	Soot Burn-off 0%	52
4	Soot Burn-off 25%	176
5	Soot Burn-off 50%	268
6	Soot Burn-off 75%	296
7 Stanmore_1999 [139]	Idle	31
8	Medium RPM	90
9	High RPM	165
10 Setiabudi_2004 [262]	Common Rail Diesel - Idle	<5
11	Common Rail Diesel - Full Load	18
12 Covitch_1988 [138]	Mack T-7 Engine Test, ceramic Thimble Exh Manifold	99
13	Mack T-7 Engine Test, ceramic Thimble Exh Manifold	227
14	Mack T-7 Engine Test, ceramic Thimble Exh Manifold	254
15	Mack T-7 Engine Test, ceramic Thimble Exh Manifold	301
16 Zerda_1999 [137]	Chevrolet Lumina 3.1L V6 Sample A	93
17	Chevrolet Lumina 3.1L V6 Sample E	138
18	Chevrolet Lumina 3.1L V6 Sample E outgassed st 673K	199
19 Smekens_2005 [155]	Carbon Black Cabot 1999	94
20	Diesel Soot	45
21	Biodiesel Soot	53
22	Domestic Heating Soot	14
23	Aircraft Exhaust Soot	31
24 Chughtai_1999 [46]	Fresh Diesel Soot (H2O adsorption)	71
25	Aged Diesel Soot (H2O adsorption)	65
26	Aviation Fuel (H2O adsorption)	65
27	Pine Needles Burning (H2O adsorption)	80
28	Coal Combustion (H2O adsorption)	84
29 Pott_1991 [276]	Diesel Soot	20
30	Extracted Diesel Soot	34
31 Lapuerta_2010 [136]	DPF Soot Unpacked	222.37
32	Soot Packed	200.64
33 Nguyen_2006 [124]	SRM2975 - From Forklift (Not heated during outgassing)	80
34	SRM2975 - From Forklift (Heated during outgassing)	87
35	SRM1650b Diesel PM (Not heated during outgassing)	48
36	SRM1650b Diesel PM (Heated during outgassing)	80
37	Hexane Soot (Not heated during outgassing)	81
38	Hexane Soot (Heated during outgassing)	87

2 2.4

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Table 2.4: Summary of Soot/Carbon Particulate Surface Area Reported In Literat	ure
(Part 2)	

Reference	Information	Surface Area (m^2/g)
39 Otto_1980 [135]	Sample 1 - burn-off 0% (CO2 gas)	86
40	Sample 1 - burn-off 11% (CO2 gas)	164
41	Sample 1 - burn-off 18% (CO2 gas)	202
42	Sample 1 - burn-off 28% (CO2 gas)	268
43	Sample 2 - burn-off 17% (CO2 gas)	260
44	Sample 2 - burn-off 38% (CO2 gas)	314
45	Sample 2 - burn-off 71% (CO2 gas)	327
46 Thiele_Case_Study [236]	Carbon Black	62.05
47	Nickel	26.3
48	TiSi2	97.25
49 Ghzaoui_2003 [268]	Diesel Tailpipe Soot - unwashed (N2 77k)	52
50	Diesel Tailpipe Soot - washed (N2 77k)	70
51 Rockne_1999 [277]	Dodecane (N2 77k)	85.3
52	Marine Diesel (N2 77k)	11.7
53	Bus Diesel (N2 77k)	1.9
54	Wood Stove (N2 77k)	1
55	Fuel Oil (N2 77k)	1.5
56 Levitt_2007 [273]	Methane Flame Soot	134
57	Propane Flame Soot	146.95
58	Kerosene Flame Soot	105.5
59 Muckenhuber_2004 [116]	Diesel Engine 315 kW, 12.7 L Soot Exhaust Manifold	100
60	Diesel Engine 315 kW, 12.7 L Soot Exhaust Outlet	40
61 Yu_2005 [140]	Activated Carbon - W660 (N2 77K)	2115
62	Activated Carbon - W602 (N2 77K)	2007
63	Activated Carbon - W269 (N2 77K)	1858
64	Activated Carbon - W101 (N2 77K)	2255
65 Collura_2004 [134]	Virgin Soot A (benzene at 25°C)	238
66	Virgin Soot B (benzene at 25°C)	168
67	Extracted Soot A (benzene at 25°C)	240
68	Extracted Soot B (benzene at 25°C)	147
69 Clague_1999 [233]	Carbon Black, Printex 85	200
70	Carbon Black, Vulcan XC-72R	260
71	Carbon Black, Printex 3	95
72	Carbon Black, Elftex 120	40
73 Lu_2011 [142]	Coal Stack Soot (N2 77k)	14.6
74 Bau_2010 [151]	SiO2 Powder (SBET Adsorption isotherm)	198.3
75	Fe3O4 Powder (SBET Adsorption isotherm)	40.3
76	AI2O3 Powder (SBET Adsorption isotherm)	36.9
77	SiO2 Powder (SBET Adsorption isotherm)	248.4
78	Fe3O4 Powder (SBET Adsorption isotherm)	27.9
79	AI2O3 Powder (SBET Adsorption isotherm)	23
	Average	: 225.4

This set of data reveals reported surface areas from 1 to over 2200 m²/g for these types of particles which attests to the earlier reported change in soot surface area due to aging, oxidation and heating. The mean for the data set is 225 m^2 /g which actually compares well to the more traditional diesel engine exhaust soot results reported in [131, 134, 135, 136, 137, 138].

The data from Otto et al. [135] and Ishiguru et al. [131] shows the effect of sample heating and burn-off discussed earlier, with marked increases in

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measured surface areas in both cases. The data from Stanmore et al. points to an increase in soot surface area with increasing engine rpm [139]. Finally, Yu et al. [140] report the surface area for activated carbon and these results stand out as the surface area is approximately 2000 m²/g and thus an order of magnitude higher than the average for the full set of data and a high surface area for adsorption would be expected for such particles.



Figure 2.3: Summary of Soot/Carbon Particulate Surface Area Reported In Literature

2.4.2.2 Porosity

For materials of a porous nature there are three different categories of porosity that have been defined by the International Union of Pure and Applied Chemistry (IUPAC, 1984): *Micropores (<2 nm), Mesopores (2 to 50 nm) and Macropores (>50 nm).* The origin of pores is important in respect to the state and structure of pores [141]. Pores which are open are ones which communicate with the surface of the soot whereas closed pores create voids in the structure of the solid and thus influence the mechanical properties. The presence of porosity in soot is a concern as it enables a higher concentration of pollutants such as PAH on the surface by virtue of the higher surface area derived from the porosity [142]. It is also important as it provides sites of discontinuity in the soot surface which could be beneficial for increasing soot reaction rate [16, 143].

A crystalline solid such as soot which is composed of atoms or ions has intrinsic voids and defects and these are called intraparticle pores. This is because relative to the organised outer crystalline shell of soot, the nucleus is

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generally more amorphous and this disorganised carbon presents plenty of opportunities for voids [114].

Between particles in an aggregate structure such as that observed for exhaust soot, there is inevitably void space created between the particles and this is called interparticle pores which can be both rigid and flexible [141]. Governing the state and population of these pores are the inter-particle forces which can include: chemical bonding, van der Waals force, electrostatic force, magnetic force, surface tension of adsorbed films on the primary particles. Thus, these pores depend on whether the group structure of primary particles is an aggregation or agglomeration of particles.

Electron microscopy of soot shows crystallites in concentric orientation and having boundary edges and these sites create boundaries [144]. The presence of foreign elements in the surface of soot most likely increases the concentration of surface irregularities [118] in these crystallites; such irregularities therefore potentially increase the porosity. The investigation of the micropores in some carbon blacks has revealed that these have a slit shape and a width of 1 nm [145] and it is possible that the pores of soot are similar.

It is thought likely that under the action of high temperatures and in the presence of oxygen, soot undergoes burning and that this possibly causes morphological change through the development and/or opening of pores [143]. Neoh et al. found evidence for increases in soot microporosity during oxidation and was attributed to micropore development [146]. Song et al. go a step further and compare the burning of soots from Fischer-Tropsch and biodiesel fuels and found that the biodiesel fuel soot was observed to undergo a hollowing of the internal core of the soot whilst the outer shell remained intact [16]. The core of the Fischer-Tropsch derived soot by contrast remained intact. This was observed to exert a strong influence on the soot oxidation rate and was initiated by the development of a micropore which facilitated internal burning with subsequent layer plane rearrangement and was enhanced by the more amorphous soot structure [16].

The mechanism of the removal of volatile matter and the subsequent increase in surface area due to micropore opening and penetration of oxygen into the soot is also considered by others [123, 130, 147]. The extent of this porosity development is known to be affected by both the gasification medium [123] and the temperature [131].

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A common technique for porosity measurement is to use N2 adsorption at 77K [141] and for soot with its porous structure this involves several mechanisms which include multilayer adsorption, capillary condensation, and micropore filling for macropores, mesopores, and micropores, respectively. Consequently, a multilayer adsorption model is required and one of the most popular is the Barret-Joyer-Halenda (BJH) [148] and Dollimore-Heal (DH) [149] models. The N2 in this method is sometimes replaced with other gases such as argon and carbon dioxide [135] and is an important decision as the gas molecule size needs to align to the size of the pores in the soot and N2 appears to be preferred for soot.

From the review of literature, a set of reported soot and carbon black porosity measurements have been collated and these are presented in Table 2.5.

Reference	Information	Porosity
Rockne_1999 [277]	Bus Diesel (%)	79
(Paper Table 1)	Marine Diesel (%)	54
	Dodecane (%)	86
	Fuel Oil (%)	65
	Wood Stove (%)	67
Zerda_1999 [137]	Chevrolet Lumina 3.1L V6 Sample A (Ave Pore Width nm)	1.258
	Chevrolet Lumina 3.1L V6 Sample E (nm)	1.254
	Chevrolet Lumina 3.1L V6 Sample E olutgassed st 673K (nm)	1.167
Lapuerta_2010 [136]	DPF Soot Unpacked (BJH total volume of pores cm3/g)	0.388
	Soot Packed (BJH total volume of pores cm3/g)	0.309
Nguyen_2006 [124]	SRM2975 - From Forklift (Not heated during outgassing) (total pore vol mL/g)	0.1965
	SRM2975 - From Forklift (Heated during outgassing) (total pore vol mL/g)	0.2547
	SRM1650b Diesel PM (Not heated during outgassing) (total pore vol mL/g)	0.1274
	SRM1650b Diesel PM (Heated during outgassing) (total pore vol mL/g)	0.2078
	Hexane Soot (Not heated during outgassing) (total pore vol mL/g)	0.176
	Hexane Soot (Heated during outgassing) (total pore vol mL/g)	0.1844
Rockne_1999 [277]	Dodecane (N2 77k) (Meso-pore volume cm3/g)	0.08
(Paper Table 2)	Marine Diesel (N2 77k) (Meso-pore volume cm3/g)	0.02
	Bus Diesel (N2 77k) (Meso-pore volume cm3/g)	0.004
	Wood Stove (N2 77k) (Meso-pore volume cm3/g)	0.004
	Fuel Oil (N2 77k) (Meso-pore volume cm3/g)	0.004
Yu_2005 [140]	Activated Carbon - W660 (N2 77K) (total pore volume cm3/g)	1.284
	Activated Carbon - W602 (N2 77K) (total pore volume cm3/g)	1.177
	Activated Carbon - W269 (N2 77K) (total pore volume cm3/g)	1.084
	Activated Carbon - W101 (N2 77K) (total pore volume cm3/g)	1.585
Collura_2004 [134]	Virgin Soot A (benzene at 25°C) (micropore volume cm3/g)	0.02
	Virgin Soot B (benzene at 25°C) (micropore volume cm3/g)	0
	Extracted Soot A (benzene at 25°C) (micropore volume cm3/g)	0.02
	Extracted Soot B (benzene at 25°C) (micropore volume cm3/g)	0
Clague_1999 [233]	Carbon Black, Printex 85 (pore volume cm3/g)	0.5
	Carbon Black, Vulcan XC-72R (pore volume cm3/g)	1.8
	Carbon Black, Printex 3 (pore volume cm3/g)	1.2
	Carbon Black, Elftex 120 (pore volume cm3/g)	0.65
Lu_2011 [142]	Coal Stack Soot (N2 77k) (total pore volume ml/g)	0.0325
Song_2007 [17]	B100 Initial Pore (Mean Diameter nm)	22
	B100 Oxidized Pore (Mean Diameter nm)	23

Table 2.5: Summary of Soot/Carbon Particulate Porosity Reported In Literature

As a result of the multiple formats available to quantify porosity it is difficult to compare directly between the different sets of data to identify the typical porosity reported for soot. The results quoted in total pore volume cm³/g consistently show that the surfaces of activated carbon and in some cases carbon black have far higher porosity than observed for soot. The high porosity for activated carbon agrees with the high surface area measurements detailed previously in Section 2.4.2.1. In literature in general, porosity results for carbon black and activated carbon are more readily available than results for diesel exhaust soot.

2.4.2.3 Density

The density of diesel engine soot is a function of the composition and the structure of the primary particles i.e. the presence of voids between the carbon crystallite. In literature there is less data available which reports the measurement of diesel soot density than was found for most of the other soot physiochemical properties considered in this review and this is attributed to the difficulty in measuring density directly [150].

The direct method used for measuring soot density is N2 Pycnometry which determines the *skeletal volume* of a sample and then the sample is weighed to get the mass, Section 3.6.4.3. This method generally requires a relatively large sample mass of several mg and most studies that state soot density therefore use a popular value generally quoted in literature [22]. There are several examples in literature where alternative methods are sought to determine density and compare the results to the pycnometry technique [150-152].

It is clear from the literature that the accurate measurement of the inherent material density of soot is reliant upon the sample preparation prior to N2 Pycnometry; the preparation process should remove any condensed volatile fraction and ideally break-up any aggregate structure via. sonication or similar.

The majority of the literature found which discusses soot density states that the density of diesel engine soot resides typically in the range 1.8 to 2.0 g/cm³ [17, 18, 123, 152, 153]. Wal at al. state that density of amorphous carbon is 2.0 g/cm³ and that most carbons are quoted to have densities between 1.8 to 2.0 g/cm³ [18].

Park et al. [152] showed that when soot was preheated to remove volatile components, the density was 1.77 ± 0.07 g/cm³; independent of particle size. However, without pre-treatment, the density of the soot increased from 1.27 to 1.78 g/cm³ as particle mobility size of the soot increased from 50 to 220 nm.

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Thus, it appeared that the heating of the soot removed the volatile hydrocarbons adsorbed into the pores and onto surface of the soot providing the much more consistent density measurement [6].

Maricq et al. found that there was a ~20% change in soot density between idle, medium and high load operating conditions but that this was averaged out over a transient test which is useful for using online particle sizing to estimate soot mass [154].

Table 2.6 and Figure 2.4 summarise the density reported in literature for diesel soot and similar substances with an emphasis on measurements made using pycnometry.

Table 2.6: Summary of Soot/Carbon Particulate Density (g/cm³) Reported in Literature

Reference	Information	Density (g/cm3)
1 Stanmore_1999 [139]	Idle	0.038
2	Medium RPM	0.061
3	High RPM	0.051
4 Rockne_1999 [277]	Bus Diesel	5.3
5	Marine Diesel	1.3
6	Dodecane	0.78
7	Fuel Oil	1.7
88	Wood Stove	1.8
9 Park_2004 [152]	Diesel Soot, John Deer 4 cylinder, 4.5 l, 75 kW & Isuzu, 3 cylinder, 1.5 l, 10 kW	1.27 to 1.78
10 Bau_2010 [151]	SiO2 Powder (SEM image derived)	2.4
11	Fe3O4 Powder (SEM image derived)	5.2
12	Al2O3 Powder (SEM image derived)	4
13 Coudray_2008 [150]	Silica particles (SEM image derived)	0.4 to 3.1
14	Silica particles (Pycnometer)	2.5
15 McMurry_2002 [283]	mass-mobility relationship used to determine atmos aerosol particle density	1.5 to 1.8
16 Choi_1995_2 [239]	Diesel Soot (helium pycnometry)	1.7 to 1.8
17 Rossman et al. (from Choi_1995_2) [239]	Acetylene black	1.84
18 Hanel_1977 [284]	Dry aerosols from atmosphere	1.8 to 3.0
Song_2007 [17], Stanmore_1999 [139],	Stated soot density ranges	1 8 to 2 0
² Park_2004 [152]		1.0 10 2.0
20 Lapuerta_2010 [136]	Soot density Assumption	1.85
	Average:	1.99





The reported soot density measurements cover the range from 0.04 to 5.3 g/cm³ with a mean value of 1.99 g/cm³. Excluding the outliners in this data set, the range is 0.75 to 2.5 g/cm³. Thus, this set of results from literature support the 1.8 to 2.0 g/cm³ density range quoted in the majority of works.

2.4.2.4 Primary Particle Diameter

The diameter of diesel engine exhaust soot is a function of the conditions in which it forms and the fuel being combusted. The typical size ranges quoted in literature for diesel soot primary particle diameter is 15–50 nm [6, 25]. The soot primary particles form aggregates of chains of ten to hundreds of primary particles and the size of these structures can be several hundred nanometres [25].

As stated previously, the size of the soot primary particles is the most important factor in the respirability of soot and is therefore very important from a human health perspective [34]. Therefore the factors that affect soot primary particle size are very important. The diameter of diesel soot is reported to decrease with increasing engine load and with increasing engine speed [34, 155]. However, Burtscher et al. report that there is also a strong dependence of the size on the type of engine [6]. There are suggestions that the size of soot primary particles have reduced with the development of new diesel engine technologies such as higher fuel injection pressure [6].

When considering the particle size distribution observed at the exhaust when diluted, most of the particle numbers emitted by engines are in the nanoparticle range (<50 nm) but most of the mass is in the accumulation mode range (50-1000 nm) [54, 83]. The nanoparticles form by nucleation from hydrocarbons or sulphate during dilution and cooling of the exhaust. The accumulation mode particles comprise of the carbonaceous soot agglomerates. The size distributions of diesel particles in the accumulation mode are very well represented by lognormal distributions with an almost constant geometric standard deviation of 1.8–1.9 nm [6]. Frequently the structure of the agglomerates is described by the concept of fractals [6, 17], with typical fractal dimensions of 2.3 quoted [152].

Presented in Table 2.7 and Figure 2.5 are the primary particle diameters taken from literature for soot, carbon black and some powdered materials. Where 'SBET' is stated, the diameter is calculated from measured surface area using assumptions of non-porous spherical particles (See Section 3.6.4.4).

2 2.4

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Table 2.7: Summary of Soot/Carbon Particulate Prin	mary Particle Diameter (nm) Reported
in Literature	

Reference	Information	Particle Diameter (nm)
1 Ishiguro_1991 [131]	Soot Burn-off 0%	34.5
2	Soot Burn-off 25%	33
3	Soot Burn-off 50%	31
4	Soot Burn-off 75%	27.5
5 Thiele_Case_Study [236]	Carbon Black (TEM meas.)	31
6	Carbon Black (SBET est.)	45
7 Wegner_2002 [279]	titania particles (SBET est.), burner nozzle dist 5mm	6
8	titania particles (SBET est.), burner nozzle dist 20mm	14
9	titania particles (SBET est.), burner nozzle dist 40mm	18
10 Clague_1999 [233]	Carbon Black, Printex 85	15
11	Carbon Black, Vulcan XC-72R	30
12	Carbon Black, Printex 3	28
13	Carbon Black, Elftex 120	60
14 Lapuerta_2010 [136]	DPF Soot Unpacked (SBET Est. from BET and density)	14.6
15	Soot Packed (SBET Est. from BET and density)	16.2
16 Johannessen_2000 [280]	Al2O3 particel size in flames (TEM imaged)	15.8 to 20.9
17	Al2O3 particel size in flames (BET calc.)	22.1 to 32.7
18 Park_2004 [152]	Diesel Soot TEM image analysis to est. primary particle diameter	45 to 215
	John Deer 4045 engine, 50% Load, 1400rpm, 360 ppm S fuel	
19 Schraml_1999 [34]	VW 1.9 TDI Engine	19-36
	Average	31.9

The range in primary particle diameters with outliners rejected is (14-60 nm) which agrees well with the generally stated ranges from literature. The average particle diameter for this set of data is 31.9 nm.



Figure 2.5: Summary of Soot/Carbon Particulate Primary Particle Diameter (nm) Reported in Literature

The quoted ranges for the three engine exhaust derived soot literature references agree well and are quite similar to the average for the sample set [34, 131, 136]. The results from Ishiguru et al. [131] are particularly interesting when combined with the same result set presented for surface area in Section 2.4.2.1. The act of heating the soot to high temperatures to initiate oxidation and burn-off

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causes both a large increase in surface area and a reduction in the primary particle size, thus implying the physical removal of any condensed organic volatiles and possibly the underlying graphene planes that form the outer shell of soot.

2.4.3 Soot Surface Acid Functionality

The surface of soot is reported to show both acidic and basic qualities in aqueous dispersions [156]. These acidic and basic sites usually coexist, however the concentration of basic sites decreases with increasing surface acidic functionality [118]. The reactive surface sites are said to be already formed a short time after nucleation as the newly formed soot reacts with oxygen, NO_x or other gases during and after combustion [116].

This results in a multitude of functional groups on the soot surface and which differ in their acidities e.g. carboxylic acids, lactones or lactols and hydroxyl groups of phenolic character [116, 118, 156]. These functional groups can each be differentiated by neutralisation with solutions of NaHCO, NaCO and NaOH respectively [118]. The basic surface groups are: pyrones, chromenes, ethers and carbonyls [156-162].

Kittelson et al. state that the surface acid/sulphate fraction of soot is roughly proportional to the fuel sulphur content [24]. Therefore, fuel sulphur concentration can change the soot behaviour quiet significantly [138]. Together, these functional groups cover the inner and outer surface of the soot and are located at the edges of graphite platelets or within the sections of amorphous carbon [156].

These surface sites remain active and can transform during the particles' lifetime due to heterogeneous reactions or adsorption processes, such as the chemisorption of O_2 [116, 156]. Surface oxides which are created with oxygen at elevated temperatures or with liquid oxidant are acid in character [118].

The foreign elements present on the surface of soot (Section 2.4.1.1) have a significant influence on the surface functionalities with oxygen being the most important [156] and these can therefore influence the reaction rate of the soot. A correlation between pH and oxygen content of carbon black has been reported by Studebaker [163], the higher the oxygen content, the more acidic the dispersion is. Conversely, carbons with low oxygen content show basic surface properties.

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Information about these functional groups can be determined by several methods: titration (i.e. selective neutralization as above), X-ray photoelectron spectroscopy (XPS), infrared-spectroscopy (IR) or temperature-programmed-desorption-mass-spectroscopy (TPD-MS) [116]. One of the most used methods is the titration method first described by Boehm [157] (See Section 3.6.5).

As mentioned above, the nature of these functional groups which are on the surface of soot are considered as important in the reactivity, hygroscopic behaviour, and potential catalytic activity of the soot [106]. In consideration of soot hygroscopic/hydrophobic properties, fresh soot from the exhaust is hydrophobic and water insoluble [106]. As the soot then oxidises, it becomes hygroscopic which is likely beneficial for the removal of soot from the atmosphere through wet deposition [92, 164]. Soot surface functionality is also important for lubricant dispersant control [138, 165]. Thus, the surface functionality of soot is very important for multiple purposes and is one of the most important soot characteristics to investigate.

In open literature the frequency of reported surface acidity of diesel engine soot is somewhat low, with many more examples of carbon black measurements. A set of reported surface acidity results have been compiled from a detailed but not exhaustive search and these are presented in Table 2.8 and Figure 2.6.

Reference	Information	Surface Acidity (mmol/g)
1 Popovitcheva_2000 [166]	Combuster Soot (NaOH titration) (mmol/g)	0.1
2 Kim_2012_1 [288]	Carbon Nano Tubes (Boehm Titration, total acidity) (mmol/g)	0.786
3	(Titration method validation)	0.79
4		0.812
5 Lopez_Ramon_1999 [286]	Activated Carbon - AZ46-24 (total acidity NaOH) (mmol/g)	2.72
6	Activated Carbon - BV46_OX (total acidity NaOH) (mmol/g)	1.1
7	Activated Carbon - BV46 (total acidity NaOH) (mmol/g)	0.22
8 Matsumura_1972 [167]	Boiler Soot I (KOH solution 1 M, (mmol/g))	3.02
9	Boiler Soot II (KOH solution 1 M, (mmol/g))	0.02
10	Boiler Soot III (KOH solution 1 M, (mmol/g))	1.13
11	Automobile Soot (KOH solution 1 M, (mmol/g))	0.02
12	Acetvlene Black (KOH solution 1 M, (mmol/g))	0
13 Goertzen_2010 [243]	Black Pearls 2000 (Boehm totration, Phenolic group, mmol/g)	0.18
14	Black Pearls 2000 (Boehm totration, Lactonic group, mmol/g)	0.024
15	Black Pearls 2000 (Boehm totration, Carboxylic group, mmol/g)	0.014
16	Black Pearls 2000 (Boehm totration, Total group, mmol/g)	0.218
17 Yu_2005 [140]	Activated Carbon W101 (total acid mmol/g)	0.92
18	Activated Carbon W101-KS (total acid mmol/g)	1.917
19	Activated Carbon W101-CN (total acid mmol/g)	2.29
20	Activated Carbon W101-HT (total acid mmol/g)	1.632
	Average:	0.89565

 Table 2.8: Summary of Soot/Carbon Particulate Surface Acid Functionality (mmol/g)

 Reported in Literature

There are only two results which specifically relate to soot, Popovicheva et al. [166] and Matsumura et al. [167] and in the case of the former a surface acidity of 0.1 mmol/g was measured but for the automobile soot for the latter it was 0.02 mmol/g. The average surface acidity for the data set is 0.9 mmol/g. The data shows a large variation with a standard deviation of 0.93. Clearly, there is a need for further detailed investigation of diesel engine soot surface acidity.



Figure 2.6: Summary of Soot/Carbon Particulate Surface Acid Functionality (mmol/g) Reported in Literature

2.4.4 Soot Polycyclic Aromatic Hydrocarbons (PAH)

PAH were associated with gasoline and diesel engine exhaust PM emissions as early as the 1950's [168, 169] and have since been recognised as some of the most toxic constituents of PM from the engine exhaust [35]. PAH are largely concentrated on the surface of soot [34] due to the condensation of PAH from the exhaust matter [25]. Their presence on the surface of soot combined with their toxicity explains why they are of such great concern. An extensive study of human cell mutagenicity for 39 PAH is reported by Durant et al. and identifies Benzo[a]pyrene (BaP) amongst others [170] as being of greatest concern with several of the 16 PAH considered in the Environmental Protection Agency (EPA) method 610 [23, 246] also highlighted, Section 3.6.6.

PAH can often be found together in groups of two or more and they can exist in over 100 different forms [171] of which Naphthalene is the simplest [171]. The most important in respect to diesel exhaust soot are a group of sixteen defined by

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EPA method 610 [23, 246]. PAH are also found naturally in the environment such as in oil, coal and tar deposits. Indeed, recent research has detected them out in space and they are thought to be potential precursors on the path to create amino acids and life; an interesting contrast to their associated toxicity to humans [172].

Diesel fuel is a source of PAH [173, 174] and generally the most abundant groups of aromatics in diesel fuel are the lighter PAH naphthalene and alkylnaphthalenes [175] though diesel fuel can also contain: fluorene, dibenzothiophene, biphenyl, benzothiophene, tetrahydronaphthalenes carbazole and their alkyl derivatives [28]. Some PAH are also thought derive from the lubricant [23, 28, 176, 177]. PAH are present in the soot precursor nanoparticles which range in size from 1-10 nm and ethane flame studies by Dobbins et al [25] show the presence of benzenoid PAH even in these young nanoparticles [25] suggesting that pyrosynthetic reactions [173, 175, 178] are producing PAH during combustion in addition to PAH which survive from the fuel [179]. Indeed, PAH are observed in diesel exhaust PM well beyond the limited molar mass range of 128 to 206 g/mol and such PAH must therefore originate from pyrosynthetic reactions rather than the fuel.

Many of the masses of observed PAH in diesel exhaust correspond to stabilomer species or their isomers that were previously found by thermodynamic analysis to be the most stable PAHs at temperatures typical of hydrocarbon flames [25, 180]. These stabilomer species account for the consistent appearance of specific PAH in diesel exhaust PM. The review by Dobbins identifies two and three ring alkylated naphthalenes and alkylated phenanthrenes as the dominant PAH components and which occupy the low to medium molar mas range 128 to 206 g/mol [181].

There have generally been reductions observed in diesel exhaust PM PAH concentrations with 80-90% reductions observed since 2000-model-year engine technology in the following decade [35, 182].

PAH condense onto the soot carbonaceous core with a wide range of other organic material and do so at different concentrations. The presence of oxygenated compounds which are common for soot (Section 2.4.1.1) can also hinder analytical measurements. The sample preparation and particularly the extraction of PAH from potentially interfering compounds is very important [183]. The other complication is that PAH concentration in modern diesel PM can often

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be at or below 1 ppm total, thus requiring very high precision to resolve accurately. The accurate determination of diesel exhaust PM PAH profile and individual PAH concentrations is thus a taxing exercise [183] and the analysis method generally used is Gas Chromatography–Mass Spectrometry (GC-MS) (See Section 3.6.6) as defined in EPA Method 610 [246].

Presented in Table 2.9 are the concentrations of 30 PAH reported for 10 different samples and highlighted in bold font are the 16 PAH identified in the EPA Method 610 [246]. Table 2.9 presents the original concentrations reported in the referenced literature for each PAH along with the PAH total concentration.

Table 2.9: PAH Percentage of Total Soot/Carbon Particulate PAH for Ten Samples

 Reported In Literature

			1	2	3	4	5	6	7	8	9	10	Mean	All Mean
Molecular	Formula	PAH Compound	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
128	C10H8	Naphthalene	-	-	27.57	25.54	76.79	-	-	7.14	6.53	4.68	24.71	17.30
142	C11H10	1-methylnaphthalene	-	-	-	-	-	1.58	1.55	-	-	-	1.57	0.47
142	C11H10	2-methylnaphthalene	-	-	-	-	-	3.56	5.32	-	-	-	4.44	1.33
152	C12H8	Acenaphthylene	-	-	0.15	0.16	1.14	-	-	7.43	6.53	4.78	3.36	2.35
152	C12H8	Biphenylene	-	-	-	-	-	-	-	-	-	-	0.00	0.00
154	C12H10	Biphenyl	-	-	-	-	-	-	-	-	-	-	0.00	0.00
154	C12H10	Acenaphthene	-	-	4.35	4.05	3.53	-	-	0.00	7.34	0.00	3.21	2.25
166	C13H10	Fluorene	-	-	15.14	14.26	4.37	-	-	7.71	6.53	4.68	8.78	6.15
178	C14H10	Anthracene	-	0.34	0.35	0.34	2.23	-	-	6.86	6.53	5.82	3.21	2.57
178	C14H10	Phenanthrene	-	15.41	44.74	48.47	1.29	-	24.16	7.14	6.53	10.19	19.74	17.77
190	C15H10	4,5-Methylenephenanthrene	-	-	-	-	-	-	-	-	-	-	0.00	0.00
192	C15H12	Methylphenanthrenes	-	43.72	-	-	-	-	-	-	-	-	43.72	8.74
202	C16H10	Fluoranthene	9.82	11.25	4.22	3.77	5.49	47.34	41.88	8.29	6.53	11.43	15.00	16.50
202	C16H10	Acephenanthrene	-	-	-	-	-	-	-	-	-	-	0.00	0.00
202	C16H10	Aceanthrylene	-	-	-	-	-	-	-	-	-	-	0.00	0.00
202	C16H10	Pyrene	15.29	10.70	2.50	2.54	2.42	1.60	1.30	8.57	6.69	17.67	6.93	7.62
226	C18H10	Benzol[ghi]fluoranthene	-	2.73	-	-	-	-	-	-	-	-	2.73	0.55
226	C18H10	Cyclopenta[cd]pyrene (CpP)	-	-	0.06	0.06	0.64	-	-	-	-	-	0.26	0.10
228	C18H12	Benzo[a]anthracene	25.07	1.43	0.08	0.09	0.10	0.56	0.29	6.86	6.53	5.82	4.68	5.15
228	C18H12	Chrysene & Triphenylene	33.05	5.86	0.20	0.21	0.09	17.40	13.42	6.86	6.69	5.93	8.97	9.87
252	C20H12	Benzo[b]fluoranthene (BbF)	9.61	1.99	0.05	0.05	0.23	20.47	9.99	7.71	7.01	6.13	6.32	6.96
252	C20H12	Benzo[b]fluoranthene (BkF)	3.44	0.59	0.05	0.06	0.30	-	-	-	-	-	0.89	0.53
252	C20H12	Benzo[b]fluoranthene (BjF)	-	0.79	-	-	-	-	-	-	-	-	0.79	0.16
252	C20H12	Benzo[e]pyrene (BeP)	-	1.68	0.23	0.15	0.81	1.98	0.83	-	-	-	0.95	0.66
252	C20H12	Benzo[a]pyrene, (BaP)	3.72	0.30	0.02	0.02	0.08	-	-	6.29	6.20	4.68	2.66	2.40
252	C20H12	Benzo(k)fluoranthene	-	-	-	-	-	1.21	0.54	7.14	6.53	4.57	4.00	2.40
252	C20H12	Perylene	-	0.04	0.02	0.02	0.09	-	-	-	-	-	0.04	0.02
276	C22H12	Indenol[1,2,3-cd]pyrene(IcdP)	-	1.27	0.03	0.03	0.10	2.49	0.37	5.71	4.08	4.78	2.10	2.10
276	C22H12	Benzol[ghi]perylene (BghiP)	-	1.46	0.03	0.03	0.14	0.89	0.12	6.29	4.89	4.78	2.07	2.07
278	C22H14	Dibenz(a,h)anthracene	-	-	0.01	0.00	0.03	0.93	0.24	0.00	4.89	4.05	1.27	1.14
300	C24H12	Coronene	-	0.45	0.20	0.17	0.13	-	-	-	-	-	0.24	0.12

Colour: EPA Method 610 PAH [246]

- 1 Bagley_1996 [79], 50% load, particulae + vapour PAH
- 2 Dobbins_2007 [25], National Institute of Standards and Technology (NIST) SRM1650a
- 3 Lin_2006 [296], diesel generator
- 4 Lin_2006 [296], diesel generator, palm 20 % blend
- 5 Lin_2006 [296], diesel generator, palm 100%
- 6 Poster_2003 [183], National Institute of Standards and Technology (NIST) SRM2975
- 7 Poster_2003 [183], National Institute of Standards and Technology (NIST) SRM 1975
- 8 Lombaert_2003 [221] DJ 5 Peugeot AFR 1.67
- 9 Lombaert_2003 [221] DJ 5 Peugeot AFR 3.52
- 10 Lombaert_2003 [221] DJ 5 Peugeot AFR 5.7

This total concentration has been used to calculate the percentage of total sample weight for each PAH and then this data has been averaged across the rows for each PAH to produce Figure 2.7.



Figure 2.7: Average PAH Percentage of Total Soot/Carbon Particulate PAH

Together Table 2.9 and Figure 2.7 provide a summary of the typical PAH profile observed for diesel exhaust PM. It is clear that the PAH of highest concentration are generally Naphthalene, Phenanthrene and Fluoranthene.

This chapter presents the methodology for all aspects of the research work. It begins with the design of experiments and then summarises the experimental apparatus and instrumentation system. There is a detailed review of the research and development of the key aspects of the system such as the engine compression ratio modification, the EGR system adaptation and exhaust soot collection apparatus. Finally, the techniques utilised for analysis of the exhaust soot are outlined.

3.1 Experimental Design

3.1.1 Fuels

This section summarises the fuel selection, procurement and presents a comparison of the fuel properties.

3.1.1.1 Fuel Selection

The selection of the fuels for the experimental work followed from the aims and objectives of the research work and the collaborative effort with Lubrizol. The first clear objective was to investigate a comparison of both mineral and biodiesel fuel soots by first establishing a baseline with a European EN590 (*henceforth denoted as* <u>EN590</u>) specification reference diesel fuel and then comparing to one of the most frequently encountered biodiesel fuels. Since the aim was to consider a very common biodiesel fuel, particularly one found in the European Union, rape seed was chosen as the feedstock for the biodiesel. It was also decided that the clearest distinctions in soot characteristics would be observed for the investigation of a pure biodiesel fuel rather than a mineral/biodiesel blend and that these distinctions could be easily ascribed to the respective fuels and their properties, which was the aim of the research work. Henceforth, **the** *Rape Seed Methyl Ester (RME) biodiesel fuel is referred to as* <u>B100</u>.

Lubrizol's experience of world fuel and lubricant test standards highlighted that a comparison of the soot produced from both a European standard diesel mineral fuel and a North American equivalent would complement the mineral-

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biodiesel comparison as it would provide an indication of the relative effects of two different but standardised mineral test fuels in relation to a biodiesel fuel. As the Western European and North American mineral diesel fuels typically derive from different crude sources (paraffinic, aliphatic) [184] and refineries and also conform to different standards; the compositions of the fuels are somewhat different. Two of the most significant differences are 1) the total aromatic content and 2) previously the North American diesel fuel specification had higher sulphur content. Each of these differences are frequently reported in literature to influence the soot produced during combustion and are thus of interest. Lubrizol specifically reported an interest in the North American PC-9 diesel test fuel as this is a fuel commonly used in standard lubricating oil high EGR engine tests [185].¹

In collaboration with Lubrizol it was therefore decided to use the North American PC-9 diesel fuel (*henceforth denoted as <u>PC9</u>*) as the third fuel in the research work as all three fuels together would provide soot characterisation results for three fuels representative of the more common mineral/biodiesel diesel engine test fuels in use across both the European and North American standardised tests. Selecting standard industry test fuels also enabled the research work to have a broad application and suitability for follow-up work.

3.1.1.2 Fuel Supply and Storage

Lubrizol arranged for the supply of all the fuels used in the research work reported herein. The two mineral diesel fuels were sourced as single batches in each case. The EN590 fuel was barrelled at Lubrizol's Hazelwood site in the UK from the EN590 reference fuel they were using at the time. The PC9 diesel fuel was specially shipped over from the United States by Lubrizol and was produced by and procured directly from Chevron Phillips. The B100 Rape Seed Methyl Ester (RME) biodiesel fuel was sourced by Lubrizol and two separate batches were required as the fuel specialists at Lubrizol advised that the fuel should be tested without any additives which meant that it had a short storage life. The batch used for the initial standard engine compression ratio experiments (referred to as the high compression ratio reference experiments at 19.5:1) was sourced from a subsidiary of ADM in Germany. The second batch which was used for the low compression ratio experiments (at 16.5:1) was sourced from Silver Group

¹ PC-9 is a lubrication oil standard test fuel established by the American Petroleum Institute which was developed for the EGR equipped engines of the late 1990s and has been later superseded by PC-10 (2007) [186]. PC-9 was widely used at the time of the experimental work.

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Fuels Ltd in the UK in 2007 prior to administration. All fuel was stored in 205 litre barrels and then moved into a fuel bund in the test cell when being used in the experiments.

3.1.1.3 Fuel Property Summary

The properties of each fuel were reported in test reports from the fuel supplier with the exception of the reference EN590 fuel which had a fuel analysis performed by SGD Germany GmbH. The fuel properties are summarised in Appendix 1 (Table A1.1).

Comparing across fuels, one of the key fundamental differences was the density which was higher for the biodiesel fuel. The other physical properties which were higher for biodiesel were the viscosity and the flashpoint temperature. The cetane number for the EN590 and the biodiesel fuel were quite similar but the cetane number for the PC9 fuel was much lower. The total acid number for the biodiesel fuel was far higher than for both the mineral fuels, particularly for the low compression ratio batch. The sulphur content for the EN590 and both biodiesel fuel batches were quite similar and low (<10 ppm) and the PC9 sulphur was a factor of 100 higher thus providing an interesting point of comparison. The water content for both batches of biodiesel was significantly higher than for the two mineral fuels and likely arose from the washing performed during the biodiesel transesterification process.

Comparing between the two mineral fuels, the PC9 fuel had 2% greater density and 14% higher viscosity but the flashpoint was lower and the cloudpoint was higher. The cetane number of the PC9 fuel was 15.8% lower than the EN590 baseline fuel and was therefore illustrative of the typical cetane number disparity between European and North American fuels. The total aromatic content of the PC9 fuel was 70% higher than for the EN590 fuel indicating a different fuel feedstock origin and refinery processes. The total acidic number for the PC9 fuel was a magnitude lower than that of the EN590 diesel and the total particulate matter for both fuels was quite similar.

Comparing between the two batches of biodiesel fuels, Appendix 1 (Figure A1.1), the differences were subtle but worthy of note. The viscosity of the 16.5:1 fuel was 5% higher than that of the higher compression batch but more importantly the cold filter plugging point for the 16.5:1 fuel was somewhat higher along with the flash point and a slightly lower cetane number and thus the lower compression batch of biodiesel may have had subtle differences in the ignition

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delay characteristics and combustion compared to the first batch used for the high compression experiments. The 16.5:1 B100 fuel also had a significantly higher total acid number and slightly higher concentrations of inorganics and metals.

3.1.2 Lubricant

A single lubricant formulation was used in this work which was selected and supplied by Lubrizol with a formulation tailored to investigate (as a separate study of principally Lubrizol's interest and not reported on in this work) whether there was any observable rheological differences in the end of test lubricant for each set of experiments with different fuel and compression ratio combinations. The outline elemental composition of this lubricant was important for reference when discussing the soot results and is summarised in Appendix 2 (Table A2.1).

3.1.3 Identification of Geometric Compression Ratio Range

During the last decade or more, newly developed Direct Injection (DI) diesel engines have shown a tendency toward lower geometric compression ratio, particularly those from the German Original Equipment Manufacturers (OEMs) and Japanese OEMs such as Honda. This trend has resulted in automotive industry companies (e.g. Lubrizol) enquiring whether this trend in compression ratio is impacting on the physiochemical characteristics of the soot produced. In Lubrizol's case, the question is acute as the soot produced in the cylinder is transported into the lubricant through the soot transportation mechanisms namely thermophoretic deposition and turbulent deposition. Thus, if there are significant changes to the physiochemical properties of the soot then there are potential concerns with regards to the performance of the Lubricant and hence Lubrizol's dispersant and detergent additives. This section therefore presents a summary of the statistical trend of geometric compression ratio in the last decade and accordingly identifies the compression ratio range which has been subsequently experimentally investigated in the work reported herein.

3.1.3.1 Engine Compression Ratio Trends

Obviously, for any given conventional engine design, it is the combination of the engine breathing system with the geometric compression ratio that determines the charge pressure, density and motion in the cylinder during the engine cycle. Thus, there is a complex interplay of an array of a significant number of factors that ultimately affect the in-cylinder charge and hence

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combustion and soot formation - especially so for modern DI diesel engines with turbocharging and EGR. However, geometric compression ratio remains a fundamental parameter of an engine and describes a group of these factors rather than any single factor and as such it can be readily compared engine-toengine with an expectation that there will be some form of correlation between it and measured parameters.

A higher compression ratio acts to increase the cylinder pressure and temperature for a given crank angle and thus generally on a CI engine with no other modifications this results in a shorter ignition delay period at a given operating speed. This plus the increased pressure during combustion leads to greater thermal efficiency and power when analysed thermodynamically. However, there is an associated reduction in mechanical efficiency as the higher cylinder pressures increase the piston-ring to cylinder wall friction and there are increased heat losses during compression and expansion as a result of the increased amount of work being done. Thus, the thermal efficiency gain with compression ratio is counteracted by a falling mechanical efficiency, explaining why there is typically a range of 15:1 to 24:1 for LD CI engines as a consequence of the different elements that form part of the whole package of the engine design.

In the late 1990s Volkswagen (VW) first introduced the 1.9I Turbo Direct Injection (TDI) engine series with DI using unit injector technology and in parallel Common Rail (CR) diesel fuel systems also saw their first application in Light Duty (LD) engines. This initiated a clear shift from the then dominant Indirect Injection (IDI) diesel engine design to the now dominant DI design. Thus, over a period from 1999 to 2011 the diesel engine has changed considerably and one of the characteristics of this change has been a general reduction diesel engine compression ratio.

To ensure that the compression ratio range investigated experimentally in this work aligned to the pattern of change in light duty LD diesel engines, a survey of reported engine geometric compression ratio for passenger car LD applications was undertaken which spanned the years of production 1999, 2005 and 2011. The respective data tables for compression ratio are presented in Appendix 3 (Table A3.1 to Table A3.5).

The statistical summary of compression ratio for the years 1999, 2005 and 2011 is presented in Table 3.1 to Table 3.3.

<u>3</u> 3.1

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Statistic	Result
Min	15.9
Max	24
Mean	20.9
Standard Deviation	1.65

 Table 3.1: Compression Ratio Statistics -1999 Engine Sample [340]

 Table 3.2: Compression Ratio Statistics -2005 Engine Sample [341]

Statistic	Result
Min	15.5
Max	20.2
Mean	18.0
Standard Deviation	0.88

Table 3.3: Compression Ratio Statistics -2011 Engine Sample [342, 343]

Statistic	Result
Min	14.9
Max	18.5
Mean	16.8
Standard Deviation	0.87

To assist the interpretation of this data it was useful to make the assumption that a Normal Distribution was a good approximation of the compression ratio distribution and to plot individually for the three data sets Figure 3.1.





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It was found that between 1999 and 2005 there was a very rapid shift from a broad distribution of relatively high compression (as there was a change from a sample set consisting of IDI and DI diesel engines to just DI) to a much narrower distribution with a mean roughly 14% lower. Then between 2005 and 2011 this trend continued at a slower rate with a reduction of 6.7% but with an almost identical distribution with engine designs solidifying on combining DI, CR, turbocharging and EGR.

As the specific power of the engines has increased, Figure 3.2, the peak cylinder pressures have also increased and now hover around 180 bar.



Figure 3.2: Engine Specific Power (kW/litre) for 1999 and 2011 Engines

Thus, for modern heavily boosted engines, a lower compression helps to achieve a better balance between the increase in mechanical losses associated with higher peak pressures whilst keeping the peak pressure lower to enable the engine block to be as light as possible and yet durable. The additional key driver in many engine designs in the same time period has been the reduction in NO_x emissions. As the kinetics of NO_x formation relate to the flame temperature, the reduction in compression ratio is a tool for directly reducing total engine NO_x emission. This has been perhaps the strongest factor in the trend towards reduced compression identified in Figure 3.1.

3.1.3.2 Selecting Engine Geometric Compression Ratio Range

Reflecting on the Normal Distribution for the 2005 and 2011 engine data in Figure 3.1 and the 6.7% reduction in compression in this period, it is projected

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that the current generation of engines will likely see a stabilisation in mean geometric compression between 16:1 and 16.5:1 with a few engines potentially tending towards 14:1. Thus, the lower range of compression ratio identified for experimental investigation was in the range 15:1 to 16.5:1. The lower value of this range was used in the review of methods of compression ratio modification (Section 3.3) and the upper value set the limit for the highest-low compression ratio configuration that was to be experimentally investigated. The upper limit of the experimental range for compression ratio was defined by the combination of the 1999 and 2005 data sets. From this data, *the upper limit was determined to be 20:1* based on estimation for the 2001 engines (i.e. constraining the range of investigation to one decade). Therefore, the lower end of this range was representative of contemporary LD diesel engines and the upper end was representative of older LD engines as well as some Medium Duty (MD) and Heavy Duty (HD) diesel engines.

3.1.4 Selection of Engine

Initially a range of options were considered for the choice of engine and the method for compression ratio change. These two considerations being clearly interrelated required careful analysis early in the research. The selection also had to be based on the desired range of compression ratio adjustment outlined in Section 3.1.3.2.

One of the first criterions for the experimental engine tests was the selection of the base diesel engine combustion system design (injectors, piston bowl, cylinder honing, valve configuration, bore-stoke, turbocharger, EGR etc.). It was decided from a review of the available research data previously gathered by Lubrizol that the VW 1.9 TDI engine was a well understood engine by Lubrizol with regard to PM emissions. This knowledge was gained through standardised tests that Lubrizol had been conducting as part of their lubricant development and certification processes. Thus, it was agreed with Lubrizol to utilise this combustion system design and review what options there existed for integrating this base design with a variable geometric compression ratio capability.

Building from this decision, analysis was undertaken into the design modifications which would enable the engine to be converted to run at various geometric compression ratios within the range 15 to 21:1, this analysis is presented in later Section 3.3 and in summary this work resulted *in the selection of two geometric compression ratios: 19.5:1 and 16.5:1*.

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3.1.5 Experimental Test Design

The experimental work was divided into three groups of experiments:

- Base Engine Performance, Emissions, Cylinder Pressure Measurements at Steady-State Conditions (Section 3.1.5.2): For the three fuels and two compression ratio permutations, the engine was operated over a set sequence of speed-load operating points and requisite measurements made to characterise the engine performance and emissions. The findings from these experiments helped to develop the experimental design for the other two groups of experiments.
- 2. Engine Soot Collection Tests (Section 3.1.5.3): For the three fuels and the two compression ratios, the engine was operated at a single condition to maximise exhaust soot mass flow rate to reduce the soot collection time requirement. Soot was collected at the exhaust manifold for all tests with an exhaust system diesel particulate filter (DPF) used at one of the compression ratios to collect soot to identify exhaust soot evolution from the exhaust manifold. Standard engine EGR was used for all tests.
- 3. Adapted Engine EGR (low 10% and high 55%) Soot Collection Tests (Section 3.1.5.4): For the EN590 reference fuel and the B100 biodiesel fuel and a single compression ratio the effect of EGR was considered. The emphasis for the experiments was the EGR based influence of soot. Soot was collected in a DPF in the exhaust system (See Section 3.5.2). The speed/load condition was necessarily different to that used for the main soot collection tests of experimental group 2.

3.1.5.1 Full Factorial or Fraction Factorial Design Consideration

For the base engine soot collection tests (Section 3.1.5.3) a consideration was initially made of whether the experiments should be of a fraction factorial or a full factorial design. The advantage of a fraction factorial approach was an optimised balance between the number of experiments to be performed and an increase in factor permutations which could be tested. During the initial design of experiments this was therefore considered with the main feature being more than two compression ratio configurations but following finalisation of the engine compression ratio modification methodology (Section 3.3) it was concluded that a full factorial approach with just two compression ratios was ultimately the more secure path to experimentally implement and to derive conclusions from with the time and resource available.
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3.1.5.2 Base Engine Performance, Emissions, Cylinder Pressure Measurements at Steady-State Conditions

A parametric experimental study of the base engine performance and emissions was undertaken to quantify the differences between the fuels and the geometric compression ratios' so that the changes in Brake Mean Effective Pressure (BMEP), fuel consumption, Air Fuel Ratio (AFR), exhaust emissions and cylinder pressure etc. could be understood and utilised to help interpret the sampled exhaust soot results. These experiments were also essential in establishing the engine operating conditions for the base engine soot collection tests and the EGR experiments detailed later in Section 3.1.5.3 and Section 3.1.5.4. The experimental results from this work are summarised in Chapter 4 and are supporting to the foremost soot characteristics results in Chapters 5-9.

The speed-load steady-state operating points used for these experiments are detailed in Appendix 4 (Table A4.1) and were designed to broadly consider the speed-load envelope of the engine, encompassing EGR and none-EGR engine operating conditions. The main limitations which constrained the range of set-points investigated were a drive line resonance below 1400 rpm which impaired the dynamometer controller speed control stability and also a dynamometer speed control instability at greater than 60% load between 1400 and 1900 rpm. Tuning of the dynamometer speed controller reduced the severity of the system oscillation at these points but failed to eliminate them completely and thus these unstable regions were avoided. The load groups were defined as follows: **A** (Torque <40 %), **B** (40<=Torque<60 %), **C** (60<=Torque<80 %), **D** (80<=Torque<95 %), **E** (Torque>=95 %). These were used to group the measurements and average the data across load groups when summarising the performance and emissions changes with fuel and compression ratio, Chapter 4.

At each steady-state point detailed in Appendix 4 (Table A4.1) the gaseous and particulate emissions, engine performance and cylinder pressure were recorded using the instruments detailed in Section 3.2.2. The approach taken to provide a fixed reference across the three fuels and two compression ratios investigated was to set the dynamometer controller to *[dynamometer-speed, throttle-direct]* mode so that the engine throttle was set to a position which achieved the same fuel injection duration and the dynamometer speed controller loop then managed the torque to achieve the required engine speed. In this way the engine performance and emissions were compared across the same fuel injection timing and thus changes in fuel density, compressibility and calorific

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value would be highlighted between the three fuels. This was considered to provide a more useful and robust basis for comparison than equating the fuel mass flow or engine power output between fuels during the experiments.

The engine performance and emissions measurements were undertaken with two different intake manifold air temperature states (<40°C and >50°C) to enable an analysis of the effect of this parameter on the overall engine performance and emissions. This parameter was a controllable experimental factor which was used to increase the exhaust soot concentration for the base engine soot collection tests and is discussed in more detail in Section 3.1.5.5.

A limitation of the experiments was that the inlet air pressure, temperature and humidity could not be controlled (test cell limitations) and thus variation in these parameters across the experiments is responsible for a fraction of the measurement changes observed.

The performance and emissions experiments were each conducted prior to the associated base engine soot collection experiment which used the same fuel and compression ratio configuration (Section 3.1.5.3). This was to align the performance and emissions results to the condition of the engine and atmospheric conditions at the time of the soot collection experiment for the same system configuration. The lubricant used for each experiment was a fresh fill to avoid any aged lubricant influence on the results.

3.1.5.3 Engine Soot Collection Experimental Design

The design of the engine soot collection experiments developed from the design and development of the ceramic thimble based exhaust manifold soot collection apparatus detailed in Section 3.5.1. The principle characteristic of this collection apparatus which influenced the design of the collection experiments was the very low (<1%) collection efficiency at the exhaust manifold confluence point which was where the sample line tapping was installed. Further, this collection efficiency declined significantly with reduced exhaust soot concentration in the exhaust. Consequently, it was necessary to maximise both the exhaust soot concentration and the exhaust mass flow rate. The engine performance and emissions parametric study described in Section 3.1.5.2 revealed this to be at **'rated engine power'** (4000 rpm, maximum load) with the original base engine mapping and EGR setting Chapter 4, Section 4.2.

Section 3.6.8 outlines that the total sample soot mass required to complete all of the soot characterisation tests was approximately 2g. Consequently, it was

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necessary to conduct preliminary experiments which were undertaken with the combination of the selection of the rated engine condition and the 2g of soot target with the EN590 fuel at 19.5:1 to determine the total hours required for soot sampling with the ceramic thimble system. It was determined that at least 20 hours were required for the EN590 fuel and that the ceramic thimbles needed to be changed every 5-7 hours to achieve this requirement. The ceramic thimble change was necessary due to the decline in collection efficiency as the thimble plugged.

For each of the fuel-compression ratio combinations (a total of 6) the design of the experiment therefore consisted of running the engine at the rated condition for a target duration of 20 hours with the ceramic thimble system sampling the exhaust soot once the engine exhaust temperature had stabilised. Isolation valves were used to control the sampling and the ceramic thimbles were replaced with a new thimble every 5-7 hours. The experiments were broken into 5 hour intervals at which point the mass of soot collected in the thimble was measured using a mass balance and also the mass of condensate (largely water) which was trapped in the ceramic thimble system catch-pot (Section 3.5.1.1) was also measured. This latter measurement was used to monitor the collection efficiency achieved in this period of time so that a decision of when to replace the thimble could be made (the sample duration for thimble change was different for each of the six test combinations). A 50 ml lubricant sample was also taken at the 5 hour interval from the engine main gallery using a tapping on the oil filter mount and this provided lubricant rheological performance information for Lubrizol. A subdivision of this 5 hour block was necessary at 2 hours after the installation of a new thimble as lagging had to be added to the ceramic thimble sample line (Section 3.5.1.1) to maintain the thimble temperature above 110°C to avoid condensation.

During each experiment the performance of the engine was monitored and recorded using the instrumentation system detailed in Section 3.2.2. Measurements were taken every 10 min with the AVL415 smoke meter and then at every 30 min the snapshot of the measurements was recorded and checked for any significant change. This process revealed a problem with injector coking for the two biodiesel experiments and in the case of the 16.5:1 experiment the problem was so acute that the soot collection experiment had to be ceased early at 12 hours as the exhaust soot concentration and hence collection rate had declined to such an extent that the experiment was no longer viable to continue,

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Appendix 9. The other 5 experiments completed the 20 hours target and the soot mass collected is summarised in Section 3.5.1.1.

For the three 19.5:1 experiments which were conducted first, just the exhaust manifold ceramic thimble system (Section 3.5.1) was employed for soot collection but for the 16.5:1 experiments a DPF exhaust collection system was also utilised (Section 3.5.2). The DPF was employed for these lower compression experiments to fulfil the project research aim of understanding how soot which originates from different fuels evolves in the exhaust. The DPF had to be used for this task in preference to a ceramic thimble system as the lower pressure in the exhaust after the turbocharger rendered the ceramic thimble method ineffectual at this sample location.

To maximise the exhaust soot concentration, the Intake Manifold Air Temperature (IMAT) was elevated to above 40°C for all experiments and this approach is summarised in Section 3.1.5.5.

3.1.5.4 Adapted Engine EGR (low ~10% and high >50%) Soot Collection Experimental Design

The main criterion of the EGR experimental tests was the exploration of the EGR range from low (~10%) to high (>50%) with the method of EGR manipulation limited to utilising the original engine vacuum actuation of the original EGR valve which is detailed in Section 3.4. The use of the existing engine EGR system required a parametric study to first identify the operating conditions where both low and high EGR could be achieved. This revealed that the EGR rates available depended on the pressure difference across the EGR valve (since the VW 1.9 TDI uses a high pressure EGR system design with the exhaust gas bleeding off before the entry to the turbine housing). At high loads with high intake boost pressures, the maximum achievable EGR was very limited as the pressure difference across the EGR valve (i.e. exhaust manifold to intake manifold) was small. Therefore the EGR tests had to be performed at lower intake pressures and therefore not at the same speed-load condition of the baseline engine soot collection experiments described earlier. From the parametric investigation the optimum speed was determined as 1400 rpm and the torque for the low EGR (10%) point was ~180 Nm (Section 8.2) with a fuel injection duration of 12.8 Crank Angle Degrees (CAD).

Having determined a suitable operating point, it was necessary to confirm the estimated exhaust manifold soot collection rate to see if the ceramic thimble

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collection method was viable. Based on the calculated soot mass flow rate for the B100 fuel 10% EGR case (3.3 g/h –Section 8.3) and the typical collection efficiency of the ceramic thimble exhaust manifold collection system (~1% - Section 3.5.1), it was estimated that the total collection period for the B100 test would be infeasible as it would need in excess of 600 hours. The EGR experiments were therefore constrained to the use of the just the DPF for soot collection. Due to time constraints the experiments were also limited to the 16.5:1 geometric compression ratio alone.

The required duration of the soot collection with the DPF was determined in two ways. Firstly, by estimation of the minimum time required based on the measured exhaust soot mass flow and the assumption that 100% of the soot mass measured by the AVL415 smoke meter (Section 3.2.2.5) was trapped by the DPF (thus ignoring collection efficiency and exhaust oxidation effects). Secondly, pressure sensors were installed pre and post DPF and the pressure drop monitored during the test and limited to (<25 kPa). Two additional thermocouples were also installed for the EGR experiments and were located in the engine intake before and aft of the EGR valve to ascertain the increase in temperature of the intake charge caused by the uncooled EGR and these measurements are summarised in Section 8.2.

An important constraint with the EGR experiments was that as the EGR was increased there was a corresponding reduction in available boost pressure as the VW 1.9 TDI engine uses high pressure EGR and there was thus a significant reduction in the pressure ratio across the turbine with higher EGR. For the high EGR condition experimentally investigated, the ECU was running at the extremities of the calibration tables and consequently fuelling was reduced (12.8 to 8.2 CAD, Section 8.2) and the torque output also therefore reduced at high EGR and thus the EGR soot results reported in this work are also subject to these associated fuel injection and boost pressure changes which were unavoidable.

At the time of the experiments the Horiba gas analyser used in this work (Section 3.2.2.6) had an incorrectly functioning intake CO_2 measurement and thus it was necessary to use a calculation approach for the estimation of the resultant rate of EGR. *This method was based on the assumption of constant volumetric efficiency with EGR*. The required data from the engine included air mass flow and manifold temperature and pressure at conditions under zero EGR and with EGR which are detailed in Chapter 8.

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From the definition of true volumetric efficiency under zero EGR conditions:

$$\dot{\mathbf{m}}_{\text{zero}} = \rho_{\text{zero}} \cdot \eta_{\text{vol}} \cdot \mathbf{V}_{\text{swept}} \cdot \mathbf{N}$$

With EGR:

$$\dot{m}_{air} + \dot{m}_{egr} = \rho_{man} \cdot \eta_{vol} \cdot V_{swept} \cdot N$$

Equating η_{vol}

$$\dot{m}_{egr} = \dot{m}_{zero} \cdot \frac{\rho_{man}}{\rho_{zero}} - \dot{m}_{air}$$

So from the definition of EGR fraction:

$$EGR = \frac{m_{egr}}{\dot{m}_{air} + \dot{m}_{egr}} = 1 - \frac{\dot{m}_{air}}{\dot{m}_{zero}} \cdot \frac{\rho_{zero}}{\rho_{man}}$$

Now assuming perfect gas behaviour:

$$\rho = \frac{\text{mass}}{\text{volume}} = \frac{\text{MP}}{\text{RT}}, \text{ so}$$

$$EGR = 1 - \frac{m_{air}}{\dot{m}_{zero}} \cdot \frac{M_{air}}{M_{air+egr}} \cdot \frac{P_{zero}T_{man}}{P_{man}T_{zero}}$$

Further assuming that the molecular weights are similar:

$$EGR = 1 - \frac{\dot{m}_{air}}{\dot{m}_{zero}} \cdot \frac{P_{zero} T_{man}}{P_{man} T_{zero}}$$
 Equation 3.1

Equation 3.1 has therefore been used to estimate the EGR rate for all four of the EGR experiments using the mass air flow, intake pressure and temperature (both measured at the same point). This calculation should only be considered an estimation due to the assumptions made in the derivation, however it provides the required indication of the extent of the change in EGR when direct measurement was not possible.

3.1.5.5 Intake Manifold Air Temperature (IMAT) Optimisation

During the base engine performance and emissions experiments the effect of manifold air temperature (measured before the EGR valve introduced exhaust gas to the intake manifold) was evaluated in regard to the engine Mass Air Flow (MAF) and AFR and the resulting impact on exhaust soot concentration. It was determined that there were several significant changes in the engine performance and emissions with the change of IMAT in the range of 20 to 80°C

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which usefully included an increase in the exhaust soot concentration with higher IMAT and an example of this effect is illustrated in Figure 3.3 for the change from low to high IMAT at the two compression ratios for all fuels. This was largely a consequence of the parallel reduction in AFR which occurred as the ECU did not successfully compensate for the increase in the IMAT. Thus, IMAT was a controlled experimental factor which was not part of the original research aims but could be optimised to increase the exhaust soot concentration at the majority of engine operating conditions. A general summary of the effect of IMAT is presented in Section 4.2.1.



Figure 3.3: Increasing IMAT - Effect on Exhaust Gas Soot Concentration (g/h) for $R_c = 16.5$:1 (a) and $R_c = 19.5$:1 (b)

The IMAT used for the base engine soot collection experiments was maintained at a high temperature in the range 74 to 86°C for the 19.5:1 experiments and the range 44 to 67°C for the 16.5:1 experiments (Section 4.3). The range in temperatures was a consequence of the ambient temperature variations across the experiment. A slightly lower temperature range was used for the 16.5:1 experiments as the turbocharger bearing seals failed twice in the 19.5:1 experiments and this was attributed to prolonged excessive turbocharger temperatures. These intake temperatures therefore maximised the soot collection rate and hence soot sample mass for the soot collection experiments. The control of IMAT was achieved through the control of the cooling water flow rate through an air-water charge air cooler, Section 3.2.1.3.

3.1.5.6 Test Sequencing

Experimental test sequencing was an important part of the experimental design in terms of the sequence in which the three separate groups of experiments were conducted and also the sequencing of the fuels, compression

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ratio and EGR. The groups of experiments (performance and emissions, soot collection, EGR) could not be conducted separately in the order detailed as the compression ratio change (19.5:1 to 16.5:1) meant that both the soot collection and performance and emissions tests were conducted such that experiments alternated between each experiment type following each change in fuel or compression ratio. The EGR experiments were distinct in the requirement to use the DPF alone for which the installation was not completed until after the engine geometric compression had been reduced to 16.5:1 thus these experiments had to be sequenced in with this constraint.

The sequencing of the fuels was important, especially with regard to B100 biodiesel which was the last fuel to be tested at the 19.5:1 compression ratio and was selected as the first fuel to be tested at the 16.5:1 compression ratio. This fuel sequencing was devised for several reasons. Firstly to try and run both experiments with the same batch of biodiesel fuel and therefore minimise the fuel storage time and the risk of fuel degradation [189]. Secondly, to sequence back-to-back experiments where the only change was the reduction of compression ratio and was thus an attempt to more clearly define the influence of the compression ratio change alone. Finally, this fuel sequence also allowed the mineral diesel experiments to be arranged back-to-back which was advantageous as there was a risk with running the engine on un-additised B100 biodiesel that there would be a measurable impact on the fuel injection system performance (e.g. injector coking: Appendix 9).

However, as stated previously, Lubrizol had advised that the biodiesel fuel was to be un-additised so that any additive based influence on the sampled exhaust soot could be avoided which meant the fuel had a limited storage life. The change to the lower compression ratio as detailed in Section 3.3.4 consumed such an amount of time that the biodiesel fuel had begun to biodegrade when the engine was ready to do the 16.5:1 B100 biodiesel soot collection test. Two different batches of B100 fuel were therefore supplied, Appendix 1 (Figure A1.1), for the test work; the first batch was used to do the base engine soot collection and the engine performance and emissions tests at the 19.5:1 compression ratio and also the 16.5:1 EGR tests with DPF soot collection. The second batch of B100 fuel was only used for the 16.5:1 compression ratio soot collection experiments.

3 3.2

Experimental Apparatus

3.2 Experimental Apparatus

This section describes the engine experimental system which was installed specifically for this work in the Powertrains Laboratory at Loughborough University. The installation originally spanned the period June 2004 to March 2006 and the engine remains in use as of 2014 for research and teaching. The system configuration is illustrated in Figure 3.4 and Figure 3.5.



Figure 3.4: Photograph of Experimental System - Test Cell



Figure 3.5: Photograph of Experimental System - Control Room

The engine was supplied from Lubrizol's Hazelwood UK research facility as a post-test engine which had been completely stripped down and inspected following a standard industry lubricant test. With the assistance of Lubrizol the engine was rebuilt with the majority of the ancillaries and fasteners replaced.

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Power curve data from the prior Lubrizol baseline tests of the engine provided validation of the installation and instrumentation system described herein.

3.2.1 Engine

This section summarises the key parts of the engine installation and where deviations exits between the experimental engine and the engine used in a vehicle. The VW 1.9 TDI engine has numerous different ratings and configurations as the engine has been widely utilised within the whole of the Volkswagen Group. In Table 3.4 the full specification of the *type AVF engine* utilised in the experiment research reported herein is outlined.

Displacement	1896cm ³ (1.91)
Power	96kW (131PS, 129bhp) at 4,000rpm
Torque	310Nm at 1,900rpm
Compression ratio (R_c)	19.5:1
Bore	79.5mm
Stroke	95.5mm
VW Engine Designation	Type AVF (Passat B5 6-Speed M Trans)
Other Common Engine Codes	ASZ & BLT
Years of Production	10/2000 to 05/2005
Fuel Injectors	Pumpe Düse, Bosch 1920bar
Block	grey cast iron
Head	cast aluminium alloy
Valves	SOHC, 2 valves per cylinder
Turbo	Garrett vacuum drivven VGT
EGR	hi-pres, non-cooled, vacuum driven valve
MAF	Hot-wire
ECU	Bosch ED16

Table 3.4: VW 1.9I TDI – Base Engine Specification [187, 188]

3.2.1.1 Engine Electrical System

Lubrizol procured an original Passat vehicle and then procured a duplicate engine loom, ECU, vehicle speedometer panel, ignition key and key transponder receiver. This duplicate set was then fitted to the Passat and the system security codes programmed by a local VW dealer so that this duplicate system functioned. This solution precluded the capability to access the ECU to adjust operating parameters and maps etc.

3.2.1.2 Engine Cooling

The engine was coupled to the test cell cooling water system using a sized Bowman heat exchanger. The engine thermostat was retained to ensure a fast warm-up time as there was no control valve on the coolant system to regulate the

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flow of coolant through the Bowman. Thus, the Bowman coolant flow was set so that the engine coolant temperature stabilised at 90°C when the engine was warmed up and would then fluctuate between 90-100°C depending on the engine operating condition.

3.2.1.3 Charge Cooler Selection and Control

The base engine was fitted with an air-to-air charge air cooler and this was unsuitable for the test cell so was replaced with an air-to-water charge cooler from a Peugeot 2.0I engine which used the laboratory cooling water.

To achieve the setting of the low and high IMAT condition (Section 3.1.5.5), the procedure was to set the water flow control valve to fully open in the case of the low IMAT configuration and to then restrict the flow control valve such that the maximum IMAT temperature was 90°C (typically either 2000 rpm 76% load or 4000 rpm full load) for the high IMAT case. 90°C was determined as the upper temperature limit due to the onset of increased engine combustion instability (coefficient of variation of the Indicated Mean Effective Pressure (IMEP)). The methodology was designed to achieve as large as possible delta in the IMAT within the limits of the system performance capability.

3.2.1.4 Exhaust System Routing

The layout of the test cell where the engine was installed dictated that the original engine exhaust required significant modification. This was a result of the exhaust side of the engine being on the opposite side of the test cell extraction duct. The exhaust was successfully modified to maintain the original system pipe lengths and intermediate and final silencer units thus ensuring that the gas flow would be as close as possible to the base engine and also as the engine was originally installed at Lubrizol, thus achieving the same back pressure characteristics.

3.2.1.5 Fuel Conditioning, Handling and Storage

The 1.9I TDI engine used in this work had a vehicle under-floor heat exchanger to cool the return (spill-back) fuel returning to the fuel tank when in service. The volume of spill-back fuel returning to the fuel metering system was considerable and required the removal of up to 2 kW of heat from the return fuel continually. This was achieved by adapting a Haake UWK90 laboratory chiller unit to remove heat energy from the fuel prior to the return fuel from the engine being returned to the measurement volume in the fuel metering system. This

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implementation helped to reduce fuel volumetric measurement variation but did not provide precise control of fuel supply temperature.

The use of multiple fuel types during this experimental work required careful fuel handling and storage practices to minimise the opportunities for crosscontamination. All fuel was stored in regular 205 litre barrels and in the test cell a fuel bund was installed into which these barrels could be placed.

To minimise cross-contamination when changing fuels, the engine fuel system was drained and the engine fuel filter replaced prior to charging the system with the next fuel. A flush test was then conducted with the engine run at high speed and load for more than an hour and the emissions and cylinder pressure were continually monitored for stabilisation. The fuel supply and metering system was also designed to prevent any backfill from the test cell fuel system to the barrel.

3.2.1.6 Lubricant Handling and Consumption Measurement

For each soot sample collection experiment with a change of fuel or compression ratio, the old engine oil was drained and a fresh fill of lubricant was added. This was then followed by a flush run and then the engine lubricant was renewed again. These precautions were undertaken to minimise any potential contamination of the soot samples from aged lubricant.

A lubricant sample line was manufactured and installed on the engine oil filter mount and during the rated condition soot collection experiments; a 50ml oil sample was taken every 5 hours to provide Lubrizol with information on the effects soot loading and oil rheology change. To measure the rate and amount of lubricant lost from the engine during the soot collection tests, the oil level on the engine dip stick was monitored and oil added gradually to maintain the oil level. These lubricant mass additions were then used to estimate the lubricant consumption rate for all rated condition experiments.²

3.2.2 Instrumentation

This section summarises the integrated instrumentation system developed in this work emphasising the critical components of the system.

² The post-experiment lubricant analysis revealed very low levels of soot loading of the lubricant (<1% weight) for all rated condition soot collection experiments and this level of soot loading had negligible influence on the rotational viscosity of the lubricant.

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Experimental Apparatus

3.2.2.1 System Overview

The instrumentation system was developed around a series of measurement instruments and sensors and utilised National Instruments LabVIEW[®] for centralised data acquisition and instrument communication for system control and monitoring. All the software was conceived and written specifically by the author for this research work and was presented at the National Instruments UK Academic Conference in 2006 [190].

An overview of the system is provided in Figure 3.6 which shows that the system was comprised of three Personal Computers (PCs) with two equipped with National Instruments DAQ cards and one running an ECU communication software (VCDS). The two PCs with DAQ cards were individually optimised for 1) low frequency (<10Hz) engine monitoring and system control and 2) for high frequency (1440 samples per cycle) cylinder pressure measurement and heat release rate online computation.

The low frequency program monitored and recorded system temperatures, emissions, fuel rate, pressures (DPF and ceramic thimble system) at a fixed sample frequency and an analysis of this data is summarised in Chapter 4 for the emissions and soot collection experiments and later in Chapter 8 for the EGR experiments. The high frequency program captured the cylinder pressure signal from cylinder 1 (cylinder adjacent to the timing belt end of the engine) with the samples triggered by an AVL 364 optical encoder and this provided information on the different burn characteristics of the three fuels for both compression ratios.

The third PC was used to monitor ECU parameters and fault codes with the software tool VCDS [191]. This was connected to the ECU via CAN and most importantly was used to determine the ECU measured throttle input signal as the engine and dynamometer control system was configured to the dynamometer-rpm, throttle-direct control mode combination for all experiments.



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3.2.2.2 Dynamometer and Control System

A Froude AG150-HS eddy current dynamometer was used in combination with a Froude Consine Texcel V4 dynamometer-engine control system. Engine torque was measured by a load cell fitted to the dynamometer and the engine speed was measured using a Hall Effect sensor and toothed wheel which were also fitted to the dynamometer. The dynamometer load cell was regularly checked throughout the experiments for calibration accuracy. Engine speed and dynamometer applied torque were configured to be transmitted via a RS232 link between the Texcel V4 controller and the low frequency LabVIEW[®] data acquisition program and this program was also utilised to program Texcel with test sequences which assisted with experimental reproducibility.

3.2.2.3 Fuel Rate Measurement

A volumetric fuel measurement system manufactured by Plint & Partners Ltd of the UK [192] was used for the engine fuel rate measurement. The fuel meter was linked to the low frequency LabVIEW[®] monitoring program to record the time for each steady-state fuel measurement. A minimum of three fuel measurements were recorded and then averaged for each experimental test point.

3.2.2.4 Cylinder Pressure and Injector Current Measurement

For the measurement of cylinder pressure a Kistler Type 6055 piezoelectric Pressure Transducer & Type 6535 Glowplug Adapter were fitted to cylinder 1 (cylinder adjacent to the timing belt end of the engine). An AVL 364 optical encoder was configured to 0.5 CAD and used to trigger the sampling of cylinder pressure 720 times per engine rotation. A Kistler 5011 charge amplifier converted the pressure transducer charge signal to a voltage signal in the range 0-10V suitable for the data acquisition hardware. This was equivalent to 0-200 bar and thus well matched to the peak firing pressure of around 160-170 bar at 19.5:1.

Accurate determination of cylinder Top Dead Centre (TDC) position was very important for correct IMEP estimation [193] and this was done by first statically aligning the AVL encoder to TDC and then motoring the engine and recording the cylinder pressure trace. This data was then post-processed with an algorithm written in Matlab[®] based on the methodology described by Hsu [193] and the encoder position was then adjusted by the correction estimated from this post processing. This sequence was repeated several times to minimise the correction calculated in the data post processing.

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3.2.2.5 Exhaust Particulate Emissions Measurement

Particulate emissions measurement was performed with an AVL 415 smoke meter with an unheated sample line. The sample point for the emissions and rated condition soot collection experiments was located approximately 2 meters down the exhaust from the turbocharger with the sample probe installed in the exhaust pipe following the guidelines of the AVL 415S manual [195] (6 exhaust pipe diameters equivalent of straight pipe section ahead of the probe). This position was then changed to be before the DPF when the DPF was installed in the exhaust, Figure 3.7.



Figure 3.7: AVL 415 Exhaust Sample Locations (with and without DPF)

However, the sample probe position relative to the DPF depended on whether the soot collection tests were for the rated power collection experiments (i.e. investigation of soot evolution in the exhaust system, Section 3.1.5.3, or the EGR experiments, Section 3.1.5.4). For the former experiment set-up, a long exhaust extension was also required to increase the distance between the exhaust manifold and DPF to reduce the exhaust gas temperature at the DPF (refer to later Section 3.5.2.1) and thus the AVL 415S sample probe was roughly 5 meters upstream of the DPF position for these experiments. For the EGR experiments, the probe was approximately 1 meter upstream of the DPF as the exhaust extension was not required.

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For the position used during the DPF experiments it was necessary to design and machine a new main body section for the AVL 415 sample probe which did not have a 45 degree angle as the new position enabled the probe to be inserted into the exhaust at a 90 degree bend downstream of the sample probe as is shown in Figure 3.7 (on the right). As a precaution the unheated sample line was cleaned with a high pressure shop air prior to each experiment to remove any residue.

3.2.2.6 Exhaust Gaseous Emissions Measurement

All exhaust gas emissions were measured pre-catalyst with the same exhaust manifold sample point used for the soot collection tests, Figure 3.8. The gaseous emissions test bench was a Horiba Mexa 7100 HEGR which included individual analysers for measuring CO, CO_2 , O_2 , THC and NO_x . Each analyser was calibrated routinely with span gases before and during each experiment to reduce the effect of analyser drift. Regular sample line purging was also conducted during the experiments to minimise the hang-up of HCs and any condensed water in the sample line. Only steady-state engine operating points were considered in this work and the emissions at each point were averaged over 30 seconds and repeated.



Figure 3.8: Horiba Mexa 7100 HEGR Exhaust Emissions Analyser and Sample Position Detail

3.3 Engine Geometric Compression Ratio Modification

The principle engineering challenge in respect experimentally investigating geometric compression ratio with the selected VW 1.9I TDI engine was to be able

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to experimentally test over the required range of relevant geometric compression ratio whilst at the same time ensuring that the generated results would be valid and not biased by other related fundamental change(s) to the engine. For example, these could have included changes to the engine breathing and or motion of the charge in the cylinder such as the squish and swirl characteristics around the piston bowl for DI diesel engines.

The change of the geometrical compression ratio could be achieved through changing either the physical swept volume or the clearance volume or both. Changing the engine swept volume was eliminated as an option as it would result in a change in the engine displacement through a change in the stroke of the engine; requiring modification of either the crankshaft, connecting rod or piston to achieve.

Thus, the following section reviews the basic design of the VW 1.9I TDI engine and considers the ideas for varying the compression ratio through modification of the clearance volume so as to meet the research objectives.

3.3.1 Measurement and Calculation of Engine Geometry

Section 3.1.3.2 defined that the identified range for the investigation of geometric compression ratio was 15:1 to 20:1. This section reviews design modifications that were considered for the VW 1.9I TDI engine to change its geometric compression ratio within this range.

Table 3.5 lists the important geometrical specifications of the VW 1.9I TDI engine [188].

Parameter	Value
Displacement:	1896 cm ³
Original compression ratio (R _c):	19.5:1
Bore:	79.5 mm
Stroke:	95.5 mm

Table 3.5: VW 1.9I TDI – Base Engine Geometry

Equation 3.2 defines the compression ratio of an engine (where; Clearance Volume V_c is the clearance volume at TDC, V_s is the swept volume and Compression Ratio R_c is the compression ratio) and was used to calculate the engine clearance volume for the baseline compression ratio of 19.5:1 and deduce what part of this volume derives from the piston bowl and valve recesses

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in the piston and what part is a consequence of the Clearance Height H_c between the piston and the cylinder head.

$$V_c = \frac{V_S}{R_c - 1}$$
 Equation 3.2

The volume of the piston bowl was measured separately with water and acetone and was found to account for ~86% of the total V_c at TDC. The H_c between the piston crown and cylinder head was estimated at approximately 0.6620mm, and thus very small which implied that the investigation of compression ratios' significantly higher than that of the base engine was unlikely to be feasible through a reduction in this clearance without issue with valve clearances etc. thus for practical purposes the compression ratio investigation was constrained to compression ratio lower than the base engine 19.5:1.

3.3.2 Analysis of Methods for Changing Geometric Compression Ratio

This section summarises the methods originally considered and investigated for changing the clearance volume of the VW 1.9I TDI engine.

3.3.2.1 Contra-Piston Method

The contra-piston method is based on the principle that a boundary of the combustion chamber consists of a piston Figure 3.9, the position of which is able to be finely adjusted such that the adjustment of the cylinder V_c and hence compression ratio can be tightly controlled. The main issue with this approach is where to site the piston as it is typically forms part of the cylinder head.



Figure 3.9: Contra-Piston [Adapted from: Heisler, H., Advanced Engine Technology]

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3.3.2.2 Auxiliary Chamber Method

The auxiliary chamber method refers to an auxiliary chamber that is connected to the main combustion chamber via a channel which can be sealed with a form of screw mechanism Figure 3.10. This creates in a very narrow passage for the reactants and products of combustion to pass through therefore introducing its own set of problems when it comes to analysing what additional effects this method has on in-cylinder gas dynamics and combustion. It is also more suited to use on IDI engines where there is a pre-chamber in which the auxiliary chamber can be located adjacent to and coupled with. In its basic form, this solution also only allows for a single change in compression ratio.



Figure 3.10: Auxiliary Chamber [Adapted from: Heisler, H., Advanced Engine Technology]

3.3.2.3 Joint Ring 'Spacer' Method

One method for achieving different compression ratios with the VW 1.9I TDI engine was to use the so called joint spacer rings methodology. This involves increasing the height of the cylinder head above the block and hence the size of the clearance volume through the incorporation of spacer rings of appropriate thickness at the head gasket interface Figure 3.11.

To determine the validity of this method, consideration was given to the maximum height increase in the cylinder head required to achieve the lowest compression ratio of 15:1. The clearance volumes and heights were calculated for compression ratios in the range 15 to 21:1 and the results are presented in Appendix 5 (Table A5.1). This showed that a geometric compression ratio of 15:1 required an increase in the cylinder head height of 2.32125-0.66198 = 1.659mm. This was equivalent to a 32.14% increase in the clearance volume V_c and was

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thus a significant change for the engine. However, in principle this could be achieved through the inclusion of a joint ring at the head gasket interface. The main concern would be how to combine with the head gasket to ensure a reliable gas seal.



Figure 3.11: Joint Ring Separating Engine Block and Cylinder Head [Adapted from: VW 1.9I Engine Workshop Manual]

Closer inspection of the 0.5 increments in compression ratio, Appendix 5 (Table A5.1), and the resulting change in the clearance height suggested that a joint ring installation would be required to be within a tolerance of 0.1 mm (100 μ m). For a unit change in compression ratio the tolerance reduces to 0.2 mm. Thus, technically there were no 'show-stopper' issues identified with implementing this method of compression ratio adjustment.

The benefit of this method shown by these calculations was that the maximum clearance height increase was approximately 9% of the piston bowl depth and thus the associated displacement of the injector tip would not have been excessively large in relation to important length scales of the engine. The 26 degree inclination of the injectors precluded that they could not be repositioned to account for this offset and so change in the relative position of the injector tip to the piston bowl with engine angular position would have to be accepted. The impact of this change on combustion and emissions would be difficult to quantify and thus such a change would always complicate the interpretation of the effect of compression ratio change on soot formation and oxidation. This is especially true in view of the fact that it was technically infeasible in this work to internally investigate the combustion process other than

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through cylinder pressure and such a measurement is global and devoid of spatial information.

3.3.2.4 Reduction of the Piston Bowl Pip

The piston bowl of the VW 1.9I TDI engine employs a re-entrant 'Mexican hat' design with a prominent piston bowl pip at the centre of the bowl Figure 3.12. A possible method of increasing the combustion chamber volume was therefore to machine down the piston bowl pip by set increments to achieve specific compression ratios'. This approach has the advantage that it avoids changes to the fundamental combustion chamber characteristics such as piston bowl and injector tip relative position with engine crank angle. Additionally, since the clearance height H_c is not being increased, the relative squish and swirl ratios of the combustion system should be impacted to a lesser extent compared to increasing H_c. Minimising such combustion system effects was fundamental to isolating the change in geometric compression ratio from other parameters such as swirl and squish and their effect on soot physiochemical characteristics.



Figure 3.12: VW 1.9I TDI Piston Bowl Top Land (sectioned detail)

The approximate volume of the piston bowl pip was estimated by assuming that the pip was essentially a circular cone in form with the dimensions as indicated in Figure 3.13, therefore the volume was calculated using Equation 3.3:

pip volume
$$\approx 0.9\pi 2^2 \left(\frac{1}{3}\right) \left(\frac{1}{4}\right) = 0.942 \ cm^3$$
 Equation 3.3



Figure 3.13: VW 1.9I TDI Piston Bowl Pip Size Estimation

Thus, if the entire piston bowl pip were to be machined down, then this is equivalent to increasing the V_c from 25.6245 cm³ to 26.567 cm³, which equated to a reduction in geometric compression from 19.5:1 to (474.0537/26.567 + 1) = 18.8:1. Therefore, the volume of material incorporated into the piston bowl pip itself proved insufficient to enable a compression ratio of 15:1 to be realised. Additional material would have to be removed from somewhere and the obvious choice would be to deepen the piston bowl below the base of the pip. Assuming that the piston bowl at the base was approximately 40mm in diameter, the remaining (5.979-0.942 cm³) = 5.037 cm³ volume increase was equivalent to an increase in depth of 4.0mm. This equated to 26.7% of the original piston bowl depth and was therefore considerable.

Arcoumanis et al. [195, 196] reported on work undertaken on an optical engine designed by VW as part of the Integrated Diesel European Action (IDEA) program. This engine employed a design fundamentally similar to the production VW 1.9I TDI engine with respect to the principle combustion chamber characteristics apart from the fact that the optical engine had a quartz window in the piston bowl base. Arcoumanis et al. commented that the absence of the piston bowl pip in the optical derivative, resulted in poor mixing and thus higher HC's and PM emissions compared to the standard production engine. Thus, when considered against the findings reported in [195, 196], this method of compression ratio reduction was concluded to be unsuitable.

3.3.2.5 Material Removal from the Piston Crown

Examining a piston crown of the VW 1.9I TDI engine in detail revealed that a significant proportion of piston material was machined away to create recesses for the intake and exhaust valve heads Figure 3.14.

These recesses were approximately 1.1 mm in depth and 34 mm (intake valve) and 39 mm (exhaust valve) in diameter. A close inspection of the piston deposits along the axis of the five radial injections, Figure 3.14; suggested the

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contaminate deposition to be very high within the piston bowl but that it also extended onto the surface of piston crown so any modification was a concern.



Figure 3.14: VW 1.9I TDI Piston Crown Recess Detail

The volume of piston material above the level of the sections that had been recessed for the inlet and exhaust valves was clearly less than the 8.236 cm³ required to reduce the compression ratio to 15:1. Indeed, it was calculated that the entire crown would have to be machined down by more than 1.659 mm, assuming it were whole, in order to achieve the required volume change.

The issue with this piston crown material removal solution concerned the fact that it would adversely affect the engine balance unless remedial action was taken to rebalance the engine for the changed piston masses. Thus, upon each change of compression ratio using this method, engine re-balancing would also be necessary. Thus, this method was ultimately considered not practical for achieving the significant reduction in compression ratio which was sought.

3.3.2.6 Addition of a Ring Groove to the Piston

The analysis of the removal of material from the piston crown of the previous Section 3.3.2.5 established that there was insufficient material on the piston crown to achieve the desired compression ratio reduction. The other proposed methods were also not ideal with the potential of secondary effects through changes in the relative position of the injector tip and piston bowl and/or swirlsquish characteristics. Thus, another method was sought to change the clearance volume but which succeeded in avoiding such issues. The only way to achieve this appeared to be increasing the clearance volume whilst avoiding changing the clearance height. The only two locations inside the combustion chamber not considered at this stage where the geometry could be changed were: 1) the top land of the piston 2) the cylinder head fire deck.

In the case of the second option the calculation in Section 3.3.2.5 identified the volume of material to be removed was equivalent to a cut-out of depth of at

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least 1.659 mm assuming a circular cut-out of diameter equal to the bore of the cylinder. As this was not considered feasible for the fire-face of the head, sections would need to be removed that were of smaller diameter and deeper than this and these would likely introduce significant areas of thermal stress in and around critical areas such as the valve bridges.

The first option, the removal of material from the piston top land, appeared somewhat more viable. The volume of material that would need to be removed in principle was achievable since the top land of the piston was approximately 12 mm deep and could thus in principle accommodate a relatively large section of material wastage. This at first appeared analogous to the addition of an extra ring groove to the piston above the first gas ring. Figure 3.15 illustrates the area concerned and shows a sectioned view of the piston in the quadrant where the distance from the piston bowl to the outer circumference of the piston is smallest. This revealed the depth of any groove would need to be less than 15 mm to avoid the bowl (based on simply the clearances and not a thorough thermal/stress analysis of the piston). It also revealed a cooling gallery adjacent to the oil scraper ring which is discussed in detail by Ohmstede et al. [197].



Figure 3.15: VW 1.9I TDI Piston, Section through Ring Pack Area

The shape of the ring groove as proposed is illustrated in Figure 3.16. The inner radius R_1 can be calculated based on the depth D of the groove using Equation 3.4. The outer radius is that of the piston top land section, R_2 (39.37 mm).³

$$V_c \text{ increase} = (R_2^2 - R_1^2)\pi D$$
 Equation 3.4

³ The piston top land was not perfectly perpendicular to the crown as the piston profile was a barrel shape to prevent it 'jamming' in the cylinder - so this calculation method was only an approximation but sufficient to estimate the general dimensions of the required ring groove.

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Based on the increase in clearance volume required for the reduction in compression ratio from 19.5:1 to 15, calculations were performed that considered a range of groove depth D from 2mm to 8mm. The resultant incision depth required (R_2 - R_1) for a groove depth D=6mm is presented in Appendix 5 (Table A5.2). At 15:1 compression it was determined that a ring groove with an incision depth of (R_2 - R_1) = 6.009 mm was required and was considered the best balance of the two variables. The calculation results for the other groove depths D are presented in Figure 3.17. These calculations showed that the required size of the additional ring groove was comparable to that of the gas ring grooves.



Figure 3.16: Piston Ring Groove Proposal

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To fully understand what possible effects the inclusion of this ring groove would have on the combustion, a thorough review of literature discussing similar piston adaptations was conducted. Several interesting points arose through this process but the one which essentially lead to the abandonment of the approach was the discovery of work done by A. Pouring et al. [198-201] and the fortunate opportunity for the Author to discuss one-to-one with Pouring at the 2004 Society of Automotive Engineers (SAE) Fuels and Lubes conference.



Figure 3.17: Ring Groove Incision (R₂-R₁) Calculation

Pouring had arrived at the same proposed method for engine compression ratio adjustment previously in the 1970s but when it was tested it was determined that there was a highly unusual 'Helmholtz - free radial' effect taking place as a consequence of the trapping of charge in the groove and this causing a fundamental change in combustion characteristics.

In essence, the groove was causing the auto-ignition process to change fundamentally from that of a DI diesel engine with conventional re-entrant bowl design. This change has been proposed to be mediated through intermediate and radical chemical species produced in the crevices [198]. Interestingly, this phenomenon enables engine designs with lower compression to run low cetane fuels and also has the added benefit of the radicals assisting the oxidation of the soot in the blowdown process. Pouring and Sonex have utilised this effect to Patent a combustion system design called Sonex Combustion System (SCS) [202-207].

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Engine Geometric Compression Ratio Modification

Subsequent further research in this area revealed Rogers et al. of Ricardo have investigated the effects of the in-cylinder cavities proposed by Pouring [208] and also there exist at least 98 patents filed at the US in other patent offices (search term: 'Piston Auxiliary Charge containing Cavity') relating to cylinder cavity based ideas as considered here.

It was concluded that the uncertain combustion auto-ignition effects reported introduced too many potential additional issues and thus the ring groove method and the other cavity based modifications were ultimately abandoned as a result.

3.3.3 Down-Selection of Compression Ratio Change Method for the VW 1.9 TDI

Following the investigation of the forgoing proposed methods for compression ratio modification it was concluded that the best solution was the joint ring 'spacer' method Section 3.3.2.3. In summary, the joint ring 'spacer' method had the least number of concerns associated with it and it was also considered as the most practical solution that could be implemented. The principle concern with this method was the unquantifiable change to the swirl and squish characteristics of the combustion system but it was considered that such changes would be almost impossible to avoid with geometric compression ratio change.

3.3.4 Modification of Engine Cylinder Head Gasket

Usefully for the AVF (Section 3.1.4) derivative of the VW 1.9I TDI engine used in this work, a number of different gaskets types and gasket versions were found to exist. For each gasket type, there was a subgroup of three derivatives that depended on the measured engine piston projection (1,2,3-hole) Table 3.6 [188].

Gasket Reference	Piston Projection
1-hole	0.091-1.00 mm
2-hole	1.01-1.10 mm
3-hole	1.11-1.20mm

Table 3.6: VW 1.9I TDI Gasket Selection Criteria

Each gasket design was based around a centrally located 'spacer' element of a prescribed thickness and bounded on either face by thinner sealing gasket layers. Figure 3.18 shows the separate elements of the 2-hole gasket used for the 19.5:1 base engine build.

Engine Geometric Compression Ratio Modification

This form of gasket construction meant that it was possible to modify the gasket thickness by means of replacing the central spacer element with either a thinner or thicker element. When the VW part inventory for the AVF engine was reviewed, a total of three different versions of the 3-hole gasket were found. The thickness of the 'spacers' for these gaskets and the original (19.5:1) 2-hole gasket are detailed upper part of Table 3.7.



Figure 3.18: Head Gasket Individual Elements for 19.5:1

This table also has the calculated values for the clearance height H_c , the compression ratio R_c and the percentage reduction in compression relative to 19.5:1.

Gasket Ref.	Part No.	Spacer Thickness	H。	R₀	-% R.
2-hole	038 383 BM	0.39 mm	0.66 mm	19.5:1	0
3-hole V1	038 383 BN	0.47 mm	0.74 mm	19.2:1	1.5
3-hole V2	038 383 DG	0.78 mm	1.05 mm	18.2:1	6.7
3-hole V3	038 383 CN	0.47 mm	0.74 mm	19.2:1	1.5
2x0.47	NA	0.94 mm	1.21 mm	17.7:1	9.2
0.78+0.39	NA	1.17 mm	1.44 mm	17.1:1	12.3
0.78+0.47	NA	1.25 mm	1.52 mm	16.9:1	13.3
2x0.78	NA	1.56 mm	1.83 mm	16.1:1	17.4
2x0.78+0.39	NA	1.95 mm	2.22 mm	15.2:1	22.1
2x0.78+0.47	NA	2.03 mm	2.33 mm	15:1	23.1
3x0.78	NA	2.34 mm	2.61 mm	14.4:1	26.2

Table 3.7	• \/\//		Gaskat	Vorcione	and P	Estimato
i able 3.7.		1.91101	Gaskel	versions	anu R _c	Estimate

As the original gasket construction was a set of five elements Figure 3.18, the replacement of the single spacer with two or more would have meant that there would have been un-coated face-to-face contact between the spacers which

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Engine Geometric Compression Ratio Modification

would have risked the gasket seal. Clearly, the greater the number of spacers, the greater the difficulty in getting the gasket to seal.

It was therefore determined that the most acceptable compromise was to use the two thickest spacers to achieve a compression ratio target of 16.1:1 and then stack them such that each spacer was between the two outer elements of the original 19.5:1 gasket Figure 3.18. This construction thereby avoided adjacent spacers and is illustrated in Figure 3.19.



Figure 3.19: Head Gasket Individual Elements for 16.5:1

After the elements were stacked in the correct sequence and orientation they were riveted together using the original rivet holes. The cylinder head was then bolted up normally following a clean of the block and cylinder head gasket contact faces.

On the first build to low compression the engine was initially cranked over with the starter to test compression. It was found that the compression pressure across the cylinders was even but coolant was seen to be leaking from one of the corners of the block. As the compression pressure was good it was believed that the leak was due to a lower bolt compression load at the corner of the block close to a coolant channel.

A second attempt at building the engine with this same type of gasket assembly was made but in an attempt to try an ensure there would be no coolant leak issues, a thin bead of high temperature silicon based sealant (Loctite 5367) was applied to each face of the gasket layers to see if this would help create a reliable seal.

Engine Geometric Compression Ratio Modification

Unfortunately this method proved very unsuccessful as the sealant, although applied sparingly, spread into the coolant and oil feed galleries from between the layers of the gasket when the cylinder head was bolted up. Thus, although a form of sealant was absolutely necessary to ensure a good coolant seal, a sealant which would not migrate into the coolant channels and the cylinder and then cure was essential. This resulted in some research and following from this a candidate sealant was found. *This sealant was Loctite 573T M which is an acrylic based anaerobic sealant*.

When the engine was rebuilt again with this sealant, Figure 3.20, both the coolant and gas seals proved to be good on the first build attempt.



A thin bead was run around all the apertures of the gasket for each element of the gasket (all six)

Once the cylinder head was torqued up, the gasket joint was inspected down the coolant channels to ensure the excess was not curing

Figure 3.20: LOCTITE® 573 Used To Seal Gasket

An inspection was made down the oil return channels from the cylinder head after the assembly had been left to cure for 24 hours and it was clear that the anaerobic sealant had worked as intended as the excess simply dispersed into the oil rather than go hard in the channel.

3.3.5 Cylinder Pressure Evaluation of Compression Ratio

Table 3.8 shows the measured peak pressure with the engine being motored by the starter motor at approximately 300 rpm for both the reduced compression configuration and the standard base engine configuration.

 Table 3.8: R_c Reduction Analysis – Cylinder 1 Motored Peak Pressure

Test Reference	Peak Pressure, bar
low R₀	30.536
base engine, R₀=19.5	39.100

Engine Geometric Compression Ratio Modification

The direct application of the relation Equation 3.5 (where P_{comp} is the compression pressure, P_0 is the pressure in the cylinder at Bottom Dead Centre (BDC), and gamma γ =1.4⁴ is the ratio of specific heats C_p/C_v) to the peak pressure data in Table 3.8 leads to R_c estimates of 11.5 and 13.7 for low and base engine compression configurations respectively. The calculated value for R_c for the base engine was somewhat lower than the actual 19.5:1 due to the compression process not being isentropic with heat loss to the cylinder walls, non-ideal piston ring sealing and non-ideal cylinder filling. However, this was the only practical measurement method to estimate the change in R_c and based upon these two R_c estimates the compression ratio was estimated to have been reduced ~16.1%. This is equivalent to a reduction from 19.5:1 to ~16.4:1 (i.e. 19.5 x 0.839).

$$P_{comp} = P_0 \times R_c^{\gamma}$$
 Equation 3.5

A further confirmation of the above compression ratio reduction estimate was made by making use of the retarded injection timing characteristics of the VW 1.9I TDI engine at idle (800 rpm). Such was the retardation in timing, that the compression stroke completed prior to auto-ignition and thus the TDC peak pressure could be approximated to the motored peak pressure that would be observed at this higher rpm. Figure 3.21 illustrates this observation; where 'Data Set 1' is the base engine idle cylinder pressure and 'Data Set 2' is the reduced compression data set (both averaged over 50 engine cycles). The peak pressures at TDC for this data is summarised in Table 3.9.

Table 3.9: Rc Reduction Analysis – Cylinder 1 Idle Peak Pressure

Test Reference	Peak Pressure, bar
Data Set 1 (Rc=19.5)	44.888
Data Set 2 (low R₀)	35.663

Table 3.9 reveals that in both cases the measured peak pressure was higher at the higher engine rpm of idle compared to the engine being cranked over with the starter motor (as would be expected with improved piston ring sealing and improved engine breathing at the higher rpm). Repeat analysis using Equation 3.5 and a value for gamma of 1.37 (i.e. slightly lower than for air to be reflective of a diesel engine lean fuel air mixture [344]) resulted in a base engine compression ratio estimation of $R_c = 16.1$:1 and for the reduced compression

⁴ Assumes ratio of specific heats for air is 1.4 (U.S. Standard Atmosphere, 1962) [344].

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Engine Geometric Compression Ratio Modification

case it was $R_c = 13.6$:1. The compression ratio was thus estimated to have reduced by 15.5% and was therefore similar to the 16.1% reduction estimated for the 300 rpm motored condition.



Figure 3.21: R_c Reduction Analysis – Cylinder 1 Idle Pressure

Table 3.7 shows that the original projected reduction in compression ratio resulting from the increase in thickness of the head gasket was 17.4%. This is greater than the 15.5 to 16.1% reduction derived from the forgoing analysis of the two sets of peak cylinder pressure measurements. Thus, the estimated achieved low compression ratio between 16.4 to 16.5:1 (i.e. 19.5 x 0.836, 19.5 x 0.845) is higher than the original calculated target of 16.1:1, Section 3.1.3.2.

The 0.4:1 difference in compression between predicted and measured equates to a clearance volume difference of 0.81 cm³ and a clearance height difference of 0.163 mm. This is equivalent to a difference of 3.2% in respect to the base engine clearance volume. The reason for this could not ascertained directly as it potentially had many causes including: wear of the bore, less than ideal measurement method for motored peak cylinder pressure, error in gasket spacer measurement etc. For simplicity, throughout the remainder of this work, the <u>low</u> engine compression ratio is henceforth denoted by <u>16.5:1</u> and the <u>high</u> compression ratio is denoted by <u>19.5:1</u>.

To ensure that the reduction in compression was even across all four cylinders, the cylinder pressure transducer was moved through cylinders 1-4 and the pressure measured for the 300 rpm motored condition and the peak pressure results are presented in Table 3.10. This showed that the standard deviation across all cylinders was 0.249bar, or 0.8% of the mean peak pressure.

Table 3.10: Rc Reduction Analysis – Cylinder 1-4 Motored Peak Pressure Check

Cylinder Number	Peak Pressure, bar
1 (low R₀)	30.536
2 (low R₀)	30.395
3 (low R₀)	30.395
4 (low Rc)	31.002

3.4 VW 1.9I TDI EGR System Adaptation

The VW 1.9I TDI EGR system was a high pressure external design and was configured with the EGR control valve mounted directly onto a cast aluminium intake manifold Figure 3.22.



Figure 3.22: VW 1.9I TDI EGR Valve

A pipe connection from the exhaust manifold confluence point delivered the exhaust gases to the EGR valve which was controlled by vacuum regulated diaphragm. Just upstream of the EGR valve was an intake manifold flap which was also actuated using a vacuum regulated diaphragm and was part of the EGR

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VW 1.9I TDI EGR System Adaptation

valve assembly. This valve was only designed to cut-off intake airflow on engine shutdown [209] and thus was left disconnected for the experimental work reported herein.

In the modification of the system, the vacuum line to the EGR valve was rerouted to a second redundant EGR valve and the engine EGR valve was then connected to a vacuum pump with a manometer connected in-line adjacent to the vacuum pump to help control the EGR valve position demand Figure 3.23.

The inability to override the ECU meant that it was not possible to maintain constant engine fuelling with EGR rate change and thus the intake manifold pressure and temperature changed and the MAF decreased with increased EGR rate. As this occurred, the ECM responded by limiting the engine fuel injection duration. Thus, to investigate both high and low rates of EGR, it had to be accepted that there would be a change in the engine fuel injection quantity. The resulting change in AFR however proved ideal for broadening the conditions of soot formation and resulting soot physiochemical properties, Chapter 8.

Vacuum line to EGR valve from vacuum pump

Second redundant EGR valve connected to ECU controlled vacuum solenoid





Figure 3.23: Engine EGR Valve Vacuum Override Detail

Exhaust Soot Collection

3.5 Exhaust Soot Collection

This section describes the two exhaust soot sampling methods used in this work: Section 3.5.1 outlines the sampling method implemented at the exhaust manifold using ceramic thimbles and Section 3.5.2 describes the use of a diesel particulate filter mid-way down the exhaust.

3.5.1 Ceramic Thimble Exhaust Manifold Soot Sampling

In the case of exhaust manifold soot which was to undergo extensive chemical and physical analysis; the ceramic thimble method was advised by Lubrizol to be the most suitable sample collection method and became the principle method used to collect the soot for the three fuels and two compression ratios investigated in this work. This method had previously been utilised by Lubrizol in several published papers starting with Covitch et al [210] which defined the collection apparatus; this apparatus and its derivatives were then utilised in subsequent reported work [115, 117, 119, 138, 165, 211-213].

3.5.1.1 Design and Function of the Ceramic Thimble System

The ceramic thimble system as described by Covitch et al. derived from the international standards [214-217] that govern the sampling of particulate emissions in effluent gases from stationary sources; most frequently the stacks at industrial installations. These standards are based on isokinetic sampling principles and as these standards relate to the collection of particulate from a stack, they serve only to establish a foundation for the development of the ceramic thimble sampling method covered in this section.

A review of literature concerning the utilisation of ceramic thimbles beyond the Lubrizol works was conducted but little was found which reported in detail on the use of the collection methodology, though some papers were found which utilised techniques similar to that employed in his work [171, 218-221]. Additionally, this review identified technical reports and publications which discussed diesel engine soot collection methods in general and these assisted the development of the general methodology [24, 222-228].

The ceramic thimbles for the tests were procured through Westech [229] in the United Kingdom. They are described by their commercial name as Alundum[®] Thimbles and are made from fused alumina oxide (Al₂O₃). Thimbles with a porosity size of 20 micron were selected for this work following Lubrizol's experience.

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Methodology

Exhaust Soot Collection

The sampling position for the ceramic thimble system was selected to be the confluence point on the exhaust manifold which connected to the inlet of the turbine housing foot of the turbocharger. This was chosen as it was relatively easy to access, had a suitable surface for tapping into and the exhaust gas at this point was as close as could be sampled to the cylinder. A further advantage of this sampling position was that the sample gas was at a relatively high pressure, thus helping to pump sampled exhaust gas through the ceramic thimble system. A Swagelok 1/8 inch NPT threaded tube fitting was tapped into the exhaust and off this ran the primary sample line which was ¼ inch 415 stainless tubing, Figure 3.24 and Figure 3.25.

The primary sample line from the exhaust manifold extended for approximately 2 meters, Figure 3.24, and then interfaced with the input end of the ceramic thimble holder, Figure 3.25. The holder was made of stainless steel and was designed so that a ceramic thimble would slide over the end of the holder and then be sealed by an O-ring which fitted on the outside of the ceramic thimble, Figure 3.26. An outer cylindrical sleeve went over the thimble, sealing against the O-ring, and this was secured with a cap that screwed to the outside of the sleeve. The gas outlet port at the end of the sleeve was connected to a 1 meter length of ¼ inch stainless steel pipe. After this a 6 mm PTFE pipe went to a zinc plated 6 mm regulating ball valve in the control room and then to an Edwards RV3 Vacuum Pump with catch-pot (to collect water condensate) and then back into the test cell and to the exhaust extract duct, Figure 3.24.

A by-pass line broke off from the primary sample line 100mm before the ceramic thimble and was designed to enable the pre-heating of the sample line with exhaust gas prior to switching the gas flow to pass through the ceramic thimble. This pre-heating of the sample line was necessary to prevent condensation forming on the inside of the sample line, which would entrain soot and also condense inside the ceramic thimble reducing the quality of the sample.

An Edwards RV3 vacuum pump was used to maintain the flow rate of the sample gas by the regulation of the pressure drop across the ceramic thimble. Reduced vacuum was required with a new ceramic thimble as there was less resistance than when soot was entrained (similar to the layer cake of a DPF). A needle valve in the control room, Figure 3.24, was used to regulate the vacuum. Research and development established that the addition of the vacuum pump increased the soot accretion rate by greater than a factor of two.

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Figure 3.24: Ceramic Thimble System Schematic

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Exhaust Soot Collection

The permissible temperature range for the ceramic thimble and hence the temperature of the sample gas was somewhat limited. The lower temperature was dictated by the need to avoid condensation inside the thimble and this necessitated a minimum temperature in the thimble canister of 120°C; this was to account for up to 2bar absolute pressure inside the sample chamber due to the exhaust gas pressure at the sampling point⁵. However, the system was configured to operate mainly above 150°C due to a rapid drop in temperature in the sample canister as the thimble plugged and the gas flow rate declined.



1/4inch 415 stainless tube tapped into the neck of the turbine housing using a Swagelok 1/8inch NPT tapping

Ceramic thimble 1





The upper temperature limit was dictated by the O-rings which sealed the thimble in the holder. These were rated to 250°C and when this was actually tested it was found that in the worst case the O-ring would not retain the thimble in the holder and the thimble would be 'blown' off the holder mount and hit the far end of the outer cylinder sleeve, breaking the fragile thimble.

A thermocouple was installed into the ceramic thimble canister by tapping a channel at the gas inlet end and fitting a 1.5 mm diameter thermocouple and then sealing with a high-temperature epoxy adhesive (Scotch-Weld DP760), Figure 3.26.

Typically, the temperature of the sample gas in the thimble (sampled from the exhaust manifold with the engine at rated power) would fall 20-30°C per hour as a consequence of the reduction in sample gas flow rate as the ceramic thimble plugged from the accretion of soot. To maintain the sample gas temperature in the range of 150 to 250°C, the length of the primary sample line was determined

⁵ Calculated using the Antoine equation.

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such that at rated power with a new thimble, the resulting temperature inside the thimble was around 230°C. As the thimble began to plug, the vacuum was increased on the exit port of the thimble to minimise the reduction in sample flow rate and this helped to reduce the rate of temperature decline. Eventually, after approximately 2 hours of sampling (EN590 base fuel) the pressure drop across the thimble would be at a maximum and the temperature had declined to 150°C and at that point lagging was placed on the sample line so that the test could continue with that thimble, Figure 3.25.



Figure 3.26: Ceramic Thimble and Holder

The high pressure drop, poor flow rate and the low thimble temperature in combination would necessitate a thimble change. From the tests conducted this would equate to about 0.5-0.7 g of total soot collected by the thimble (for the mineral diesel fuels) and about 7 hours of continuous testing at rated engine power. Thus, to achieve the required 2 g of soot (Section 3.6.8) for each mineral based fuel and compression ratio, it was necessary to test for approximately 20 hours and use three thimbles for each mineral fuel and compression ratio combination.

The test duration would have been much longer with a lower speed-load operating point which had both reduced exhaust soot concentration and lower exhaust manifold pressure. Hence, the ceramic thimble collection methodology as outlined in this section was the principle reason for limiting the engine speedload point to full load rated speed (maximum power).

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It was essential to ensure that the ceramic thimble and holder were above (>100°C) prior to letting the sampled exhaust gas enter the thimble. So a heating element which clamped around the outside of the ceramic thimble holder was sourced Figure 3.27. The heat output of the element was controlled by a variac (variable autotransformer). A process was developed for pre-heating the thimble to (>120°C) using just the heating element and a pre-set variac setting and the warm-up time was 30min.



Figure 3.27: Ceramic Thimble Holder Heating Element

The gas pressures both before and aft of the ceramic thimble were measured using a pair of Keller 5bar absolute pressure transducers Figure 3.28. This was essential as this pressure differential had to be maintained to maximise the gas flow rate but it could not be made to exceed approximately 1.5 bar else there was a risk of breaking the ceramic thimble.



Figure 3.28: Ceramic Thimble Sample Line Pressure Tapping

Initial tests prior to the implementation of the vacuum pump showed clearly that there would be a lot of water condensing out in the system pipework after the

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Exhaust Soot Collection

sample gas had passed out of the ceramic thimble (hence the requirement for careful temperature control to avoid condensation). This was collected in a catchpot that was installed atop the Edwards RV3 vacuum pump. The mass of water collected in the catch-pot trap was a reasonable indication of the total mass flow of sample gas through the ceramic thimble and was therefore measured.

Even though the ceramic thimble soot collection rate was much lower for the biodiesel fuel; the mass of the collected water proved that there was increased total mass flow through the thimble as a consequence of there being proportionally less soot blocking the thimble with time relative to the mineral fuel tests. Table 3.11 illustrates this point.

Fuel	Exhaust Gas Soot Concentration (mg/m³)	Ceramic Thimble Soot Ave. (g/h)	Ceramic Thimble Soot Total (g)	Condensate Water Total (g)
EN590	38.04	0.063	1.206	0.951
PC9	44.36	0.108	2.012	1.109
B100	5.92	0.0267	0.477	1.606

Table 3.11: 19.5:1 Ceramic Thimble Soot and Water Condensate Collection

Table 3.11 shows an 85% reduction exhaust soot concentration in the exhaust between the mineral and biodiesel fuels and a corresponding reduction in the total soot collected by the ceramic thimble. However, the total water condensate collected increased by 56% for the biodiesel fuel as the mass of sample gas which has passed through the thimble was so much higher as a consequence of the less contaminated thimbles. Therefore, this method of soot collection, whilst it worked satisfactorily for the mineral fuels, proved very challenging to execute successfully with the biodiesel fuel due to the significantly lower exhaust soot concentration observed.

3.5.1.2 Performance of the Ceramic Thimble System

Table 3.12 presents a summary for the soot collection system performance for the experiments described in Section 3.1.5.3. Table 3.12 illustrates that for the biodiesel fuel for both compression ratios, the effect of the reduction in exhaust soot concentration was to increase the collection efficiency of the ceramic thimble system whilst the total soot yield at the end of the tests was less than 25% of what was ideally required for the soot analysis tests.

Exhaust Soot Collection

Fuel	Rc	Engine Air Mass Flow (kg/h)	Exhaust Gas Soot Concentration (mg/m ³)	Soot Rate (g/h)	Thimble (g/h)	Collection Efficiency (%)	Thimble Soot (g)
B100-1	19.5	925.4	5.9	2.1	0.027	1.24	0.477
B100-2	16.5	947	4.4	1.6	0.043	2.58	0.462
EN590	19.5	888.1	38.0	13.2	0.063	0.48	1.206
EN590	16.5	943.9	40.5	15	0.09	0.6	1.722
PC9	19.5	915.5	44.4	15.9	0.108	0.68	2.012
PC9	16.5	935.4	48.0	17.6	0.127	0.72	2.388

Fable 3.12: Anal	vsis of Ce	ramic Thimble	Collection	Efficiency
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This phenomenon occurred because the accumulation of soot in the thimble resulted in a rapid increase in the resistance to the flow of the sample gas through the thimble. Thus, within the first hour of the test, the collection rate reduced significantly for the mineral diesel fuels. With the biodiesel fuel having 85% lower exhaust soot concentration, this 'throttling' took much longer to occur and hence over time the total flow through the thimble was higher - increasing the collection efficiency. Hence two ceramic thimbles were used for the biodiesel tests whereas three were used for the mineral diesel tests.

Figure 3.29 details the average soot collection rate vs. the exhaust soot rate for each fuel-compression ratio permutation and reveals an approximately exponential increase in the thimble collection rate and hence the total ceramic thimble collected soot with increased exhaust soot concentration. This explains why the ceramic thimble sample method proved so ineffective for sampling the biodiesel soot. Unfortunately, as this had not been documented by Lubrizol or in in literature previously, it was unforeseen when the soot collection method was chosen prior to the commencement of the experimental work.

The exponential reduction in thimble soot accretion rate vs. exhaust soot concentration which was determined during the course of this research, makes the ceramic thimble collection technique very difficult to implement on diesel engines with low exhaust particulate concentrations when the required sample mass is several grams as was necessary in this work. This finding explains why Lubrizol were able to apply the sampling method to US Tier III MD diesel engines successfully and yet the method proved far more challenging to translate across to the VW 1.9I TDI engine.

To illustrate the difficulty with the biodiesel fuel; it was found that soot yield was roughly 0.24 g of soot for every 10 hours for each new ceramic thimble.

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Thus, to achieve the full 2 g would have necessitated more than 8 thimbles and in excess of 80 hours of testing at rated condition. This was simply infeasible in respect to the available time and resources for the experimental work.



Figure 3.29: Ceramic Thimble Collection Rate

3.5.2 Diesel Particulate Filter

A single non-catalysed DPF filter-canister was supplied by Lubrizol and was used for all the reported DPF soot collection results in this work. This section describes the DPF canister soot collection method.

3.5.2.1 DPF installation and Soot Collection

For the EGR experiments (Section 3.1.5.4) the DPF was located in a section of exhaust between the exhaust manifold and the central silencer Figure 3.30. To achieve a flexible installation the DPF was connected into the exhaust using a pair of quick-release V-band clamps. The DPF could be removed and a straight section of exhaust inserted in its place thus avoiding any significant exhaust system re-configuration when doing the DPF experiments. A tapping for the AVL 415 smoke meter was installed upstream of the DPF to measure the soot concentration (Section 3.2.2.5). A thermocouple on the DPF inlet measured temperature and a pair of Keller 5bar absolute pressure transducers measured the pressure drop across the DPF. Exhaust Soot Collection



Figure 3.30: DPF Canister Installation Configuration

To collect soot at the peak power condition where the ceramic thimble soot was collected required a very long extension of the exhaust system pipe work to maintain DPF temperatures below 250°C and prevent soot from oxidising once trapped in the filter matrix. This was achieved via an inelegant though practical solution which employed two 2m lengths of semi-flexible 60mm outer diameter convoluted exhaust pipe Figure 3.31 which were joined together and connected to the exhaust using two V-band flanges. This solution avoided any need to completely deconstruct the installed exhaust system and thus ensured it was simple to return to the baseline exhaust system when the DPF soot collection was complete.

Due to the two quite different DPF installation positions required for the experimental work it was infeasible to implement a bypass system like that used for the ceramic thimble. For this reason, the test methodology was designed so that the engine was first warmed up without the DPF and a straight pipe section instead installed. Once the engine was warmed up, the DPF was fitted; the quick release clamps enabling this to be done within two minutes. The engine was then started and guickly ramped to the operating condition required by the test. At the end of the test, the engine was shut down quickly. This helped to minimise the level of contamination of the DPF with soot from engine operating conditions outside those of interest.

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Exhaust Soot Collection



Figure 3.31: DPF Installation with Extended Exhaust

3.5.2.2 DPF Soot Extraction Method

The method for the extraction of soot from the DPF canister involved backflushing with compressed air. This was achieved by partially sealing the inlet end of the DPF with an evacuated polythene bag and then at the other end forcing air through the filter matrix at high velocity in a concentrated area using a high pressure airline at about 4 bar and a fine nozzle Figure 3.32. As the bag pressurised, the pressure was released at the point where the bag was partially sealed to the outlet of the DPF. The tip of the nozzle of the airline was then traversed across the outlet face of the filter block and soot carried by the reverse flow air was caught in the bag. This was the only method which could be conceived as the DPF canister was a sealed unit and the only one available; thus having to be reused for each test.



Figure 3.32: DPF Soot Extraction with Air Line and Polythene Bag

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Exhaust Soot Collection

To clean the DPF of soot it was first allowed to cool to room temperature (24-48 hours) and it was then weighed and its mass compared to the original clean canister mass. It was then installed in the position used for the EGR experiments Figure 3.30. The engine was then operated at 3000 rpm 200 Nm, generating a temperature in excess of 500°C at the DPF inlet. This condition was then maintained and the pressure drop across the DPF monitored as it dropped to (<2 kPa). At which point the engine was quickly stopped.

The process of collecting soot with the same DPF and then cleaning at elevated exhaust temperatures was repeated a total of eight times in this work. The first time was a developmental test to determine the operational parameters of the DPF which was then followed by the four EGR soot collection experiments (Section 3.1.5.4) and then the three rated power experiments (Section 3.1.5.3) at the low compression ratio of 16.5:1. Since the same DPF was used for all experiments there was a concern of progressive ash contamination of the DPF with each successive test.

To identify whether there was likely to have been any impact on soot physiochemical analysis from the build- up of ash in the DPF over the course of the experiments, the amount of ash produced from the worst case experiment for potential ash vs. carbonaceous soot loading is calculated as follows:

B100 16.5:1 soot collection experiment:

 $DPF \ collection \ duration = 2h$ $Fuel \ consumption \ rate = 23.8 \ kg/h \ \{Table \ 4.10\}$ $B100 \ \%wt \ Ash = 0.002\% \ \{Appendix \ 1 \ (Table \ A1.1)\}$ $Lubricant \ consumption \ rate = 13.3 \ g/h \ \{Table \ 4.10\}$ $Estimated \ Lubricant \ \%wt \ Ash = 1\%$ $Estimated \ total \ mass \ of \ ash \ from \ fuel = (2 \times 23.8 \times (0.002/100)) \times 1000 = ~1g$ $Estimated \ total \ mass \ of \ ash \ from \ lubricant = 2 \times 13.3 \times (1/100) = ~0.27g$ $Estimated \ total \ ash \ for \ experiment = ~1.27g$

A similar calculation for the EN590 and PC9 16.5:1 DPF soot collection experiments resulted in a total ash estimate for both tests combined of around

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0.3g (collection duration was only 20min). For the four EGR tests the total was again about 0.3g. *Thus, cumulatively for the experimental tests the total ash loading was less than 2g total.* In contrast, the estimated total soot produced in these tests was (0.3x14.96 + 0.3x17.58 + 2x1.64) Table 4.10 and ($0.16 \times 216.6 + 1.365 \times 17.0 + 85.8 \times 0.53 + 3.3 \times 3.5$) Table 8.2 which totals to ~ 128g. *Thus, the ash loading of the DPF is estimated to have been 2/128g = 1.6% of the soot loading.* Thus the DPF ash loading was considered as insignificant. Additionally, to minimise ash loading over the course of the experiments the DPF was backflushed with air after it had been regenerated (using the same technique as used to remove the soot) to remove any free ash.

3.6 Soot Analysis Techniques

In this work a total of eight physiochemical analysis methods were used to characterise the soot sampled from the exhaust with one soot parameter calculated for a total of nine characterisations. This section first summarises the down-selection process for the selection of each analysis method and then summarises the details of each.

3.6.1 Down-Selection of Measurement Methods

The literature review of Chapter 2 identified the important soot physiochemical characteristics for the understanding of soot and its behaviour in the exhaust. The same literature was also utilised to develop a picture of the common soot characterisation methods used to quantify these soot characteristics. A total of over 50 methods have been reported in the 178 publications reviewed and for each method the frequency of occurrence in the literature has been determined. Appendix 6 (Table A6.1) presents the identified top twenty-two analysis methods used for each soot characterisation.

The identified methods of Appendix 6 (Table A6.1) were then considered in association with Lubrizol by evaluating the following criteria to select the soot analysis methods to be used in this work: 1) result relevancy 2) usefulness and depth 3) mass of soot required 4) cost and accessibility of the method. Based on this set of criteria, the frequency of application and the previous experience of Lubrizol, a total of nine soot analysis methods were selected Appendix 6 (Table A6.2). For each of these methods a fairly comprehensive literature survey was undertaken and the references for each method are summarised in Appendix 6 (Table A6.3 and Table A6.4) which may be of use to other researchers.

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3.6.2 Surface Elemental Analysis - X-Ray Photoelectron Spectroscopy (XPS)

X-Ray Photoelectron spectroscopy (XPS) {Appendix 6 (Table A6.3)} is a technique which is used to provide information about the elemental composition and oxidation state of a surface. In XPS a monochromatic X-ray beam of known energy is emitted by an X-ray source and is absorbed by an atom in the top 1-10 nm of the surface of a sample [63]. The incident photon causes ionization and the emission an electron from a K-shell orbital (inner shell) of one of the atoms in the surface of the sample.

XPS is also sometimes referred to as Electron Spectroscopy for Chemical Analysis (ESCA) and is one of the most widely used surface analysis techniques because of the relative simplicity of the test and the data interpretation. Advanced forms of XPS can also be used to identify the Oxygen Functional Groups i.e. the oxidation state of the surface [230] as detailed in Section 2.4.1.1.

The kinetic energy distribution of all photoelectrons emitted (i.e. the number of emitted photoelectrons as a function of their kinetic energy) from the sample surface is simultaneously measured in an electron spectrometer to generate a photoelectron spectrum and from this the composition and electronic state of the surface region of a sample can be determined.

For each and every element, there is a characteristic binding energy ($E_{binding}$) associated with each core atomic orbital. Thus, each element will give rise to a characteristic set of peaks in the photoelectron spectrum at energies determined by the photon kinetic energy ($E_{kinetic}$) (measured by the electron spectrometer) and the energy of the incident photon (E_{photon}) and is described by the relation ($E_{binding} = E_{photon} - E_{kinetic}$). The photoelectron spectrograph therefore has peaks corresponding to each element in the sample region exposed to the X-ray source. The intensity of the peaks indicates the concentration of the element within the sample region.

The most commonly employed X-ray sources are those giving rise to Mg K α radiation (hv= 1253.6 eV) and Al K α radiation (hv = 1486.6 eV) and this is therefore the range of the kinetic energies of the emitted photoelectrons. The fact that such electrons have very short Inelastic Mean Free Paths (IMFPs) in solids is what *limits the analysis to the top 1-10 nm of the sample surface*. However, special treatment methods are used in some circumstances to expose the bulk chemistry so that this may also be analysed.

3 3.6

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Soot Analysis Techniques

For most applications, XPS is generally a non-destructive technique due to the use of monochromatic X-ray sources which result in very little degradation. This fact was taken advantage of in this work when the soot sample mass collected was small. In such situations, the XPS sample was later re-used for one of the other soot physiochemical analysis tests.

It must be remembered however that the XPS method does require an Ultra-High Vacuum (UHV) and this can lead to the removal of various gases (e.g. O_2 , CO) and liquids (e.g. water, hydrocarbons) that were initially trapped within or on the surface of the sample. This form of sample degradation is difficult to estimate and detect and is therefore a potential source of error in the application of the method to soot. The UHV also means that it is possible for the chemistry and morphology of the sample to change until the surface achieves a steady state, a source of further error.

For the soot analysed in this work, the XPS test measured the surface atomic weights for (C,O,S,N,Cl and total atomic %). These were then converted to percentage weight so that the results could be directly compared to the bulk soot results.

All soot sample surface elemental analysis was outsourced by Lubrizol, Wickliffe, Ohio.

3.6.3 Bulk Elemental Analysis (ICP-MS)

Inductively coupled plasma mass spectrometry (ICP-MS) {Appendix 6 (Table A6.3)} is a type of mass spectrometry which is able to determine a range of metals and non-metals at concentrations of less than 1 part per trillion. The method uses inductively-coupled plasma to produce ionization of a sample and a mass spectrometer then separates and detects the ions produced. The ICP-MS technique was commercially introduced in 1983 and has gained general acceptance in many types of laboratories particularly in geochemical laboratories. It is a flexible technique that offers many advantages over more traditional techniques for elemental analysis, including Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) and Atomic Absorption Spectroscopy (AAS). [231].

The sample needs to be introduced into the plasma as an aerosol with as small a size as possible so that it can be transported easily into the plasma. There exist a variety of techniques to achieve this and these include: aspirating a

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Soot Analysis Techniques

liquid, the acid digestion of a solid sample into a nebulizer and using a laser to directly convert solid samples into an aerosol. The acid digestion process is the one selected in the majority of literature for preparing soot for analysis. Typically, either pure or mixed solutions of hydroflouric (HF), nitric (HNO₃) or hydrochloric (HCl) acid are used.

For the analysis of the soot samples in this work, the soot sample was dissolved using an acid-digestion technique with a spectrally pure nitric acid as reported in [232-234] and then placed into a nebulizer.

Following the sample preparation step the sample aerosol is introduced into the ICP torch and it is completely desolvated and the elements in the aerosol are converted first into gaseous atoms and then ionized towards the end of the plasma. Thus, this is a destructive test and the sample mass required is typically 300mg.

Once the elements in the sample are converted into ions, the ions from the plasma are extracted through a series of cones into a mass spectrometer, usually a quadrupole mass filter. This is essentially electrostatic filter which only allows ions of a single mass-to-charge ratio to pass through the cones to the detector at a given instant in time and the detector then receives an ion signal proportional to the concentration. The concentration of a sample is determined through calibration with certified reference material which can be either a single or multi-element reference [235].

The elements reported for the soot samples analysed in this work include: (Ca,Cu,Fe,Mg,Mn,Na,P,S,Si,Zn).

All soot sample bulk elemental analysis was outsourced by Lubrizol, Wickliffe, Ohio.

3.6.4 Soot Morphological Analysis

The soot morphological characteristics investigated in the work reported herein included: surface area, porosity, density and primary particle diameter.

3.6.4.1 Surface Area (BET)

The surface area of the soot was measured using a technique based upon the principle of physisorption (physical adsorption) where a gas or vapour phase is brought into contact with a solid (the sample) with part of this being taken up and remaining on the outside of the sample attached to the surface. Weak Van

Soot Analysis Techniques

der Waals forces are responsible for the attraction between the adsorbate and the solid surface. The technique is highly suited to porous materials as it enables the determination of specific surface area, pore size and porosity.

The most commonly used method to calculate the surface area is the **Brunsuer, Emmett and Teller (BET) approach** {Appendix 6 (Table A6.3)}. This is an equation which uses an Adsorption Isotherm which is a plot of the amount of gas adsorbed across a wide range of relative pressures (p/p_o) at a constant temperature. The surface area which this technique describes is the external surface of a material which includes the surface attributable to pores. The surface area is typically quantified as the specific surface area (m^2/g).

The shape of an isotherm is non-linear as the adsorptive transitions from a monolayer on the surface to the onset of capillary condensation and to multi-layer formation and then finally the filling of the voids of any pores, this multi-layer adsorbate is the condition modelled by the BET model. The point on the isotherm where the monolayer formation is valid ($p/p_o = 0.05$ to 0.3) is the part which is used to estimate the surface area using a BET plot. A single point on the BET plot, typically at a $p/p_o = 0.3$, can be selected to determine the specific surface area but quite often multiple points are used to provide a more reliable estimation. For the samples analysed in this work multiple points were used.

Sample pre-treatment is very important to ensure an accurate measurement. This is because the surface and pores should be free for the adsorptive and also because during the process of desorption, guest species can interfere with the analysis. A cleaning procedure is recommended which involves elevating the temperature of the sample in a vacuum to desorb gas and vapour molecules but presents a risk of phase transitions in the sample itself. A flow of dry, inert gas is also a technique used to remove any desorbed molecules.

When using this technique, the accurate estimation of the soot surface area is reliant on the sample not containing significant aggregations of the soot primary particles as these are not considered in the BET theory [141, 236]. Reports in literature fail to reliably state the procedure undertaken to reduce the risks of error because of this problem. A typical method is sonication for a period time [237] and the results reported in this work were from samples that had been sonicated. Degassing and heat treatment techniques are also described in various forms in literature an example being the sample preparation by

degassing under N2 atmosphere at 150°C for 1 hour [237] and even higher temperatures (400°C) are reported elsewhere [137].

All soot sample surface area analysis was outsourced by Lubrizol, Wickliffe, Ohio.

3.6.4.2 Porosity (BJH)

The porosity of the soot analysed in this work was determined by utilising the **Barrett-Joyner-Halenda (BJH) adsorption theory** {Appendix 6 (Table A6.3)} which was originally proposed in 1951 and has been a popular technique for pore size determination in many fields. This theory is applicable to the same adsorption isotherm used in the BET surface area determination outlined in the previous section. It applies from the point of onset of capillary condensation (the pressure ratio p/p_o is > 0.35) in the assumed cylindrical pores until the upper limit of the isotherm is reached (p/p_o = 0.5).

The BJH model assumes that pores have a cylindrical shape and that pore radius is equal to the sum of the Kelvin radius and the thickness of the film adsorbed on the pore wall [141]. The method is therefore based on a modified kelvin equation which predicts the pressure at which adsorptive will spontaneously condense (and evaporate) in a cylindrical pore of a given size.

There is a limitation in the BJH method that needs to be considered when using it to quantify the porosity of soot; is it is known to underestimate the size of small to medium mesopores (2-25 nm). For this reason it is advised to limit use of the method to broad size distributions of medium to large mesopores (25-50 nm) [238]. As a result, the BJH method is now being slowly superseded in some fields with a more recently developed method called Density Functional Theory (DFT) which is essentially a far more complex method of utilising the adsorption isotherm to calculate the average pore volume and size [238]. However, the majority of the literature found which considers diesel soot porosity uses the BJH method (Chapter 2) and this is the method adopted in this work.

In this work the BJH porosity results are reported as 'average pore diameter' which is calculated on the basis of an assumed cylindrical pore geometry using the BET surface area and the volume of the pore [345], Equation 3.6.

average pore diameter =
$$\frac{4V_{liq}}{S_{BET}}$$
 Equation 3.6

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Here, V_{liq} is the volume of the pore which is calculated from the volume of gas adsorbed when measuring the N2 adsorption isotherm. S_{BET} is the BET surface area outlined earlier. This is a useful relation as it shows that pore volume is directly proportional to average pore diameter and surface area reported in this work.

One of the practical issues of both the BET and BJH methods (i.e. they both relay on the N2 adsorption isotherm) when applying to an aerosol such as soot is that most commercial apparatus requires a sample of several milligrams [151]. In this work this constraint resulted in some of the soot samples not being analysed for surface area and porosity due to soot sample mass limitations, specifically the 19.5:1 soot samples at the exhaust manifold.

All soot sample porosity analysis was outsourced by Lubrizol, Wickliffe, Ohio.

3.6.4.3 Density (N2 Pycnometry)

The method utilised to determine the soot density was based on *N2 Pycnometry* {Appendix 6 (Table A6.4)} which uses the measured pressure of nitrogen gas displaced between sample and reference chambers. The pressure of the gas in the original sample chamber is measured and then measured again once it has expanded into a chamber with a calibrated volume. This is then used along with the volume/pressure relationship of Boyle's Law to calculate the volume of the sample. The density is then simply calculated by the mass/volume relationship using the sample mass determined using a precision mass balance.

The volume determined by a Pycnometer is the space occupied by the sample and this is therefore the space which is inaccessible to the gas used in the device. A limitation of the method arises with closed pores which form voids as these are included as the volume of the sample causing errors in the subsequent density calculations. The molecular size of the gas used is important for taking into consideration the finest scale of surface features. Generally, Helium is used due to its small molecular size and it also being inert. Helium can however present issues with some samples which have low density and can be permeable to the gas and thus this can cause errors with the volume measurement. Therefore Nitrogen was chosen for the soot sample analysis in this work as they are reported in literature to have low density, Section 2.4.2.3.

There is much difficulty with the application of this technique to soot as the particle size and low sample mass mean that it is very difficult to get accurate measurements as the volume of the sample is very small and the accuracy

Soot Analysis Techniques

demands on the pycnometer pressure sensing apparatus is very high. For example, Choi et al. [239] quote the density of the soot to be 1.74 g/cm^3 with uncertainty of +/-0.10 g/cm³ (i.e. +/-5%).

The density calculated from the volume measured by a gas Pycnometer is sometimes referred to *skeletal density*, true density or helium density [240].

Similar to the surface area and porosity measurements the main constraint of the N2 pycnometry analysis method is that several milligrams of sample are required for accurate determination and this is reported in literature as common reason for the technique not being that widely used for diesel engine soot even with the advantage of the accuracy and confidence in the method [150]. Thus, providing results for diesel soot using this method is very useful.

All soot sample density analysis was outsourced by Lubrizol, Wickliffe, Ohio.

3.6.4.4 Primary Particle Diameter Estimation

The primary particle diameter in this work was determined not through direct measurement but by *calculation using the measured soot surface area (from the BET calculation) and the density (from the N2 Pycnometry),* both of which were detailed earlier {Appendix 6 (Table A6.4)}.

The calculation was based on the following principle which assumes that the primary particles are nonporous and spherical:

$$\frac{volume}{surface area} = \frac{\frac{4}{3}\pi r^3}{4\pi r^2} = \frac{r}{3} = \frac{d}{6}$$
 Equation 3.7

If we insert both volume and surface area as specific parameters of the particle mass, then:

$$\frac{volume}{surface area} = \frac{d}{6} = \frac{m^3/g}{m^2/g} = \frac{1/\rho}{m^2/g}$$
 Equation 3.8

Thus, the primary particle diameter can be estimated as [241]:

$$d = \frac{6}{\rho \times (m^2/g)}$$
 Equation 3.9

Where the specific surface area (m^2/g) is found using the BET method and the density p is found by the N2 pycnometry. Thus, this method leverages on the indirect measurement of surface area (BET method) and the indirect measurement of density (N2 Pycnometry). The estimation is therefore subject to any error in these two measurements and thus a direct method of measurement such as TEM would likely yield more reliable results for diesel exhaust soot [236]. Methodology

Soot Analysis Techniques

However, due to the limited sample mass collected in this work the decision was taken to concentrate on the specific quantification of key physiochemical soot characteristics which cannot be derived through TEM as these are less frequently reported than the soot TEM images popular in literature. The other consideration was that the application of the outlined primary particle size calculation method appeared to provide fairly reasonable estimations as reported in Section 2.4.2.4 and thus TEM was not considered in this work.

A further consideration with this approach was the assumption of a *nonporous spherical particle*. Such an assumption overly simplifies the description of the soot particles since soot primary particles are frequently reported in literature to be porous (Section 2.4.2.2) with the primary particles grouped together forming aggregates [137]. Porosity will result in a larger surface area measurement with the BET technique leading to an underestimation of the primary particle diameter. This is countered by the reduction in primary particle surface area measurement caused by the aggregation of more than one primary particle.

With this in mind, Equation 3.9 cannot therefore be relied upon for absolute precision. It does however permit a reasonable estimation of the primary particle diameter to facilitate the analysis of the influence of the investigative parameters when the above highlighted limitations are acknowledged.

3.6.5 Surface Acid Functionality (Boehm Titration)

The review of the surface acidity analysis of carbon black and soot (Section 2.4.3) revealed that one of the frequently cited methods for surface acidity quantification is the method referred to as **Boehm titration** {Appendix 6 (Table A6.4)}.

The method was first detailed by Boehm in 1964 [156, 242] and is capable of the determination of the acidic oxygen surface functional groups on carbon samples. The method is based on the principle that oxygen groups on carbon surfaces have different acidities and can be neutralized by bases of different strengths. These bases include NaHCO₃, Na₂CO₃, NaOH and sometimes NaOC₂H₅ [243, 244]. The surface functional groups which can be determined include phenolic group (–OH), lactone group (C=O) and carboxylic group (– COOH) [245].

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The strongest base generally used is sodium hydroxide (NaOH) and this is assumed to neutralise all the Brønsted acids (including phenols, lactonic groups and carboxylic acids). Sodium carbonate (Na₂CO₃) is used to neutralize carboxylic and lactonic groups (e.g. lactone and lactol rings) and the weakest base sodium bicarbonate (NaHCO₃) neutralizes carboxylic acids [243, 244]. The concentration and types of oxygen surface groups present on the soot can be determined by the differences in the uptake of these various bases [242]. In this work both the carboxylic and the total surface acidity of the soots were quantified.

Sample agitation is important and there are various methods reported in literature including: shaking [242], stirring and sonication [244]. Stirring and sonication have been shown to result in changes to the macroscopic surface of the carbon particles [244] and thus the original Boehm method of shaking was used.

The duration of the shaking is important as the diffusion into the pores can affect the results. Therefore, soot which has a high surface area and hence a likely significant porosity, requires a longer period of agitation [242, 244]. However, too much shaking can potentially physically change the soot surface and therefore different groups use different durations for shaking. In this work the method of Boehm [242] was followed closely to ensure a clear point of reference.

All soot sample Boehm titration tests were conducted by Lubrizol, Wickliffe, Ohio.

3.6.6 Poly Aromatic Hydrocarbon (PAH) Profile

The most widely encountered method for PAH quantification in soot literature is **Gas Chromatograph Mass Spectroscopy (GC-MS)** {Appendix 6 (Table A6.4)} with numerous examples of this technique applied to soots formed in many different environments (e.g. premixed flames, laminar diffusion flames, turbulent flames, microgravity flames) as summarised comprehensively by the review paper Dobbins et al. [25].

In this work the precise method utilised for the analysis of the PAH content is based on test method 610 'Methods For Organic Chemical Analysis Of Municipal And Industrial Wastewater' defined by the United States Environmental Protection Agency (EPA) [246] which is stated as the method applied in recent diesel soot literature [23].

3

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Soot Analysis Techniques

Using method 610 as the basis of the method; first the sample was solubilized in methylene chloride to extract the soluble organic fraction (SOF) using a soxhlet extractor. This methylene chloride extract was then dried and concentrated to a volume of several ml. This extract was then evaporated under a nitrogen flux before being injected into the gas chromatography mass spectrometer (GC-MS). This produced a gas chromatogram for the poly aromatic hydrocarbons based on the retention time.

A total of sixteen PAH, as detailed by EPA Method 610 [246], were tested for and include: Naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, Acenaphthylene or biphenylene, Acenaphthene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Benz(a)anthracene, Chrysene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Indeno(1,2,3-cd)pyrene, Dibenz(a,h)anthracene and Benzo(g,I,h)perylene.

All sample PAH analysis tests were conducted by Lubrizol, Wickliffe, Ohio.

3.6.7 Thermogravimetrical Analysis (TGA)

Thermogravimetrical analysis (TGA) is a common technique {Appendix 6 (Table A6.4)} which is applied to study the SOF, carbonaceous part and ash content of soot samples from diesel particulate filters DPF and is used in this work to determine the composition of the soot for the diesel particulate filters (DPF) samples alone due to the previously identified ceramic thimble soot sample mass constraints. The method involves heating the sample to a sufficient temperature to cause the decomposition of the solid/liquid phase components into a gas which dissociates into the air. It is common to use oxygen or nitrogen gas environments in which the sample is heated to control the processes by which material liberated from the sample into the gaseous phase so that different sample fractional parts can be accurately determined. The main advantage of the method is that it allows for the discrimination of the volatile fraction condensed onto the soot from the carbonaceous part and the non-combustible part which are typically metals from the fuel, lubricant, engine and exhaust system (ash).

The technique used for the analysis in this work followed that outlined by Covitch et al (Lubrizol) [210] which in turn references Swarin et al. [247]. This involved heating the soot sample (<30 mg) at 20°C/min under nitrogen to 585°C, at which temperature the nitrogen stream was replaced by air and the heating then continued to 1000°C.

Soot Analysis Techniques

The results in this work are reported in the form of percentage of mass reduction in each temperature region through which the sample was heated. The conventional descriptions of the material removed during each region are defined in this work as summarised in Table 3.13.

Table 3.13: Definition of TGA Temperature Ranges

Temperature Range (°C)	Mass Reduction Attribution
25 to 300	Oil residue & lighter ends e.g. SOF
300 to 400	Polymers and Sludge
400-700	Traditional soot (Carbon)
700-1000	Additional carbonaceous content
Residue at 1000	Non-combustible ash

All sample thermogravimetrical analysis tests were conducted by Lubrizol, Wickliffe, Ohio.

3.6.8 Soot Sample Mass Requirement

Based upon all eight physiochemical test based soot characterisation techniques it was estimated that a soot sample total mass of approximately 2g was required to enable all tests to be fully completed for a specific soot sample. Therefore this was the sample mass requirement which focussed the ceramic thimble apparatus development and design of the soot collection experiments.

3.6.9 Repeatability of Test Methods

The limited mass of soot which could be collected for the thirteen individual soot collection experiments performed in this work, precluded that limited repeat tests could be performed for each soot analysis technique described in Section 3.6.1 to Section 3.6.7. Where possible the precision and error was determined for each soot analysis technique and this is summarised in this section. This information is reported in each table and figure herein where available.

There were no repeat experiments performed of the individual soot collection experiments due to resource and time constraints and thus there were no separate soot samples tested to validate general result repeatability and reproducibility.

The **XPS** analysis being non-destructive enabled repeat testing of individual samples and in the work reported herein the precision of the O/C ratio is reported Correction of the Soot Bulk Inorganic Observations (ICP-MS) for Foreign Contaminates

for the thirteen samples analysed. The range of precision was 0.0113-0.0143, which was equivalent to 7.6% to 19.8% error, with the highest O/C ratios having the greatest precision.

The **ICP-MS** tests were performed on all thirteen samples but this destructive test required such a mass of soot that it precluded performing any repeat tests on individual samples. The ICP-MS results are reported to the nearest 0.01 wt % of the sample mass throughout the work herein.

For a total of ten soot samples the **BET** surface area was measured; the measurement error is reported in each case and falls within 0.5 % +/- 0.01 % for all samples. The same ten soot samples were also analysed using **N2 Pycnometry** and the measurement error ranged from 0.33% to 0.84%, being larger where the available mass of sample to measure was the smallest.

Boehm titration was repeated where sample mass permitted and the mean and standard deviation results are reported herein for each of the nine samples that were analysed in this work. For total surface acidity (mmol/g); where acidity was detected the coefficient of variation ranged from 0.49% to 13.37%. For carboxylic acid the coefficient of variation range covered a smaller range of 0.13% to 5.14%.

PAH analysis could not be repeated on any of the singular soot samples due to soot mass constraints, indeed it was only possible to test nine out of the thirteen total soot samples due to soot mass limitations. All PAH measurements reported herein are to a resolution of 0.001 μg PAH/g sample.

The soot sample mass availability limited the **thermogravimetrical** analysis to just seven of the thirteen soot samples and there were no repeat analysis of singular samples due to it being a destructive test. Results are reported to the nearest 0.1% weight of sample.

3.7 Correction of the Soot Bulk Inorganic Observations (ICP-MS) for Foreign Contaminates

Following careful examination of the original ICP-MS results, it became clear that there were a series of inconstancies which pointed to several of the soot samples being contaminated with elements which either had no identifiable source (i.e. foreign to the experiment) or were attributable to known uncontrollable factors that could not be avoided when the soot was experimentally collected from the engine.

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Injector Coking Issues

The ICP-MS results presented in the main body of this work have therefore been carefully corrected to remove the masking effects of identified foreign sample contamination. The identified contaminates were sodium, silicon and sulphur and these have been negated from the affected sample results according to the methodology described in Appendix 8.

3.8 Injector Coking Issues

To collect sufficient soot mass at the exhaust manifold, the soot collection experiments in this work had to be run at rated engine power as detailed in Section 3.1.5.3. However, when the soot collection experiments collectively were nearing 50% completion, it became clear that there was a general trend for loss of engine torque over the course of each 20 hour collection experiment. This trend was exacerbated with the B100 fuel and ultimately forced the 16.5:1 B100 soot collection experiment to be concluded early at 12hrs.

Examination of the fuel injectors identified coking around the nozzles as the cause of the loss of engine torque and this subsequently required the replacement of all four engine fuel injectors so as to complete the experimental work. A review of literature suggested that prolonged operation at high loads and high cylinder temperatures increases the likelihood of injector coking, Argueyrolles et al. [328]. Indeed, it was identified that prolonged operation at the rated engine power condition is the standard method of evaluating injector coking tendency [328]. Since the soot mass constraint forced the soot collection tests to be conducted at rated engine power, it was not possible to adjust the engine operating point to avoid the issue.

An examination of the injector coking issues encountered in this work is presented in Appendix 9 and details a hypothesis for the much greater extent of coking observed for the B100 fuel. This therefore contains information that may be of assistance to future investigations where RME biodiesel fuel is used at high engine power for extended duration.

3.9 Overview of the Collected Soot Samples and the Analysis Techniques Performed

A summary of the measured soot physiochemical results and the chapters in which they are presented and discussed is provided by Figure 3.33.



Results and the Result Chapters in which they are Discussed

4 Engine Performance, Gaseous and Particulate Emissions Summary

4.1 Introduction

This chapter presents a summary of the results for the engine performance and emissions for two of the three experimental groups (Section 3.1.5). The first set of data presented in Section 4.2 summarises the engine performance and emissions for the parametric study of the engine speed/torque operating envelope as described in Section 3.1.5.2 which was used to establish the operating condition for the soot collection experiments. The second set of data presented in Section 4.3 derives from the six fuel and compression ratio rated power experimental conditions where exhaust soot was sampled as detailed in Section 3.1.5.3. Thus, the first section provides an overview of the general influence of fuel and compression ratio on the VW 1.9I TDI engine performance and emissions and is a reference for later discussion of the soot results. The second section is a reference for the operating conditions, fuelling and AFR etc. for the soot collection experiments which produced the soot results presented across Chapter 5 to Chapter 9.

4.2 Engine Performance and Emissions Summary for the Parametric Experiments

The parametric study of engine performance and emissions was performed according to the experimental design described in Section 3.1.5.2. This experimental study enabled the evaluation of the differences in a broad array of measurement parameters arising from the three fuels and two compression ratios investigated in this work. The result discussion in this chapter focuses on the parameters of exhaust soot concentration and exhaust hydrocarbon emissions. These parameters specifically relate to the soot physiochemical analysis in Chapter 5 to Chapter 9.

4.2.1 Effects of IMAT Change (Low to High)

The engine performance and emissions measurements were undertaken with two different intake manifold air temperature (IMAT) states (<25°C and >40°C) herein denoted as *low* and *high* IMAT which followed from preliminary work that had indicated IMAT strongly influenced the gaseous and particulate emissions. This was also useful as the ECU was a production part and would not accept overrides, thus IMAT control was an indirect mechanism which could be used to manipulate engine fuelling and AFR.

The most useful attribute of the increase in IMAT from the low to high range was to force an increase in the exhaust soot concentration. To illustrate this behaviour, Figure 4.1 and Figure 4.2 present the EN590 fuel specific soot emissions (g/kWh) measured for torque groups C to E (Section 3.1.5.2) of the parametric study at 19.5:1 and 16.5:1 compression and for low and high IMAT. This comparison reveals that the increase in IMAT to >40°C resulted in increased exhaust soot concentration and that the effect was more pronounced above 3000 rpm for the torque groups D and E at 19.5:1.





A critical observation from both Figure 4.1 and Figure 4.2 was that the highest exhaust soot concentration was observed at rated engine power (4000 rpm, maximum torque) with the concentration relatively low from less than 3000 rpm until at 1500 rpm where it increased rapidly as the engine speed reduced further.

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The increase in soot concentration below 1500 rpm was only evaluated up to torque group C (<80% peak torque, Section 3.1.5.2) as torque higher than this at this engine speed was found to result in engine-dynamometer speed control instability, Section 3.1.5.2. *Consequently, the rated power operating point was chosen as the engine operating point for the fuel and compression ratio exhaust soot collection experiments Section 3.1.5.3*.





Figure 4.1 and Figure 4.2 are both illustrative of the parametric study measurements which were also performed for a large number of other parameters. Thus, for the purposes of this work a method of data processing and presentation was required which concisely consolidates the findings to assist with the soot physiochemical result discussion which follows in subsequent chapters.

The method devised to do this involved calculating the percentage change for like fuel and compression ratio configurations with the IMAT change from low to high and this is presented in flow diagram form in Appendix 7 (Figure A7.1). In summary, percentage change was calculated for each measured parameter at each speed-torque point with the change in the factor IMAT from low to high. The individual percentage change results were then collated into each respective engine torque group to produce an average for the points within that torque group – Result 1. This way the general effects of a parameter such as IMAT could be summarised for like torque regions via a simplified presentation. The individual

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speed-torque % percentage change values were then averaged across all speedload points to establish an overall 'total average percentage change' for all torque groups C to E – Result 2.

This approach was devised so as to summarise the multi-parameter influence of factor changes such as IMAT, compression ratio and fuel for local torque regions and also globally for the entire engine speed-torque operating envelope. The results presented in this chapter focus on the most important torque groups for the exhaust soot investigation; namely C to E (torque from 60% to 100% of maximum at each engine speed) as these were the torque groups which had the highest exhaust soot concentrations.

A summary of this percentage change data is presented in Table 4.1 with each row being one of the important measurement parameters and each column being a specific fuel and compression ratio condition at which the IMAT was changed from the low to high range. On the right of Table 4.1, further averaging of all the fuel observations is presented first at each compression ratio and then finally overall.

	EN590 Vs	5. EN590	PC9 V	s. PC9	B100 V	s. B100	ALL F	UELS	ALL FUELS
Rc:	16.5:1	19.5:1	16.5:1	19.5:1	16.5:1	19.5:1	16.5:1	19.5:1	16.5 & 19.5
BMEP (bar)	-3.76	-3.39	-4.20	-3.79	-2.65	-1.57	-3.54	-2.92	-3.23
BSFC (g/kWh)	2.30	2.34	2.92	2.78	3.35	2.62	2.86	2.58	2.72
AFR	-8.75	-6.71	-8.77	-6.89	-12.25	-4.72	-9.92	-6.11	-8.02
MAF (kg/h)	-10.53	-8.14	-10.16	-8.00	-11.85	-3.77	-10.85	-6.64	-8.74
Fuel (kg/h)	-1.60	-0.98	-1.42	-1.12	0.60	1.01	-0.81	-0.36	-0.58
Soot (g/h)	32.82	79.89	72.31	52.47	15.47	41.58	40.20	57.98	49.09
Soot (g/kWh)	38.13	86.48	80.05	58.38	18.50	43.80	45.56	62.89	54.23
CO2 (g/kWh)	2.48	10.60	10.13	20.93	1.67	3.97	4.76	11.83	8.30
CO (g/kWh)	33.18	96.54	113.92	87.58	28.67	40.90	58.59	75.01	66.80
O2 (g/kWh)	-17.71	-9.83	-15.66	-18.41	-17.83	-10.06	-17.07	-12.77	-14.92
NOx (g/kWh)	7.03	9.89	12.29	5.54	10.56	17.29	9.96	10.91	10.43
HC (g/kWh)	-39.44	-13.10	-27.19	-7.70	-46.54	15.70	-37.72	-1.70	-19.71
Delta IMAT (°C)	264.68	118.21	252.86	96.97	232.39	96.06	249.98	103.75	176.86
Exhaust Temperature	11.27	9.59	11.79	9.01	12.77	6.75	11.94	8.45	10.20
Soot (mg/m ³)	48.04	96.81	91.28	64.98	29.97	46.67	56.43	69.48	62.96
Start of Injection	-0.09	-1.33	-0.03	-0.35	0.83	0.00	0.24	-0.56	-0.16
Injection Duration	-0.02	0.51	0.12	0.00	-0.64	0.00	-0.18	0.17	-0.01
CO2 (mole fraction)	9.69	17.10	16.85	25.92	11.40	6.03	12.65	16.35	14.50
CO (mole fraction)	42.69	110.12	127.28	95.65	41.08	43.69	70.35	83.15	76.75
O2 (mole fraction)	-11.98	-6.46	-10.66	-15.09	-10.01	-8.28	-10.89	-9.94	-10.42
NOx (mole fraction)	14.57	14.30	19.03	9.87	21.08	19.60	18.23	14.59	16.41
HC (mole fraction)	-35.13	-9.38	-23.10	-3.93	-41.26	18.06	-33.16	1.58	-15.79
MAF + Fuel Change	-12.13	-9.12	-11.58	-9.12	-11.25	-2.76	-11.66	-7.00	-9.33
MAP (mbar)	0.22	0.01	0.02	-0.21	-0.02	1.36	0.07	0.39	0.23
Fuel Supply Temp (°C)	9.21	-0.49	4.40	10.44	-0.19	-0.55	4.47	3.14	3.80

Table 4.1: Summary of the Percentage Change in Engine Performance andEmissions for Low-to-High IMAT Change (Torque groups C to E)

Table 4.1 details how the achievable increase in IMAT was greater for the 16.5:1 compression condition by virtue of the low IMAT temperatures for the 16.5:1 experiments being lower as these were undertaken in the winter when the

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laboratory cooling water had a lower average temperature than for the 19.5:1 experiments conducted in the summer months. The high IMAT conditions were much more consistent as these resulted from highly restricted water flow through the charge air cooler Section 3.2.1.3 thereby limiting the influence of water temperature.

The increase in IMAT was observed to have a very similar effect on both mineral fuels (EN590 and PC9) with the Brake Mean Effective Pressure (BMEP) reducing between 3.4 and 4.2%, the AFR reducing between 6.7 and 8.8% and the soot mass flow rate increasing between 30-80% depending upon the fuel and compression ratio configuration.

For the B100 fuel the influence of IMAT on BMEP was smaller and the increase in soot mass flow was also lower at between 15 to 42%. For all but the 19.5:1 B100 experimental condition the HC emissions were generally observed to fall with the increase in IMAT with the reductions consistently more significant for the low compression ratio 16.5:1. This result implied that the higher IMAT benefitted the fuel combustion process through the reduction in HCs possibly through improved fuel atomisation. *This observation was important as it implied the higher IMAT, in addition to increasing the exhaust soot concentration, also potentially reduced the soluble organic fraction (SOF) component of the soot.* This was an important observation in respect to the soot characterisation results discussed in proceeding chapters where the soot samples were all collected under high IMAT conditions.

These measured parameter changes occurred with generally consistent injection timing parameters and boost pressure implying the soot and HC observations derived largely from the IMAT induced AFR reduction and associated effects.

4.2.2 Effects of Fuels at Different Compression Ratios and IMATs

The data from the parametric experimentation presented in the previous IMAT section was evaluated to extract information concerning the relative influences of the three fuels. Focussing first on the specific exhaust soot emissions; Figure 4.3 presents the measurements at 16.5:1 compression for the three torque groups C, D and E for both EN590 and PC9 fuels at low IMAT conditions. Figure 4.3 shows that for most of the operating conditions

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> investigated the specific exhaust soot emission was higher for the PC9 fuel, particularly for higher speed and torque operating conditions. Figure 4.4 presents the same results for the B100 fuel measurements and the distinct reduction in specific exhaust soot emissions for this fuel is very clear though the pattern with engine speed and torque persisted.



Figure 4.3: 16.5:1 EN590 vs. PC9 Fuel Specific Soot (g/kWh) Speed and Torque Parameterisation



Figure 4.4: 16.5:1 EN590 vs. B100 Fuel Specific Soot (g/kWh) Speed and Torque Parameterisation

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The method of percentage change based data analysis described in the previous IMAT section has been repeated to extract the individual fuel-based effects on measured parameters but in this case the percentage change was calculated as the parameter change from the B100 and PC9 fuel measurements relative to the baseline EN590 fuel. This data is presented in Table 4.2 and Table 4.3 which describe the four different conditions of compression ratio (high and low) and IMAT (low and high) and together define the interrelationships of these fundamental factors and each fuel.

Table 4.2: Summary of the Percentage Change in Engine Performance andEmissions for Different Fuels (Torque groups C to E)

		PC9 Vs	. EN590			B10	0 Vs. EN590		PC9 Vs. EN590	B100 Vs. EN590
	16.	.5:1	19.	.5:1	16.	5:1	19	.5:1	Total	Total
IMAT:	low	high	low	high	low	high	low	high	Average	Average
BMEP (bar)	3.80	3.59	2.53	2.11	-3.88	-3.13	-4.13	-2.30	3.00	-3.36
BSFC (g/kWh)	-2.18	-1.02	-0.89	-0.54	14.18	15.68	10.91	15.91	-1.16	14.17
AFR	-1.54	-2.30	-1.33	-1.79	-9.52	-12.62	-5.43	-9.37	-1.74	-9.23
MAF (kg/h)	-0.21	0.17	-0.13	-0.29	-0.81	-2.16	0.13	2.55	-0.11	-0.07
Fuel (kg/h)	1.52	2.54	1.62	1.31	9.73	12.08	6.32	13.26	1.75	10.35
Soot (g/h)	19.27	43.72	3.03	0.41	-79.92	-83.42	-87.96	-80.75	16.61	-83.01
Soot (g/kWh)	14.79	39.37	0.33	-1.74	-79.13	-82.89	-87.43	-80.31	13.19	-82.44
CO2 (g/kWh)	-4.00	3.17	-3.93	2.50	0.71	0.20	2.88	-6.83	-0.57	-0.76
CO (g/kWh)	-7.64	38.68	7.81	9.59	-33.89	-35.13	-32.48	-40.20	12.11	-35.42
O2 (g/kWh)	-9.23	-7.23	-2.04	-10.64	5.43	5.85	5.36	-0.18	-7.29	4.12
NOx (g/kWh)	-0.85	4.33	4.19	1.16	15.21	19.48	14.84	10.28	2.21	14.95
HC (g/kWh)	-34.91	-22.45	-3.13	-3.88	92.35	-15.18	-3.66	53.54	-16.09	31.76
Delta IMAT (°C)	8.32	9.40	0.58	-1.17	16.94	10.85	-3.99	-9.56	4.28	3.56
Exhaust Temperature	4.79	5.35	2.68	3.22	-6.38	-5.76	-7.38	-9.26	4.01	-7.19
Soot (mg/m ³)	19.52	43.86	3.00	0.16	-79.79	-83.12	-87.96	-81.34	16.64	-83.05
Start of Injection	-0.04	0.17	0.07	1.52	-0.68	0.17	-0.31	3.37	0.43	0.64
Injection Duration	0.48	0.59	0.58	0.13	0.45	-0.17	0.32	0.89	0.44	0.37
CO2 (mole fraction)	-0.16	6.62	-0.12	5.13	-2.65	-1.30	-0.37	-10.67	2.87	-3.75
CO (mole fraction)	-3.93	43.04	11.02	10.16	-36.17	-35.79	-35.18	-43.26	15.07	-37.60
O2 (mole fraction)	-5.58	-4.13	0.26	-8.03	1.88	4.22	0.43	-5.16	-4.37	0.34
NOx (mole fraction)	3.14	7.85	6.31	3.69	11.34	17.60	9.24	4.70	5.25	10.72
HC (mole fraction)	-32.29	-19.90	-0.75	-1.05	86.12	-15.96	-7.58	44.60	-13.50	26.79
MAF + Fuel Change	1.31	2.71	1.48	1.02	8.92	9.92	6.45	15.81	1.63	10.28
MAP (mbar)	0.10	0.04	0.13	-0.14	-0.02	-0.12	0.23	1.06	0.03	0.29
Fuel Supply Temp (°C)	5.37	1.31	5.06	20.45	12.91	1.52	-3.79	2.05	8.05	3.17

	Load Gr	oup Avera	ge PC3	Load Gro	genwik qui	te Bloo	PO AV	Reage all Load	d Groups	B100 A W	rage all Load	Groups	PC9 Average a	Load Groups	B100 A we rage a	I Load Groups
•	0		-	0			High & Low		High	High & Low	Low I we use used in	High	16.6:1	19.6:1	16.6:1	19.61
EMEP (bar)	3.10	3.11	2.27	3.69	2.57	58 7	2.83	3.13	2.53	89	3.67	2.89	3.29	2.37	-3.17	68 7
BSFC (g/W/h)	8	÷,	4.42	15.11	13.82	12.82	8	-1.68	0.50	13.95	1224	15.08	-175	ę P	14.61	13.28
AFR	9 7	5.41	124	θ.71	9.59	8 9	1.70	-126	2.15	9'3	88. 77	-11.15	-157	1- 8-	-11.12	87
(MAF(HgM)	6.2	0.16	8	021	0.16	6	₽	0.13	0.20	đ. Q	Ę	8	62	무	-1.49	1.1
Fuel (Hgh)	1.38	2.49	1.08	10.92	10.87	9.72	1.64	138	1.90	10.50	8.32	12.08	1.47	1.81	10.98	10.03
Soot(mg/m ²)	7.55	21.89	33.84	83.30	얺	튭	21.99	17.36	88	-8251	-83.46	81.8	37.B1	6.17	81.34	-83.67
soot(gh)	7.55	218	1.8	63.25	8 8	-81.76	21.82	12.22	8	-82.47	83.9	8 1.#	31 24	8 .8	81.56	63.38 6
Soot(g#\Mh)	4.08	21.19	30.16	-82.64	-81.91	93 93	18.48	13.49	23.46	-8193	-82.91	-80.96	33.16	3.79	-30,96	-82.91
002 (mole fract)	2.62	3.32	3.28	384	-2.86	93 7	308	80	5.76	8	-0.61	6 .83	3.11	3.04	-1.86	88. T
002 (g/h/vh)	8.9	0.03	0.10	-0.53	-0.49	8	8	-3.53	2,86	89. 0	2.05	3.63	0,40	-0.27	024	-1.61
CO(mole fact)	9.87	8	2.41	31.31	814	9.6	12.74	5,89	88	-38.70	-38.50	-38.89	22	13.23	80.85	-39.31
(hwh)	6.30	18.94	19.32	28.09	88	8 F	14.85	2,33	23 28	-36.72	-36.26	-37.18	18.28	11.45	-36.89	-36.95
O2 (mole fact)	B	5.1	8	0.83	0.61	224	1	2.90	6.98	0.27	83	0.15	-4,80	6.¥	3.52	2.88
O2 (g/h/vh)	5.0	-2.08	7 18	3.18	2.47	5.41	-1.28	684	-8.69	3.68	8	3.17	+09+	-6.49	5.75	1.62
NOR (mole fact)	5,98	4 G	3.38	10.07	11.88	11.01	16	¢.19	5,68	10.91	10.66	11.16	5.07	ŧ.81	87	7.47
(HV/Mg) ION	2.67	2.89	0.76	14,60	15.23	11.52	201	1.17	2.84	14.78	15.00	11.88	1.49	2.52	16.83	12.73
HC (mole fract)	8.4	-19.34	-23.35	24.03	36.96	159.42	-16.98	88	-12.31	91°19	9104	23.87	30.28	-2.84	88	29.36
HC (g/h/vh)	9.70	-22 23	-25.03	-20.79	42.22	167.63	-18.99	-23.16	-14.82	60.02	97.49	28.66	-22.62	-6.36	90.12	35.91
MAF + Fuel (right)	1.10	2.8	88.0	10.71	11.04	9.65	44	8	1.69	10.46	83	12.71	123	17.1	6 1 .6	11.44
Eshaust Temperature	101	4.72	3.12	181	-6.22	5.0	\$ 0 \$	380	4 29	98.9	-6.73		5.27	2.83	-687	6.00
Start of Injection (CAD)	1.48	0.01	80	2.37	0.05	89 97	023	8	2470	0.59	8	1.7.1	000	0.47	-0.39	1:51
Injection Duration (CAD)	11.0	8.0	0. 1 1	8	0.37	0.18	0.42	50	0.26	0.38	0	8	0.49	9.34	0.12	8.0
Fuel Supply Temp (C)	8.92	10.08	8	2.84	4.38	2.81	7.89	5.85	9.92	334	4.54	2.15	3.62	12.15	7.56	-0.87
Delta IMAT (°C)	101	9.09	2.62	4.12	3.57	91	ē.	3,86	4.73	3.06	5.61	0.51	9.27	89	11 20	9 ^{.0}
MAP (m bar)	≓. P	22	0.12	¥:	200	0.87	200	0.11	0.03	0.46	0.47	0.45	0.11	0.0	-009	1.01

Table 4.3: Summary of the Percentage Change in Engine Performance and Emissions Relative to EN590; Segmented for each Fuel, Torque Group (C,D,E), IMAT and Compression Ratio

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Engine Performance and Emissions Summary for the Parametric Experiments

4.2.2.1 Comparison of PC9 Fuel to EN590

Relative to EN590, Table 4.2 reveals that the PC9 fuel achieved slightly improved BMEP by an average of 3.0% across the three torque groups with a slight reduction in BSFC (1.16%) but the fuel mass flow rate was higher as a result of the approximately 1.8% relative increase in fuel density (EN590 = 830 kg/m³, PC9 = 845.1 kg/m³). The increase in BMEP relative to EN590 appeared to be slightly greater for the low compression configuration but the effect was very small at around 1%. Table 4.3 shows that these BMEP observations were consistent across the torque groups (C, D, E) when averaged across the two compression ratios and low and high IMAT.

The BSFC change aligned to the BMEP change suggesting there was increased fuel conversion efficiency with the PC9 fuel relative to EN590 for the low compression ratio compared to the high compression, Table 4.2, which was supported by the generally close agreement in AFR between the fuels across the high and low compression ratios and the reduced PC9 fuel HC emissions.

The PC9 fuel generally had higher specific soot emissions (g/kWh) with an overall average increase of 16.6%, Table 4.2. This higher concentration appeared to be related to the reduction in compression ratio with the soot concentration up to 3% higher at 19.5:1 but between 19.5 and 43.8% higher at 16.5:1.

There was no clear indication what was responsible for this compression ratio bias from the measured data presented in Table 4.2 and such a bias was not observed for the B100 fuel.

The HC specific emissions for the PC9 fuel were lower than those of EN590 for all conditions. Generally, with increasing torque the reduction in HC emissions for the PC9 fuel compared to EN590 became more significant, though for both torque groups D and E the reduction was quite similar Table 4.3.

Analysing the PC9 vs. EN590 HC emissions across IMAT and compression ratio conditions in Table 4.3, it is clear that the PC9 fuel produced lower HC emissions at the 16.5:1 compression ratio and this effect was amplified at low IMAT. This observation implied there was a reduction in fuel-air mixing caused by the compression ratio reduction which impacted on the PC9 HC emissions in a far less significant way than was the case for the EN590 fuel and especially the B100 fuel which is discussed later. The increased IMAT condition at 16.5:1 resulted in both PC9 and EN590 emissions reducing but the effect on EN590 was

more significant and hence the PC9 fuel's inherent advantage of lower HC emissions was reduced.

These results demonstrate that the PC9 fuel, compared to EN590, was far less sensitive in terms of HC emissions to the reduction in compression ratio. The increase in IMAT at 16.5:1 acted to reduce both PC9 and EN590 HC emissions but less so in the case of the PC9 fuel. These findings are very useful in understanding the soot physiochemical observations reported from Chapter 5 onwards.

The PC9 fuel summary engine performance and emissions changes relative to the EN590 baseline fuel (average of compression ratios, IMATs, and speed/ torque points) are detailed in Table 4.4.

Parameter	Relative % Change to EN590
BMEP	+3
BSFC	- 1.2
AFR	- 1.7
IMAT	+ 4.3
fuel inlet temperature	+ 8
exhaust manifold temperature	+ 4
exhaust manifold soot	+ 13.2
exhaust manifold CO	+ 12.1
exhaust manifold O2	- 7.2
exhaust manifold NOx	+2
exhaust manifold HC	- 16.1

Table 4.4: Overall Summary of PC9 vs. EN590 Performance and EmissionsParametric Experiments

4.2.2.2 Comparison of B100 Fuel to EN590

The B100 BMEP average reduction relative to the EN590 fuel was 3.36%, Table 4.2, and thus almost opposite to the 3% gain observed for the PC9 fuel, Table 4.2. This reduction in BMEP was largely explained by the combination of increased fuel mass flow rate due to a higher fuel density and a 12.7% lower fuel energy content.

Comparing the BMEP reduction across the three torque groups in Table 4.3 shows there was observed a very similar pattern as for the PC9 fuel but of opposite sign. This indicated that at high torque the relative differences in the torque produced by each fuel were smaller than observed for lower torque though the differences were small.

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The BSFC increased significantly relative to EN590 with an overall average of 14.17% Table 4.2. The original volumetric flow measurements indicted that the volumetric fuel flow rate was consistent across the three fuels due to the measures used to achieve consistency. Thus, the increase in B100 BSFC relative to EN590 arose from the combined effects of a 10.35% increase in fuel mass flow rate (due to the increase in fuel density relative to the EN590 fuel) combined with the 12.7% reduction in lower heating value of the fuel. The increase in BSFC was observed to be higher for torque group C (60-80% peak torque) and low speed conditions, potentially indicating reduced fuel conversion efficiency particularly at the 16.5:1 low IMAT conditions.

By far the greatest differentiation observed between the B100 and EN590 fuels was the specific exhaust soot emission; over all the test conditions the average reduction observed was 83%, Table 4.2, and almost identical to the exhaust concentration difference.

Unlike observed for the PC9 fuel, the exhaust soot mass reduction was found to be uniform over torque, compression ratio and IMAT conditions, Table 4.3. The lowest overall soot emissions were observed at 19.5:1 with low IMAT and for a number of the torque group C speed-torque points the AVL 415 smoke meter was unable to resolve a concentration above 0 mg/m³. The other characteristic of the B100 soot emissions was a substantially reduced sensitivity to a low AFR and thus for the high speed-high- torque test points the relative increase in soot with torque was far less in the case of the B100 fuel, Figure 4.4. Interestingly, the highest B100 specific exhaust soot measurement was 0.03g/kWh which was for 19.5:1 high IMAT at rated power; by reference the Euro V limit (2008.10) is 0.02 g/kWh and thus combined with B100 fuel the VW 1.9 TDI Euro III engine without a DPF was almost able to achieve the much tougher limit. This helps to put into perspective the difficulties experienced and highlighted later in this work with collecting sufficient B100 soot mass.

The overall average analysis presented in Table 4.2 implied that the B100 fuel relative to EN590 had a 31.8% overall increase in HC specific emissions. However, when this was broken down across the test conditions it was clear that the result was dominated by large increases for the two conditions 16.5:1 low IMAT and 19.5:1 high IMAT. The cause of the former case was isolated to a very substantial increase in HC emission of 1185% at rated power relative to the EN590 fuel. For the latter 19.5:1 case, this was again caused by a large increase at high torque conditions but not specifically rated power. *A review of the raw*

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4.2

measurement data made it clear that at all maximum fuelling conditions (torque group E), the B100 fuel experienced a very dramatic rise in HC emissions relative to EN590. Furthermore, unlike for torque group E, there were inconsistent relative changes in HC for torque groups C and D across the different speed-torque points. These observations are captured in Table 4.3 where the overall percentage change in B100 HC emissions relative to EN590 saw a swing from a reduction of 20.8% for torque group C to an increase of 167.6% for torque group E (>95% peak torque).

The IMAT breakdown in Table 4.3 shows the sensitivity observed for B100 HC emissions to IMAT conditions with the increase in HC emissions relative to EN590 being reduced from 97.5 to 28.6% as the IMAT transitioned from low to high. Finally, the increase in compression ratio resulted in a reduction in the relative difference in B100 and EN590 HC emissions from 90.1 to 35.9%, Table 4.3. This result summary indicates that the mechanisms of HC emissions were not connected directly to those of the mineral fuels but included additional processes that likely related to the fuel's fundamental properties and principally the fuel spray and atomisation behaviour with changes in the cylinder charge density. This was most likely caused by the factor two higher fuel viscosity for B100 compared to EN590 which would have impaired the fuel atomisation process and exacerbated any impairment in atomisation from the reduction in cylinder charge density [87].

The B100 fuel summary engine performance and emissions changes relative to the EN590 baseline fuel (average of compression ratios, IMATs, and speed/ torque points) are summarised in Table 4.5.

Parameter	Relative % Change to EN590
BMEP	- 3.4
BSFC	+ 14.2
AFR	- 9.2
IMAT	+ 3.6
fuel inlet temperature	+ 3.2
exhaust manifold temperature	- 7.2
exhaust manifold soot	- 84.4
exhaust manifold CO	- 35.4
exhaust manifold O2	+ 4.1
exhaust manifold NOx	+ 15
exhaust manifold HC	+ 31.8

Table 4.5: Overall Summary of B100 vs. EN590 Performance and EmissionsParametric Experiments

4.2.3 Effects of Compression Ratio Change (High to Low)

This section analyses the effects of the compression ratio reduction from 19.5:1 to 16.5:1 across the three fuels and at both low and high IMAT conditions. Section 4.2.1 described how there was greater consistency in the high IMAT temperature control across the different experiments which means that the analysis of compression ratio change effects should be more robust with the emphasis placed on the high IMAT i.e. the high IMAT experiments should have a smaller variation in cylinder charge density derived from IMAT fluctuation.

For continuity, the same percentage change analysis methodology is used in this section as with the two previous sections to understand the average overall compression ratio influence over a broad range of speed and torque. The summary of this is presented in Table 4.6 and Table 4.7.

LIIISSI					que group	5 C (0 E)		
	EN590 V	s. EN590	PC9 V	s. PC9	B100 V	s. B100	ALL F	UELS
IMA	T: low	high	low	high	low	high	low	high
BMEP (ba	r) -5.19	-5.58	-4.00	-4.89	-5.79	-5.50	-4.99	-5.32
BSFC (g/kWI	h) 4.81	4.29	3.68	4.47	7.63	6.82	5.37	5.20
AF	R 6.72	4.40	5.76	2.87	2.71	-1.46	5.06	1.94
MAF (kg/l	h) 5.36	2.66	5.17	2.08	3.93	-0.57	4.82	1.39
Fuel (kg/l	h) -0.62	-1.72	-0.49	-0.64	1.38	0.95	0.09	-0.47
Soot (g/I	h) 0.80	-23.63	13.61	0.67	19.53	-21.75	11.31	-14.90
Soot (g/kWI	h) 5.89	-19.65	17.76	5.57	26.80	-17.26	16.82	-10.45
CO2 (g/kWl	h) 2.61	-4.73	2.76	-6.58	-0.48	1.44	1.63	-3.29
CO (g/kWI	h) 55.42	0.12	26.53	18.81	55.80	22.49	45.92	13.81
O2 (g/kWl	h) 16.81	7.56	7.15	10.34	20.37	10.09	14.78	9.33
NOx (g/kWl	h) -12.95	-15.66	-17.24	-12.35	-13.07	-10.80	-14.42	-12.94
HC (g/kWI	h) 67.25	-2.08	-0.38	-26.09	133.79	-56.49	66.89	-28.22
Delta IMAT (°	c) -44.36	-10.60	-39.98	4.08	-35.38	5.81	-39.90	-0.24
haust Temperatur	e -0.15	1.30	2.14	4.51	-0.43	7.07	0.52	4.29
Soot (mg/m ³	³) -4.29	-25.54	8.13	-1.32	15.46	-21.43	6.43	-16.10
Start of Injectio	n -0.24	1.38	-0.39	-0.26	-0.37	0.00	-0.33	0.38
Injection Duratio	n -0.63	-1.12	-0.75	-0.80	-0.93	-2.39	-0.77	-1.44
CO2 (mole fraction	n) -6.13	-11.92	-5.91	-12.80	-9.62	-3.69	-7.22	-9.47
CO (mole fraction	n) 39.90	-8.27	15.89	11.12	41.25	16.44	32.35	6.43

-1.89

-24.17

-8.73

4.68

-0.51

-19.26

-0.36

-22.12

-9.00

0.94

-0.30

-10.45

2.91

-18.18

-30.99

1.45

-0.08

-21.93

9.17

-20.96

111.48

5.32

-0.68

-7.99

4.45

-15.29

-58.70

0.38

-1.58

-21.75

4.12

-22.32

51.04

4.91

-0.56

-15.37

2.33

-18.53

-32.90

0.92

-0.65

-18.04

Table 4.6: Summary of the Percentage Change in Engine Performance andEmissions for High-to-Low Compression Ratio (Torque groups C to E)

Table 4.6 details the averaged effects of the compression ratio reduction for each of the three fuels at the low and high IMAT conditions and also indicates the averaged effects for the three fuels lumped together at low and high IMAT. Table 4.7 is a continuation of Table 4.6 and segments the observations across torque group, fuel and IMAT. Together both tables describe the overall observed effects of the compression ratio reduction from 19.5:1 to 16.5:1.

Table 4.6 and Table 4.7 show that the compression ratio reduction was responsible for a consistent but not quite universal increase in AFR across all

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Ex

O2 (mole fraction)

NOx (mole fraction)

HC (mole fraction)

MAP (mbar)

MAF + Fuel Change

Fuel Supply Temp (°C)

5.08

-21.84

50.35

4.74

-0.47

-18.86

4

4.2

experiments. This increase in AFR was observed to be mostly associated with an increase in MAF.

Table 4.7: Summary of the Percentage Change in Engine Performance and Emissions for High-to-Low Compression Ratio Segmented for each Fuel, IMAT and Torque Group (C, D, E)

	Load Gro and bo	oup Average All oth high & low IM	Fuels ATs	Fuel A and bo	Average all G th high & low	roups IMATs	IMAT Ave Fuels an	erage All d Groups
	С	D	E	EN590	PC9	B100	LOW	HIGH
BMEP (bar)	-4.76	-6.35	-4.79	-5.43	-4.67	-5.80	-5.23	-5.37
BSFC (g/kWh)	4.98	4.92	6.99	5.31	4.03	7.55	5.88	5.38
AFR	3.78	4.02	1.75	4.79	4.45	0.31	4.49	1.87
MAF (kg/h)	3.45	2.11	3.48	4.02	3.49	1.53	4.56	1.46
Fuel (kg/h)	-0.04	-1.85	1.85	-0.52	-0.83	1.30	0.32	-0.35
Soot (mg/m ³)	3.37	-13.50	-15.80	-19.75	-0.39	-5.78	0.75	-18.03
Soot (g/h)	7.39	-11.95	-12.93	-16.42	2.99	-4.06	5.16	-16.82
Soot (g/kWh)	12.04	-5.87	-8.83	-12.04	7.65	1.72	10.59	-12.37
CO2 (mole fract)	-8.25	-9.08	-7.62	-8.91	-9.35	-6.69	-6.72	-9.91
CO2 (g/kWh)	-0.74	-1.37	-0.22	-0.98	-1.83	0.48	2.12	-3.67
CO (mole fract)	34.07	3.54	0.58	9.92	8.77	19.50	22.39	3.07
CO (g/kWh)	45.71	13.28	8.69	21.44	17.60	28.64	34.78	10.34
O2 (mole fract)	3.88	2.57	2.70	1.66	0.47	7.01	4.24	1.85
O2 (g/kWh)	12.71	11.38	11.69	11.49	8.79	15.51	14.92	8.94
NOx (mole fract)	-21.69	-21.62	-15.63	-21.06	-20.60	-17.28	-20.68	-18.60
NOx (g/kWh)	-15.13	-14.72	-8.43	-13.22	-14.09	-10.97	-12.62	-12.90
HC (mole fract)	-6.22	29.95	42.23	22.57	-22.07	65.45	78.56	-34.59
HC (g/kWh)	2.39	41.91	56.74	34.89	-15.52	81.66	97.33	-29.97
MAF + Fuel (kg/h)	3.40	0.26	5.33	3.50	2.65	2.83	4.88	1.11
Exhaust Temperature	3.43	1.48	0.00	0.32	3.36	3.16	0.50	4.06
Start of Injection (CAD)	0.29	-0.19	-0.53	-0.01	-0.32	-0.10	-0.23	-0.05
Injection Duration (CAD)	-0.97	-1.59	-0.52	-0.80	-0.75	-1.54	-0.67	-1.39
Fuel Supply Temp (°C)	-19.37	-16.25	-14.13	-14.61	-20.04	-15.11	-15.60	-17.57
Delta IMAT (°C)	-22.65	-19.04	-13.31	-25.54	-15.93	-13.54	-36.36	-0.32
MAP (mbar)	-0.71	-1.03	-0.10	-0.30	-0.22	-1.33	-0.63	-0.60

Considering the raw MAF (kg/h) measurements, Figure 4.5 presents the data for the high IMAT EN590 experiments for both compression ratios and shows that the MAF was observed to be quite similar at both compression ratios for torque group C but at higher torque (>80%) there was an increase in MAF with the compression ratio reduction. This observation was repeated for both mineral fuels and also at low IMAT for these fuels Table 4.6 and Table 4.7. This was likely because of the increase in cylinder volume with the compression reduction. In the case of the B100 fuel, the overall MAF change did not mirror that of the mineral fuels as it was not possible to run all the speed- torque points due to limited fuel batch reserves (fuel had to be conserved for the subsequent soot collection experiments).

This MAF change resulted in a proportional effect on the AFR as the fuel mass flow rate increased and decreased by the same amount overall for each of the two IMAT cases (IMAT average all fuels and all groups column, Table 4.7). This is illustrated in Figure 4.6 for the EN590 fuel for high IMAT conditions and torque groups C, D and E. This was an interesting overall result as the fuel injection duration managed by the ECU was observed to be slightly lower for all

conditions at lower compression, Table 4.6 and Table 4.7, with the measured fuel mass flow fluctuating between increases and decreases across the categories in Table 4.6 and Table 4.7.



Figure 4.5: Geometric Compression Ratio Effect on MAF at high IMAT for EN590 and Torque Groups (C, D, E)



Figure 4.6: Geometric Compression Ratio Effect on AFR at high IMAT for EN590 and Torque Groups (C, D, E)

It is important to mention that the fuel rate measurement utilised a volumetric approach (Section 3.2.2.3) and the accuracy was subject to stable fuel

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temperature which could not be precisely controlled with the compression ratio change as shown in Table 4.6 and Table 4.7.⁶

Table 4.6 and Table 4.7 detail how there was a universal reduction of 4-5% in BMEP with the reduction in compression ratio over all experimental combinations and Figure 4.7 illustrates this for the EN590 fuel at high IMAT for torque groups C, D and E. This followed from the associated reduction in thermodynamic efficiency.

The change in exhaust soot concentration and mass flow was observed to be complex with regard to compression ratio and the different fuels. For all fuels at low IMAT, there was an increase in soot mass flow with the lower compression ratio but for the high IMAT condition this trend was reversed with the exception of the PC9 fuel (the concentration for the PC9 soot did decrease but to a much lesser extent).





These changes in exhaust soot were set against a general increase in AFR which the IMAT analysis of Section 4.2.1 associated with a decrease in soot concentration. Thus, with the compression ratio reduction there was a change in exhaust soot concentration which was coupled to IMAT but not AFR change. As there was an associated consistent small reduction of (<~1%) in IMAP, the IMAT appeared to have had an isolated influence on the cylinder charge density in

⁶ With the reduction in compression there was a reduction in global cylinder temperature and thus less heat in the cylinder head to absorb into the fuel causing a secondary effect on fuel temperature.

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parallel with the compression ratio reduction such as to be able to switch the effects of the compression ratio change on exhaust soot concentration.

As the compression effect on soot was not consistent across all three fuels and had this association with IMAT, it proved quite difficult to isolate the precise causative processes behind the observations. The observations were very likely related to the effects of compression and IMAT on the fuel injection, atomisation and mixing processes as all of these would have been sensitive to fuel and cylinder charge density.

Categorising the changes in specific exhaust soot across the three torque groups C, D, E in Table 4.7; group C was observed to have 12% increase but groups D and E both showed reductions of 5.9 and 8.8%. These observations again failed to follow the AFR pattern emphasising the disassociation of the soot observations from AFR with compression ratio change.

It is useful to finally illustrate these exhaust soot observations through the original raw measurement data and presented in Figure 4.8 and Figure 4.9 are the data for the EN590 fuel for torque groups C,D,E for low and high IMAT respectively.



Figure 4.8: Geometric Compression Ratio Effect on Soot (g/kWh) at low IMAT for EN590 and Torque Groups (C, D, E)

Figure 4.8 and Figure 4.9 together illustrate the complexity of the interdependency of compression ratio and IMAT with the main feature being an increase in the distribution of the exhaust soot rate measurements at high IMAT

conditions, particularly for the higher torque groups D and E. The generally increased specific soot emission with higher IMAT is also illustrated and is the behaviour described in Section 4.2.1.



Figure 4.9: Geometric Compression Ratio Effect on Soot (g/kWh) at high IMAT for EN590 and Torque Groups (C, D, E)

Table 4.6 and Table 4.7 both detail how the effect of the compression ratio reduction on HC emissions was analogous to that observed in the case of soot, being dependent on IMAT. There was a general increase in HC emissions with low IMAT and a decrease with high IMAT. Interestingly Table 4.7 details that whilst there were overall increases in HC emissions observed for the EN590 and B100 fuels, in contrast there were general decreases observed for the PC9 fuel. This was largely because with the PC9 fuel there was not the large increase in HC at low IMAT with the compression reduction like observed for the other two fuels. The summary of HC emissions change with compression ratio reduction across torque groups (C, D, E) in Table 4.7 shows that as the torque increased the HC emissions generally increased when averaged over both IMAT conditions.

These HC measurements aligned with the qualitative observations during the experiments where the engine was more difficult to start with the EN590 and B100 fuels with substantial wetting of the exhaust manifold with the B100 fuel during engine warm-up. Furthermore, for all fuels at the lower compression ratio, white smoke was observed coming from the engine exhaust during the engine warm-up phase.

The observed coupling between IMAT and compression ratio change and the use of high IMAT during the soot collection experiments make it important to take the findings presented in Table 4.6 and Table 4.7 and summarise further the most essential parameters for the compression ratio reduction at the two IMAT ranges investigated. With the IMAT below 40°C, the reduction to 16.5:1 compression for all fuels resulted in an average overall change in engine performance and emissions as summarised in Table 4.8.

Table 4.8: Overall Summary of Compression Ration Reduction Performance andEmissions Parametric Experiments (IMAT<40°C)</td>

Parameter	19.5:1 to 16.5:1 % Change
BMEP	- 5
BSFC	+ 5.4
MAF	+ 4.8
AFR	+ 5
fuel inlet temperature	- 15.4
exhaust manifold temperature	+ 0.5
exhaust manifold soot	+ 15.8
exhaust manifold CO	+ 45.9
exhaust manifold NOx	- 14.4
exhaust manifold HC	+ 67

With the IMAT above 50°C, the effects of the reduction to 16.5:1 compression for all fuels is summarised in Table 4.9.

Table 4.9: Overall Summary of Compression Ration Reduction Performance andEmissions Parametric Experiments (IMAT>50°C)

Parameter	19.5:1 to 16.5:1 % Change
BMEP	- 5.3
BSFC	+ 5.2
MAF	+ 1.4
AFR	+ 1.9
fuel inlet temperature	- 18.0
exhaust manifold temperature	+ 4.3
exhaust manifold soot	- 10.5
exhaust manifold CO	+ 13.8
exhaust manifold NOx	- 12.9
exhaust manifold HC	- 28.2

The soot collection experiments were conducted solely at high IMAT (Section 3.1.5.3) and clearly from Table 4.8 and Table 4.9 the low and high IMAT were

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observed to result in quite different responses in specific soot and HC emissions.⁷

4.3 Engine Performance and Emissions for the Soot Collection Experiments

The engine exhaust soot collection experiments were conducted according to the experimental design detailed in Section 3.1.5.3 and the results from the analysis of the soot produced by these experiments is presented across Chapter 5 to Chapter 7. The engine was operated at rated power (4000 rpm, maximum fuelling - equivalent to 13.5 to 14.6 bar BMEP) for each of the six fuel-compression ratio configurations.

4.3.1 Summary of Performance and Emissions Data

The engine operating condition, performance and emissions are summarised across Table 4.10 part A, B and C *(located at the end of this chapter)* and are the averaged values across all the measurements made for each soot collection experiment.

Table 4.10 Part A reveals the engine power, fuel and air measurements for the three fuels at each of the two compression ratios and also presents the AVL 415 smoke meter measured exhaust soot concentration and computed soot mass flow rate. The effects of the higher B100 fuel density and lower energy content are clearly seen in the higher fuel mass flow rate and lower output power when the engine was fuelled with this fuel. Detailed is how the 16.5:1 B100 experiment was aborted at around 12 hours and thus short of the target 20 hours. This was because the rate of injector coking observed at 16.5:1 for the B100 fuel was more than twice that observed at 19.5:1 at the 12 hour point in the experiment and was also rapidly increasing, Appendix 9. Thus, the B100 exhaust soot concentration was far lower at 16.5:1 and very little mass of soot was being collected at the exhaust manifold to the point that the continuation of the experiment was of no value.

Table 4.10 Part A importantly summarises the mass of soot collected for each experiment as well as the mass of condensed water collected in the water trap in the ceramic thimble exhaust manifold sampling apparatus, Section 3.5.1.1.

⁷ The impact of the compression ratio reduction on soot physiochemical characteristics reported in Chapter 6 in this work specifically apply under high IMAT conditions and should not be taken as generally representative of engine geometric compression ratio influence.

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These latter two parameters were useful as they illustrated that for the B100 experiments, the much lower concentration of exhaust soot meant there was overall more sample gas which flowered through the ceramic thimble sampling apparatus (as the thimbles were less plugged). However, the total mass of soot collected was much lower due to the +80% lower exhaust soot concentration. This coupling was ultimately what limited the soot mass which could be collected for the B100 fuel in particular at the exhaust manifold. Presented in the last column of Table 4.10 Part A is the measured lubricant consumption rate which was measured from the mass of lubricant added to the engine during the experiments to maintain the lubricant level.

Table 4.10 Part B presents both the controlled and uncontrolled experimental parameters and the temperatures of the engine and soot sampling system apparatus. The ambient temperature was the temperature local to the engine in the test cell and this fluctuated across the experiments as it could not be precisely controlled with the experiments distributed over all the seasons. The fuel inlet temperature was regulated by an adapted laboratory air-to-liquid chiller Section 3.2.1.5 and the change in test cell temperature affected the heat energy the chiller could remove from the fuel and consequently the fuel temperature also fluctuated across the experiments with the ambient temperature change. An additional effect as detailed in Section 4.2.3 was that the temperatures in the fuel system were reduced by the reduction in compression ratio. The measured injection duration was the maximum the engine ECU would deliver at 4000 rpm and the small variation was due to the ECU calibration and variation in ECU measured parameters across the experiments.

Table 4.10 Part C summarises the exhaust gaseous emissions both in terms of the concentration and specific units. These measurements reflect the results presented earlier in Section 4.2 with the two mineral diesel fuels being similar with the B100 fuel quite distinct. The B100 fuel saw higher HC emissions at both compression ratios but especially at 16.5:1. There was also an increase in the concentration of exhaust oxygen for all fuels at 16.5:1 and a corresponding decrease in exhaust CO₂ which aligned with an increased AFR for these experiments. This was related to a consistent increase in MAF which followed the reduction in compression ratio as observed generally for the broader operating conditions reported on in Section 4.2.

The data in Table 4.10 Parts A, B and C have been further processed to compute the % change in respect to compression ratio reduction and the

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comparison of each fuel to the EN590 reference fuel at each compression ratio. These results are presented in Table 4.11, Table 4.12 and Table 4.13 *(located at the end of this chapter)* for Table 4.10 Part A, Part B and C respectively and outline the influence of the reduction in compression ratio for each fuel and also the differences of the PC9 and B100 fuels relative to the reference EN590 fuel.

The comparison across like fuels with the compression ratio reduction 19.5:1 to 16.5:1 in the first part of Table 4.11 reveals that there was a loss in power output for all fuels and that the fuel rate for the PC9 fuel reduced when that observed for EN590 and B100 increased. The exhaust soot concentration and mass flow rate increased for both the mineral fuels but was reduced for the aborted 16.5:1 B100 experiment due to the rapid coking of the injectors at 16.5:1 which restricted fuel injection, Appendix 9.

Consequently, the mass of soot collected at low compression at the exhaust manifold was higher for both mineral fuels but reduced for the B100 fuel, reinforcing the importance of maximising the exhaust soot concentration to make the ceramic thimble collection apparatus viable in this work. The rate of the exhaust soot collection in the ceramic thimble apparatus was higher in the 16.5:1 experiments in general and this caused a reduction in the mass of sample drawn through the thimble as indicated by the reduction in the rate of collection of condensed water. This further emphasises the conflicting characteristics of this soot collection methodology.

The comparison between PC9 and B100 fuels to EN590 in the second and third parts of Table 4.11 shows that for both these fuels at both compression ratios, the AFR was lower compared to EN590. The exhaust soot concentration for the PC9 fuel experiments was between 16.6 and 18.6% higher than the equivalent EN590 experiments and in the case of the B100 fuel the concentration was between -84.4 and 89% lower during the soot collection experiments. This significant disparity between the fuels emphasises the difficulty experienced with collecting sufficient soot mass across all experiment conditions.

Table 4.12 reveals that there was variation in some of the important experimental parameters across the six experiments, the more critical being the fuel inlet temperature and IMAT disparities across the compression ratio reduction. The IMAT had to be lowered for the low compression experiments to reduce the stress on the turbocharger as two turbochargers had failed during the 19.5:1 experiments. As explained previously, the fuel inlet temperature reduced

with compression ratio reduction as less heat energy was absorbed into the return fuel.

Finally, Table 4.13 presents the gaseous emissions measurements for the rated power condition and it can be observed that the trends in the individual fuel responses to compression ratio reduction generally followed those summarised for all operating conditions in Section 4.2 earlier. The consistent pattern across all fuels with reduced compression included reductions in CO_2 , CO and NO_x with an increase in O_2 . Importantly for the later soot analysis, the HC emissions were observed to reduce with the reduction in compression ratio for the mineral fuels but to increase significantly for the B100 fuel. Thus in summary, the emissions of the two mineral fuels were observed to have similar responses to the reduction in compression ratio. The B100 fuel, although exhibiting the same response direction for all but HC emissions, had response magnitudes that were quite different. Hence, when comparing PC9 and B100 to EN590, the differences were more significant for the biodiesel fuel.

4.3.2 Fuel Soot Factor Definition and Calculation

A non-dimensional parameter has been utilised in this work to characterise the **'sooting tendency'** of each fuel at a specific operating condition and this is referred to as the **Fuel-Soot-Factor (FSF)**. The definition of the FSF is shown in Equation 4.1:

$$FSF = \frac{mass flow rate of exhaust soot (g/h)}{fuel mass flow (g/h)}$$
 Equation 4.1

The FSF describes simply the fraction of the fuel which combusts to produce soot as measured by the AVL 415 smoke meter, Section 3.2.2.5. It is designed to account for the change in fuel mass flow across the three fuels investigated due to their respective density differences. For all six rated condition soot collection experiments the FSF has been computed and these results are summarised in Table 4.14 which is located at the end of this chapter.

The data of Table 4.14 shows that the PC9 fuel produced more soot at both compression ratios in proportion to the fuel consumption rate than was observed for the other two fuels. The FSFs for the two mineral fuels were quite similar in contrast to the significantly lower FSF (factor –10) for the B100 fuel. As presented in Table 4.14, the B100 measured exhaust soot concentration was lower by a factor of 8 compared to EN590. Thus, the inclusion of the consideration of the higher B100 fuel consumption rate (due to its higher density)

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means that the fuel effectively had an even lower soot producing tendency than the measured soot concentration alone revealed.

The FSFs detailed in Table 4.14 are utilised later in Chapter 5 and Chapter 6 to better understand the overall soot bulk elemental results by taking into consideration the fuel rate and exhaust soot concentration both of which are highly associated with soot bulk inorganic concentration (refer to Section 5.4).

4.3.3 Cylinder Pressure Combustion Parameters

Cylinder pressure measurements (Section 3.2.2.4) were taken for all the engine operating conditions investigated according to the experimental design described in Section 3.1.5.2. A summary of the fundamental combustion parameters derived from this data for the engine operating conditions of the soot collection experiments is presented in Table 4.15 and this also includes the comparison of the low and high IMAT experimental configurations.

This data illustrates firstly that there was a roughly 17.5% reduction in the average peak cylinder pressure (data averaged over 50 engine cycles) with the reduction in compression ratio, this reduction in pressure correlates with the compression ratio reduction assessment presented previously in Section 3.3.5. Importantly, the change in IMAT from low to high was observed to not have any significant and consistent influence on cylinder peak pressure or the crank angle position of peak pressure at both engine compression ratios. This is likely linked to the associated reduction in MAF with low to high IMAT change, Table 4.1.

The reduction in compression correlated with retardation of the crank angle position of the maximum pressure rise rate by around 8 degrees from 351.3 to 359.4 crank angle degrees and there was also a slight reduction in the maximum pressure rise rate of about 10%. Together these changes occurred due to the retarded start of auto-ignition that resulted from the reduced in-cylinder temperature and pressures at a given crank angle during the compression phase.

At the high engine speed and engine power conditions of the soot collection tests, there was little or no sensitivity in regard to the coefficient of variation of combustion to the reduction in compression ratio regardless of IMAT condition. IMAT did however influence the maximum rate of heat release (J/degree crank angle) with a reduction in the maximum rate of heat release across the three fuels of 7.4% at 16.5:1 and a reduction of 4.2% at 19.5:1 compression ratio. These reductions were likely the result of the reduction in MAF with the increase

Concluding Remarks

in IMAT, Table 4.1, which would have slowed the diffusion process in the cylinder leading to a slower rate of heat release.

Estimations for the average in-cylinder temperature during the closed section of the engine cycle are also presented in Table 4.15 and provide a quantitative estimate of the magnitude of the change in average in-cylinder temperature with the compression ratio and IMAT changes e.g.

16.5:1 compression ratio, IMAT low to high:

7.5% increase in average closed cycle in-cylinder temperature

19.5:1 compression ratio, IMAT low to high:

6.0% increase in average closed cycle in-cylinder temperature

Low IMAT, change from 16.5:1 to 19.5:1 compression ratio:

3.6% increase in average closed cycle in-cylinder temperature

High IMAT, change from 16.5:1 to 19.5:1 compression ratio:

2.3% increase in average closed cycle in-cylinder temperature

The above result derived from Table 4.15 is important as it indicates that in respect to in-cylinder temperature, the change in IMAT resulted in roughly double the increase in in-cylinder average temperature compared with the change in in-cylinder temperature associated compression ratio. However, on the contrary, IMAT failed to change the peak cylinder pressure (as discussed earlier).

Since the exhaust soot was collected under high IMAT conditions in this work, the reduction in compression can be seen to have reduced the average incylinder temperature by 2.3% and the peak cylinder pressure by 17.5% and these findings are important in respect to the soot discussion in Chapter 6.

4.4 Concluding Remarks

The investigation of IMAT and engine speed and torque revealed that the highest exhaust soot concentration occurred at 4000 rpm maximum torque (engine rated power) with greater than 40°C IMAT. *To minimise fuel cost and the duration of individual tests, this operating point was selected as the operating point for the fuel and compression ratio exhaust soot collection tests, Section 3.1.5.3.*

Concluding Remarks

With increased IMAT the measured HC emissions generally reduced which likely resulted in a reduction of the SOF component for the soot in the exhaust. Thus, the soots collected from the fuel and compression ratio exhaust soot collection tests described in Chapters 5-7 are postulated to have had lower SOF than would generally be observed for soot sampled from the engine used in this work with the exception of the B100 soot. This high IMAT also reduced the AFR through reduced MAF and this caused an increase in exhaust soot concentration due principally to a lower availability of free oxygen molecules in-cylinder resulting in a greater incidence of locally rich equivalence ratio in-cylinder during the initial soot forming conditions around auto ignition. A reduced exhaust oxygen concentration also likely contributed but less so as the soot was sampled from the exhaust manifold when the soot was relatively 'young'.

The increase in exhaust soot concentration with increase in IMAT for the B100 fuel was somewhat lower than the increase observed for the two mineral diesel fuels. It is thought that this is related to the different physiochemical properties of the B100 soot (see Chapters 5-9) that enable it to more readily oxidise in-cylinder and in the exhaust following formation; the reduction in AFR is therefore postulated to have impeded the B100 soot oxidation process less than was the case for the mineral diesel soots.

The comparison of PC9 and B100 fuels to the baseline EN5690 fuel showed that generally the two mineral fuels (PC9 and EN590) resulted in similar engine performance and emissions compared to the much greater differentiation observed between the B100 and EN590 fuels. The majority of the significant engine performance parameter changes between the B100 and mineral diesel fuels (BMEP, BSFC, exhaust temperature etc.) derived from the B100 fuel's combination of higher fuel density and lower energy density. Such were these changes that the AFR was between 5-12% lower with the B100 fuel compared to EN590 and yet there was an 80-90% reduction in exhaust soot concentration. This observation combined with the work presented later in Chapters 5-9; leads to the postulation that the divergent AFR and exhaust soot concentration changes for B100 soots vs. the mineral diesel soots are explained partly by the much higher oxidation rate of the B100 soot in the cylinder and exhaust in addition to a lower soot formation rate during combustion. This higher rate of oxidation is attributed later in this work to the quite different physiochemical properties of the B100 soot that were observed.

Concluding Remarks

4 4.4

The B100 fuel by comparison to EN590 was also observed to have a >30% overall increase in HC emissions which was exacerbated at high loads. This observation was attributed to the higher density of the fuel combined with a factor two higher viscosity which together impaired the fuel atomisation and likely caused much greater fuel spay impingement. This observation is very important as it links to key B100 soot physiochemical properties discussed in Chapters 5-9 and also the fuel injector coking issues documented in Appendix 9.

The reduction in compression ratio resulted in a general increase in AFR of a few percent that stemmed from an increase in MAF and which in turn derived from the increase in cylinder volume. The reduction in compression was observed to reduce the estimated average in-cylinder temperature by 2.3% and the peak cylinder pressure by 17.5%; thus the influences on exhaust soot discussed in Chapter 6 are likely dominated by effects of peak and average cycle pressure reductions rather than temperature changes.

With the compression ratio reduction there was a change in exhaust soot concentration which was coupled to IMAT but not the observed AFR change. Indeed, the IMAT appeared to have an isolated influence on the cylinder charge density in parallel with the compression ratio reduction such as to cause opposed effects from the compression ratio change on exhaust soot concentration. This likely stemmed from the insignificant changes in peak cylinder pressure observed with changes in IMAT.

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Part A: 4000rpm Soot Collection Experiments

	Collection Tune	Compression				Fuel	Fuel	NAF.	014	0100	415	415	110	1110	Soot	Soot Collection	Condensed	Condensed	Lubricant
		Ratio	anha	BMOL		Fate	Rate		2	0.00	FSN	mg/m3	1000	1000	Collected	Rate	Water	Water Rate	Consumption
	(Hrs:mins)	(19.5 or 16.5)	(mu)	(VV)	(bar)	(lh)	(kg/hr)	(hg/hr)		(d/k/Wh)	(0-10)	(mg/m/3)	(g/hr)	(d/k/Wh)	(0)	(ghr)	(Hg)	(Kg/h)	(g/hr)
19.5:1 EN590	20 hr 3.9 min	19.5	218.0	91.3	14.5	25.85	21.5	426.3	19.9	235.5	1.63	38.04	13.17	0.14	1.21	0.06	0.95	90'0	27.9
13.51 PC9	20 hr	19.5	21.6	92.8	14.7	27.13	22.6	439.4	19.5	243.3	1.81	44.36	15.88	21/0	2.01	0.11	1.11	90'0	28.8
19.5:1 B100	20 hr 1.6 min	19.5	209.9	88.0	13.9	26.67	23.5	444.2	19.0	266.8	0.41	5.92	2.15	0.02	0.48	0.03	1.61	0.0	16.8
16.5:1 B100	12 hr 9.4 min	16.5	203.3	85.1	13.5	27.35	23.8	456.5	19.2	280.6	0.32	4.44	1.64	0.02	0. 4 6	0.04	0.63	8	13.3
16.5:1 EN590	20 hr	16.5	217.3	91.0	14.4	26.35	21.9	463.1	2.8	240.9	1.72	40.47	14,96	0.16	27	0.09	1.30	90.0	24.6
16.5:1 PC0	19 hrs 30 min	16.5	202.7	87.0	13.7	26.29	21.9	449.0	20.5	251.4	1.90	47.99	17.58	0.20	2.39	0.13	0.79	0.04	37.8

Part B: 4000rpm Soct Collection Experiments

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ECHARIST CI	Temp. Temp	ດ ດ	630.2 156.3	629.8 100.7	541.6 177.5	2121 1222	004.6 139.5	660.2 171.9
MAT	Č.	ç	8,69	79.6	73.8	0'79	44.0	8.5
Pre Intercooler	Temp.	° C	137.3	142.5	133.7	135.9	119.9	132.5
oil Sump	Temp.	ပူ	128.6	128.7	126.0	123.0	124.1	126.1
Codant	Temp	ပ္	38.4	8.8	8.8	97.16	87.8	8°2
-uel	Return	ပ္စ	91.7	91.8	80.6	2'62	75.2	79.3
- ne	Temp.	ပ္	44.6	46.9	34.7	37.9	32.2	37.8
Ē	Duration	F)	61'9Z	25.48	24.71	09 9Z	13.51	23.48
Stat of hi	oran or min	("CA BTDC)	24.2	24.2	24.2	24.2	24.2	24.1
Manifold	Pres.	(mbar)	2282.9	2307.2	2316.6	2316.6	2202.1	2212.4
Atmos.	Pres.	(mbar)	1007.4	1000.2	301 4	0/06	996.2	1000.8
Ambient	Temp.	(2) (2)	29.6	33.2	26.0	27.0	18.0	29.1
Fuel Conversion	Efficiency	(%)	2.36	34.4	36.2	34.2	34.8	32.9
			19.5:1 EN50	19.5:1 P 00	19.5:1 8100	16.5:1 8100	16.5:1 EN590	16.5:1 P C0

Part C: 4000rpm Soot Collection Experiments

	C02	00	02	NOX	THC	C02	8	02	NOX	THC
	(IoV &)	(mqq)	(% Vol)	(mqq)	(mqq)	(4W/M)	(d/k/Wh)	(HWMA)	(4W/Mp)	(dW/Mb)
19.5.1 EN590	12.61	367.93	6.73	1105.67	57.43	944.21	1.73	363.46	8.58	0.13
19.5:1 PC9	13.16	395.00	6.14	1140.00	52.20	963.37	1.84	326.89	8.72	0.14
19.5.1 B100	11.07	159.00	6.68	1169.00	88.40	876.00	080	384.44	29'6	0.25
16.5:1 B100	866	122.00	8.11	965.00	601.00	858.91	18.0	507.62	89.68	1.86
16.5.1 EN590	10.27	220.00	7.73	850.00	48.00	861.56	21/1	471.62	7.45	0.14
16.5-1 PC9	10.24	261.00	7.00	833 DD	25.MD	831.27	130	413.28	7.07	0.07

Part A : 4000r	pm Soot Collecti	on Experimer	- San	pression	Ratio % C	hange Ar	alysis													
	Collection Time	Compression Ratio	Torque	Power	BMEP	Fuel Rate	Fuel Rate	MAF	AFR	BSFC	415 FS N	415 mg/m3	Soot	Soot	Soot Collected	Soct Collection Rate	Condensed Water	Condensed Water Pate	Lubricant Consumption	
	(Hhs:mins)	(19.5 or 16.5)	(independence) I	(ww)	(par)	(4J)	(kghr)	(kg/hr)		(d/k/Wh)	(0-10)	(mg/m/3)	(սկն)	(dw/vh)	9	(սկսն)	(6)	(4,6y)	(44)B)	
ENS	AN D	19.5 to 16.5	0.3	0.4	-0.9	1.92	6.1	6.3	4.1	2.3	5.39	8.9	13.55	13.82	42.81	42.38	37.01	-16.67	-11.8	
P	AN NA	19.5 to 16.5	6.3	-6.2	-6.4	-3.09	3.1	2.2	5.4	3.4	4.95	8.8	10.73	17.95	18.89	17.59	-28.34	-33.33	31.3	
B10	DI NA	19.5 to 16.5	3.1	3.3	-2.9	2.54	1.5	2.8	1.2	6.2	-22.97	-25.07	-23.71	-21.49	-3.31	39.55	-60.65	-33.33	- <mark>2</mark> 0.6	
		Composition				Fiel	E e				415	415			Sort	Sort Collection	Condensed	Condensed	lubricant	
	Collection Time	Patio	Torque	Power	BMEP	Rate	Rate	MAF	AFR	BSFC	FS N	£m/gm	Soot	Soot	Collected	Pate	Water	Water Rate	Consumption	
	(Hhs:mins)	(19.5 or 16.5)	(ind)	(wy)	(bar)	(H)	(kghr)	(kg/hr)		(d/k/Wh)	0-10)	(mg/m ⁴ 3)	(Jhr)	(dWM)	9	(Jhh)	(Kg)	(kg/h)	(440) (440)	
ENS	AN D	19.5	0.0	0.0	8	000	0.0	0.0	0.0	0:0	0.00	8.0	000	8.0	0.0	000	00.0	000	0.0	
PC	AN NA	19.5	1.6	1.6	10	4.96	5.0	3.1	-2.0	3.3	11.04	16.61	20.53	18.63	66.94	71.43	16.51	000	3.3	
810	NA DI	19.5	3.7	3.6	-4.4	3.19	9.1	4.2	-4.6	13.3	-74.80	-84.44	-83.70	-83.16	-60.41	-57.62	28.83	20.00	8.8.	

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all Six Rated Condition Soot Collection Tests

Table 4.11: (Part 1 of 3): % Change of Engine Performance and Emissions Summary for

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Lubricant Consumption	(4y6)	0.0	3.3	9.00 [.]
Condensed Water Pate	(kgh)	00'0	00.0	20.00
Condensed Water	(6))	00'0	16.51	68.87
Soct Collection Pate	(uy6)	00'0	71.43	-57.62
Soot Collected	(6)	00'0	66.84	-60.41
Soot	(W/Wh)	8.0	18.63	-83.16
Soot	(սպյե)	00.0	20.53	-83.70
415 mg/m3	(E^mgm)	8.0	16.61	84.44
415 FS N	(01-0)	0.00	11.04	-74.80
BSFC	(4WAMg)	0.0	3.3	13.3
AFR		0.0	-2.0	-4.6
MAF	(կկնի)	0.0	3.1	4.2
Fuel Rate	(kg/hr)	0.0	5.0	9.1
Fuel Rate	(4/I)	000	4.96	3.19
BMEP	(par)	00	10	-4.4
Power	(wy)	0'0	1.6	3.6
Torque	(mN)	0.0	1.6	3.7
Compression Patio	(19.5 or 16.5)	19.5	19.5	19.5
Collection Time	(Hrs:mins)	٨A	NA	ΝA
		EN590	PS	B100

Part A: 4000rpm Scot Collection Experiments - 16.5:1 Fuel % Change Analysis, Relative to EN590

	illection Time Compression Tornue Power RMEP Fuel Fuel MAF AFR RSFC 415 415 Sout Sout Sout Office Officertion Condensed Conde	Ratio reverse meter Water Water Water Water Water Water Water	(Hs:mins) [(19.5 or 15.5) (Nm) (KW) (bar) (kg/hr) (kg/hr) (kg/hr) (g/k/hr) (g/hr) (g/k/hr) (g/k/hr) (g/hr) (g/hr) (kg/hr) (kg/hr)	- 500 - 500	Collection Time (Hs:mins) NA NA	Compression Ratio (19.5 or 16.5) 16.5	Torque (Nm) 0.0 4.5	Power (k'\V) 0.0 4.4	BMEP (bar) 0.0	Fuel Rate 0.00 0.00 0.19	Fuel Rate 0.0 -0.2	MAF (kg/hr) 0.0	AFR 0.0	BSFC (g/k/Mh) 0.0 4.4	415 FSN (0-10) 0.00 10.57	415 mg/m3 (mg/m/3) 0.00 18.58	Soot (g/hr) 17.54	Soot (g/k/v/h) 22.94	Soot Collected (g) 38.86 38.90	Soct Collection Rate (g/hr) 0.00 41.58	Condensed Water (kg) 0.00 -39.06	Conder Water (kg/ 20.1	Rate 1)
ime Compression Torque Power BMEP Fuel Fuel MAF AFR BSFC 415 415 2001 Soot Soot Collection Condensed Condensed 3) (19.5 or 16.5) (Nm) (kW) (bar) (Nh) (kghr) (kghr) (kghr) (ghr) (ghWh) (0-10) (mghm ³) (ghr) (ghr) (ghr) (ghr) (ghr) (ghr) (kgh) (kghr)	(Hasmins) [(19.5 or 16.5)] (Nm) (kW) (bar) (M) (kgAn) (kgAn) (kgAn) (gAkWh) (0-10) (mgAn'3) (gArWh) (g) (GMKWh) (g) (gAn'h) (g) (kgh) (kgh) (kgh)	(Hasimins) [(19.5 or 16.5) (Nm) (KW) (bar) (kg/hr) (kg/hr) (kg/hr) (g/k/hr) (g/khr) (g/k/hr) (g/k/hr)			٨A	16.5	0:0	0.0	8	000	0:0	0.0	0.0	0.0	0.00	8.0	000	8	0.0	000	000	000	
Compression Torque Power BMEP Fuel Fuel Fuel MAF AFR BSFC 415 A15 Soot Soot Soot Collection Condensed Omdensed Condensed Condensed <td>Ratio Water Pare Pare Pare Pare Water Water Pare Water Pare Water Pare Water Pare Pare Pare Water Pare Pare Pare Pare Pare Pare Water Pare Pare</td> <td>(Hs:mins) [19:5 or 16.5) (Nm) (kW) (bar) (Nh) (kg/hr) (kg/hr) [g/k/Wh) (p.10) (mg/hr⁽³) (g/hr) (g/k/Wh) (g) (g/hr) (kg) (kg) (kg/h) NA 16.5 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0</td> <td>NA 16.5 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.00 0.00 0.00 0.00 0.00 0.00 0.00</td> <td></td> <td>٨A</td> <td>16.5</td> <td>4.5</td> <td>4.4</td> <td>-4.6</td> <td>-0.19</td> <td>-02</td> <td>0.9</td> <td>-0.7</td> <td>4.4</td> <td>10.57</td> <td>18.58</td> <td>17.54</td> <td>22.94</td> <td>38.86</td> <td>41.58</td> <td>-39.06</td> <td>-20.00</td> <td></td>	Ratio Water Pare Pare Pare Pare Water Water Pare Water Pare Water Pare Water Pare Pare Pare Water Pare Pare Pare Pare Pare Pare Water Pare	(Hs:mins) [19:5 or 16.5) (Nm) (kW) (bar) (Nh) (kg/hr) (kg/hr) [g/k/Wh) (p.10) (mg/hr ⁽³) (g/hr) (g/k/Wh) (g) (g/hr) (kg) (kg) (kg/h) NA 16.5 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0	NA 16.5 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.00 0.00 0.00 0.00 0.00 0.00 0.00		٨A	16.5	4.5	4.4	-4.6	-0.19	-02	0.9	-0.7	4.4	10.57	18.58	17.54	22.94	38.86	41.58	-39.06	-20.00	
Image Compression Torque Power BMEP Fuel Fuel MAF AFR BSFC 415 415 Soot Soot Soot Collection Contensed Contensed </td <td>Ratio Water Parte Parte Parte Water Water Parte Water Water Parte Parte Water Parte Parte Parte Water Parte Parte Parte Parte Parter Pa</td> <td>(Hs:mins) (19.5 or 16.5) (Nm) (kW) (bar) (kghr) (kghr) (gghr) (ghr) (ghr) (g (ghr) (g) (g) <</td> <td>NA 16.5 0.0 0.0 0.0 0.0 0.0 0.00<!--</td--><td></td><td>× 14</td><td></td><td></td><td>•</td><td>(</td><td></td><td>1</td><td>1</td><td>0</td><td></td><td>2</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td>L</td></td>	Ratio Water Parte Parte Parte Water Water Parte Water Water Parte Parte Water Parte Parte Parte Water Parte Parte Parte Parte Parter Pa	(Hs:mins) (19.5 or 16.5) (Nm) (kW) (bar) (kghr) (kghr) (gghr) (ghr) (ghr) (g (ghr) (g) (g) <	NA 16.5 0.0 0.0 0.0 0.0 0.0 0.00 </td <td></td> <td>× 14</td> <td></td> <td></td> <td>•</td> <td>(</td> <td></td> <td>1</td> <td>1</td> <td>0</td> <td></td> <td>2</td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td>L</td>		× 14			•	(1	1	0		2								L

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Part B: 4000rpm Soot Collection Experiments • Compression Ratio % Change Analysis

CT Temp	°	-10.8	7.0	-13.5
Exhaust Temp.	°	-4.1	3.2	-1.8
IMAT	°C	-48.6	-32.8	-9.3
Pre Intercooler Temp.	°.	-12.7	0'2-	1.6
Oil Sump Temp.	°C	-3.5	-2.0	-2.4
Coolant Temp	°.	-0.6	-0.3	12.3
Fuel R <i>e</i> turn Temp.	°C	-18.0	-13.5	-1.4
Fuel In Temp.	°	-27.8	- 17.6	9.2
Inj. Duration	(°CA)	-6.7	-7.9	3.2
Start of Inj.	(°CA BTDC)	0.0	-0.5	0.0
Manifold Pres.	(mbar)	-3.5	-4.1	0.0
Atmos. Pres.	(mbar)	-1.1	0.1	0.6
Ambient Temp.	(0°)	-39.2	-12.4	3.7
Fuel Conversion Efficiency	(%)	-2.7	-4.6	-6.7
		EN590	PC9	B 100

Part B: 4000rp m Soot Collection Experiments • 19.5:1 Fuel % Change Analysis, Relative to EN590

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CT Temp	°	0.0	2.8	13.5
Exhaust Temp.	°c	0.0	-0.1	-14.1
IMAT	°	0.0	6.9	-13.7
Pre Intercooler Temp.	°C	0.0	3.8	-2.6
Oil Sump Temp.	°C	0.0	0.1	-2.0
Coolant Temp	°C	0'0	0.4	-11.8
Fuel Return Temp.	°	0.0	0.1	-12.1
Fuel In Temp.	°	0.0	3.0	-22.3
Inj. Duration	(°CA)	0.0	1.2	6.1-
Start of Inj.	(°CA BTDC)	0.0	0.0	0.0
Manifold Pres.	(mbar)	0.0	1.1	1.5
Atmos. Pres.	(mbar)	0:0	-0.7	-1.6
Ambient Temp.	(0°)	0.0	12.2	-12.0
Fuel Conversion Efficiency	(%)	0.0	-3.6	1.5
		EN590	PC9	B100

Part B: 4000 pm Soot Collection Experiments • 16.5:1 Fuel % Change Analysis, Relative to EN590

	Fuel Conversion	Ambient	Atmos.	Manifold	Start of Ini	Ē	Fuel In	Fuel	Coolant	Oil Sump	Pre Intercooler	INAT	Exhaust	ст
	Efficiency	Temp.	Pres.	Pres.	fundamente de la competencia d	Duration	Temp.	R eturn	Temp	Temp.	Temp.	(Temp.	Temp
	(%)	(c)	(mbar)	(mbar)	("CA BTDC)	(°CA)	ç	ပ္	°	ő	ç	ပ္	°	°
EN590	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
PCS	-5.5	61.7	0.5	0.5	-0.5	Ó.1	17.6	5.5	2'0	1.6	10.5	21.7	2'2	23.2
B100	7.1-	8	5	5.2	00	40 00	17.6	5.7	e Q	6 Ģ	13.4	52.3	-12.1	00

Table 4.13: (Part 3 or 3): % Change of Engine Performance and EmissionsSummary for all Six Rated Condition Soot Collection Tests

	CO2	CO	O2	NOx	THC	CO2	CO	O2	NOx	THC
	(% Vol)	(ppm)	(% Vol)	(ppm)	(ppm)	(g/kWh)	(g/kWh)	(g/kWh)	(g/kWh)	(g/kWh)
EN590	-18.5	-40.2	14.9	-23.1	-16.4	-8.8	-32.2	29.8	-13.1	13.5
PC9	-22.2	-36.5	14.0	-26.9	-52.1	-13.7	-29.5	26.4	-19.0	-46.9
B100	-9.8	-23.3	21.4	-17.5	579.9	-2.0	-16.6	32.0	-10.2	639.4

Part C: 4000rpm Soot Collection Experiments - Compression Ratio % Change Analysis

Part C: 4000rpm Soot Collection Experiments - 19.5:1 Fuel % Change Analysis, Relative to EN590

	CO2	CO	O2	NOx	THC	CO2	CO	O2	NOx	THC
	(% Vol)	(ppm)	(% Vol)	(ppm)	(ppm)	(g/kWh)	(g/kWh)	(g/kWh)	(g/kWh)	(g/kWh)
EN590	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
PC9	4.4	7.4	-8.7	3.1	-9.1	2.0	6.2	-10.1	1.6	7.7
B100	-12.2	-56.8	-0.7	5.7	53.9	-7.2	-53.8	5.8	12.7	97.2

Part C: 4000rpm Soot Collection Experiments - 16.5:1 Fuel % Change Analysis, Relative to EN590

	CO2	CO	O2	NOx	THC	CO2	CO	O2	NOx	THC
	(% Vol)	(ppm)	(% Vol)	(ppm)	(ppm)	(g/kWh)	(g/kWh)	(g/kWh)	(g/kWh)	(g/kWh)
EN590	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
PC9	-0.3	14.1	-9.4	-2.0	-47.9	-3.5	10.4	-12.4	-5.2	-49.6
B100	-2.8	-44.5	4.9	13.5	1152.1	-0.3	-43.1	7.6	16.5	1184.5

Table 4.14: Fuel Soot Factor Computation for all Six Rated Condition Soot

Collection Tests

4 4.4

	Fuel Rate	MAF	AVL415	Soot	FSF	FSF	Normalised FSF
Description	(kg/h)	(kg/h)	(mg/m^3)	(g/h)		(%)	
19.5:1 EN590	21.5	426.3	38.04	13.2	0.000613	0.061255	0.762
19.5:1 PC9	22.6	439.4	44.36	15.9	0.000703	0.070341	0.875
19.5:1 B100	23.5	444.2	5.92	2.1	9.15E-05	0.009146	0.114
16.5:1 B100	23.8	456.5	4.44	1.6	6.87E-05	0.006871	0.085
16.5:1 EN590	21.9	453.1	40.47	15.0	0.000682	0.068244	0.849
16.5:1 PC9	21.9	449.0	47.99	17.6	0.000804	0.080371	1.000

Table 4.15: Cylinder Pressure Combustion Parameters at Rated Engine Power

(Including Low and High IMAT Comparison)

Compression Ratio	IMAT STATE	FUEL	Mean calculated Peak Pressure	Mean CA for Peak Pressure	Maximum Pressure Rise rate	CA of Maxium Pressure Rise rate	Mean calculated IMEP	COV IMEP	Est. peak HR for the main combustion phase	Ave. Cyl. Temp for Closed Cycle
			(bar)	(CAD)	(bar/CAD)	(CAD)	(bar)	(%)	(J/deg)	(deg C)
		EN590	127.43	371.96	4.02	360	17.27	0.80	62.69	1149.0
	Low IMAT	PC9	129.38	371.89	4.52	360.5	17.66	0.85	64.20	1157.3
5:1		B100	131.85	370.75	3.99	358.5	16.76	0.82	60.57	1126.4
16.		EN590	127.26	371.03	3.37	358.5	16.81	0.95	58.70	1219.3
	High IMAT	PC9	130.31	370.34	3.51	358	17.17	1.12	56.24	1242.9
		B100	129.78	370.86	3.41	361	16.43	0.85	58.73	1229.4
		EN590	157.17	370.15	4.15	349.5	18.91	0.71	65.60	1195.2
	Low IMAT	PC9	158.44	370.51	4.42	359.5	19.05	0.84	68.06	1197.5
5:1		B100	157.13	370.43	4.24	350.5	18.38	0.85	65.67	1170.0
19		EN590	154.36	369.92	4.16	349.5	18.08	0.83	62.40	1275.1
	High IMAT	PC9	157.51	370.13	4.15	349.5	18.41	0.87	64.84	1281.9
		B100	157.71	370.13	4.19	349.5	18.13	0.77	63.71	1222.4

5 Soot Physiochemical Properties for Mineral and Biodiesel Fuels

5.1 Introduction

This chapter presents the results and analysis for the soot sampled from the engine exhaust system with the engine fuelled with a total of three different fuels at rated engine power. The aim of this chapter is to *understand how the fundamental differences between the fuels affected the soot physiochemical properties.* The samples were collected during the experiments described in Section 3.1.5.3 and the majority of the soot samples discussed were collected at the exhaust manifold with the ceramic thimble sampling system Section 3.5.1.

5.2 Data Selection and Grouping

As a consequence of the constrained mass of soot which could be collected with the ceramic thimble collection method; it was not possible to undertake all eight physical and chemical soot analysis techniques employed in this work for any one of the individual ceramic thimble soot samples. Therefore, in this chapter results are drawn from samples taken at different compression ratios and also sample location to facilitate the consideration of fuel type on all of the soot physiochemical properties investigated. The result sets selected and discussed in this chapter are summarised in Table 5.1.

Soot Characteristic	Data Groups	Section
Surface Elemental Composition	19.5:1 Exhaust Manifold	5.3
Bulk Elemental Composition	19.5:1 Exhaust Manifold	5.4
Morphology	16.5:1 Exhaust Manifold	5.5
Surface Acid Functionality	19.5:1 Exhaust Manifold	5.6
Polycyclic Aromatic Hydrocarbon Profile	19.5:1 Exhaust Manifold	5.7
Thermogravimetrical Analysis	16.5:1 DPF	5.8

Table 5.1: Fuel-Soot Analysis, Data Selection and Grouping

Soot Surface Elemental Composition

<u>5</u>.3

Table 5.1 illustrates that the discussion in this chapter largely focusses on the samples from the 19.5:1 compression ratio configuration which was the base engine compression ratio. Therefore it is worth noting that the fuel-soot results and analysis for this compression condition have relevance to previous Lubrizol internal research and broader published results for the VW 1.9 TDI engine.

5.3 Soot Surface Elemental Composition

Table 5.2 summarises the soot surface carbon, oxygen, sulphur and chlorine as well as the ratios of surface oxygen/carbon and sulphur/carbon for the three fuels investigated.

	wt% C	wt% O	wt% S	wt% Cl	0	/C	S/C		
Description					ratio	precision	ratio	precision	
19.5:1 CT, EN590	92.5	7.5			0.0805	0.0118			
19.5:1 CT, PC9	88.3	9.9	1.545	0.3	0.1121	0.0127	0.018	0.0059	
19.5:1 CT, B100	92.0	8.0			0.0865	0.0119			

Table 5.2: 19.5:1 Exhaust Manifold Soot Surface Elemental Composition (XPS)

Note: In Table 5.2, 'CT' denotes the soot sample was collected with the ceramic thimble system (Section 3.5.1) at the exhaust manifold and this notation is used throughout this work in the soot physiochemical results presentation.

Table 5.2 reveals that the three fuels were found to produce soot with markedly similar surface elemental composition with the dominant element being carbon, typically constituting between 88-94% (all samples) of the surface elements. The coefficient of variation in carbon content was 2.1% and largely driven by an apparent association of the carbon and sulphur content in the surface of the soots from the mineral PC9 fuel.

The next most significant surface element was oxygen with the observed content in the range 5.9-9.9% (all samples). Thus, the oxygen content was observed to be slightly more consistent across the three fuels than the carbon content. Table 5.2 details the oxygen/carbon (O/C) ratio for the soot and shows that the highest O/C ratio is observed for the mineral PC9 fuel. The degree of sensitivity of the O/C ratio to fuel type is clear with a coefficient of variation of 14.7%. The O/C ratio for the mineral EN590 fuel and the biodiesel fuel were both very similar. The surface oxygen content is thought to be closely associated with the local equivalence ratio during combustion and the free oxygen available in the exhaust gases when soot undergoes oxidative reactions [117] – specifically for low (<10ppm) sulphur fuels like those investigated in this work.

Soot Surface Elemental Composition

The PC9 fuel sulphur content was 497 ppm, Appendix 1 (Table A1.1), a factor of 10 greater than the EN590 and B100 fuels (Section 3.1.1.3) and this was observed to influence the surface composition of the soot from this fuel significantly at 19.5:1. The sulphur present on the PC9 soot surface appeared to displace carbon and increase the oxygen fraction observed on the surface. This is in agreement with Kittelson et al. [24] (Section 2.4.3), and aligns with the surface acidity findings presented later in Section 5.6. Indeed, this link is extended further in later Chapters of this work to produce an improved understanding of the relationship of surface acidity to soot surface O/C ratio for diesel exhaust soots, Chapter 9. Consequently, the surface elemental composition of the EN590 and B100 fuel soots appeared to have greater similarity than the mineral EN590 and PC9 soots. This finding of alignment between the surface elemental composition of the EN590 and B100 soots contrasts with the findings from the other physiochemical properties discussed later in this chapter.

Chlorine was detected at 0.3% weight in the surface of soot from the PC9 fuel experiment and was not observed for any other soot samples in this work. Identifying a source for this isolated case was important due to the PC9 soot also having the highest O/C ratio which could therefore be co-related. The only fuel reported in the fuel composition summary, Appendix 1 (Table A1.1), to have chlorine was EN590 fuel which had 3 ppm chlorine and thus the PC9 fuel did not appear to be a source attributable for the chlorine. Two other possible sources were considered to be the lubricant and sample contamination. The lubricant composition, Appendix 2 (Table A2.1), does not include chlorine and since there was no chlorine detected in any other samples, it is postulated that the most likely source was sample contamination. The means through which the sample contamination may have occurred is unknown; however it was more likely to have been at a stage after the sample was sealed up following removal from the soot collection apparatus since the chlorine was not detected in any other soot sample.

The effect of this chlorine on the PC9 soot results is not certain, however it is more likely the chlorine would have behaved akin to the sulphur from the fuel and been adsorbed onto the surface of the soot rather than strongly bonded like the oxygen molecules. Combined with the source of the chlorine likely having been external sample contamination, it is postulated that the effect in the sample XPS analysis was to reduce equally the wt % concentrations of the other elements

5.3

thus leaving the O/C unaffected. Thus, the high O/C ratio of the PC9 soot relative to the other soots is believed to be primarily associated with the adsorbed sulphur compounds which is intuitive given that the fuel borne sulphur typically oxidises to form sulphates such as SO_2 and SO_3 [24, 30, 31].

Since the soot samples detailed in Table 5.2 were collected at the exhaust manifold, the soot surface composition observed for the soots is assumed to be representative of the surface at the end of combustion and thus describe relatively young soot. This point is important as soot evolution in the exhaust will tend to result in the chemisorption of oxygen to the surface through oxidation [118] (Section 2.4.1.1 and Section 7.3) and thus result in the increase of the surface O/C ratio. Consequently, for the soots detailed in Table 5.2 it is expected that the results are generally representative of soots which have not undergone significant exhaust oxidation and thus the reported carbon content is considered high for typical exhaust sampled diesel exhaust soot. This conclusion is emphasised by the low AFR of the experiments, Table 4.10, which would have limited surface oxidation due to the relative paucity of free oxygen molecules at the end of combustion. Indeed, in respect to the surface elemental summary presented in Section 2.4.1.1, the surface O/C results of Table 5.2 are all at or below the reported mean O/C of 0.091 and agree well with the findings of Bardasz et al. [115, 211] in which the soot was also sampled from the exhaust manifold using a similar technique.

5.4 Soot Bulk Elemental Composition

Table 5.3 presents the percentage weight of inorganics for the bulk composition of the sampled exhaust soot and is also presented in the form of the percentage contribution of each element to the total sample inorganics Table 5.4.

#1269 ICP: Bulk Inorganic Contaminants by Acid-digestion ICP (wt%) Description %Ca %Cu %Fe %Mg %Mn %Na %Р %S %Si %Al %Cd Total wt% %Zn 19.5:1 CT, EN590 0.083 0.003 0.034 0.002 0.012 0.000 0.016 0.001 0.001 0.033 0.000 0.000 0.185 19.5:1 CT. PC9 0.078 0.002 0.043 0.002 0.006 0.000 0.002 0.282 0.001 0.028 0.000 0.000 0.444 5.1 CT B100 0 2 7 7 0.015 0 17 0.005 0.010 0.083 0.051 0.000 0.017 0 1 0 5 0 000 0.000 0 734

Table 5.3: 19.5:1 Exhaust Manifold Soot Bulk Elemental Composition (% weight)(ICP-MS, Corrected)⁸

⁸ Table 5.3 and Table 5.4 present corrected ICP-MS results; this involved negating foreign element contamination which was identified in some samples (Refer to Appendix 8).

5.4

Table 5.4: 19.5:1 Exhaust Manifold Soot Bulk Elemental Composition (%weight/Total % weight) (ICP-MS, Corrected)

	#1269 ICP: Bulk Inorganic Contaminants by Acid-digestion ICP (% of Total wt% Inorganics)												
Description	%Ca	%Cu	%Fe	%Mg	%Mn	%Na	%Р	%S	%Si	%Zn	%AI	%Cd	Total %
19.5:1 CT, EN590	44.865	1.622	18.378	1.081	6.486	0.000	8.649	0.541	0.541	17.838	0.000	0.000	100.000
19.5:1 CT, PC9	17.568	0.450	9.685	0.450	1.351	0.000	0.450	63.514	0.225	6.306	0.000	0.000	100.000
19.5:1 CT, B100	37.738	2.044	23.297	0.681	1.362	11.308	6.948	0.000	2.316	14.305	0.000	0.000	100.000

Analysis of the soot bulk inorganic contaminants was important as it indicated the composition of the soot and thus provided insight into the formation process for the soot and to what extent the sampled soot was contaminated with elements other than carbon and oxygen. The soot bulk inorganic contaminants could have originated from the fuel, lubricant, metallurgy of the engine and fuel system, atmosphere and sample contamination resulting from the collection method or sample handling procedure. These latter two sources proved to be an issue in the work reported herein and the results presented in Table 5.3 and Table 5.4 represent ICP-MS results that have been corrected for specific inorganic elements that could be isolated to known foreign contamination of the samples. The reader is advised to refer to Appendix 8 for the details of the ICP-MS data corrections performed after reading Section 5.4 in entirety to help understand why result correction was required and the corrections that have been made. In the proceeding discussion, reference is made to Appendix 8 where it is considered appropriate that the reader consider the corrections applied to the ICP-MS data.

Considering first the total weight of inorganics for each soot sample from Table 5.3, it is clear that there was general differentiation in the soot sample inorganics concentration between all three fuel soots and this is illustrated in Figure 5.1.



Figure 5.1: 19.5:1 Exhaust Manifold Bulk Total % Weight Inorganics (% weight) (ICP-MS, Corrected)

Comparison between the two mineral diesel fuels total inorganics in Figure 5.1 shows that the PC9 soot had an appreciably larger concentration of inorganics at the exhaust manifold than was the case for the EN590 soot. The concentration of inorganics in the B100 soot was greater still. To understand what was driving these differences, it is first necessary to consider the individual element contributions to the soot inorganics. The individual element wt % data from Table 5.3 is presented in Figure 5.2 and this reveals immediately that the increase in total inorganic contaminate of the mineral PC9 fuel soot relative to that of the mineral EN590 fuel soot was due to the presence of significant sulphur in the PC9 soot. The source of the PC9 soot sulphur was clearly the PC9 fuel itself as the concentration of sulphur in the fuel was 497 ppm, a factor of 10 greater than for the EN590 and B100 fuels, Appendix 1 (Table A1.1).



Figure 5.2: 19.5:1 Exhaust Manifold Bulk Inorganic Contaminants (% weight) (ICP-MS, Corrected)

Looking across all metals for the results reported in Table 5.3 and depicted in Figure 5.2, it is clear that there were three principal metals that constituted the bulk of the metal based inorganic content in all the 19.5:1 exhaust manifold soot samples and these were (Ca, Fe, Zn). Calcium was found both in the fuel, Appendix 1 (Table A1.1), and the lubricant, Appendix 2 (Table A2.1), and was therefore likely to have been contributed to by both sources. The Iron likely originated from both the engine and to a smaller extent the sampling system. For the two mineral diesel fuels, the percentage weight contribution of these metals was roughly equivalent but was found to be substantially higher for the B100 soot sample. Indeed, Referral to Table 5.3 and Figure 5.2 reveals that the increased

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level of biodiesel soot contamination was observed across all the principle inorganic elements (Ca, Cu, Fe, Mg, Na, P, Si, Zn).

As the overall concentration of inorganics across the three fuel soot samples was so different, the analysis of individual elemental contributions as wt % (Figure 5.2) of the sample was limiting and even slightly misleading. It is far more useful to consider the elemental contributions to inorganics as a percentage of the total inorganics for each sample and this is the data from Table 5.4 which is presented in Figure 5.3. The most notable observation from this figure is how significant sulphur was in respect to the contribution to the PC9 soot total inorganics, constituting some 63.5%. Figure 5.3 illustrates that this was a singular isolated result for the three fuel soots with no other single element contributing so uniquely.



Figure 5.3: 19.5:1 Exhaust Manifold Bulk Inorganic Contaminants (% wt/total % wt) (ICP-MS, Corrected)

Ignoring the unique PC9 sulphur concentration, Figure 5.3 depicts that the most significant inorganics for the three fuel soot samples were (Ca, Fe, Zn) in order of their contribution to the total sample inorganics and as outlined earlier these had a combination sources including the fuel, lubricant and engine metallurgy. The next most prominent inorganics were (Na, P, Mn) but the contributions these elements made to the total soot inorganics were sensitive to the fuel indicating that these inorganics primarily derived from the fuels investigated. Finally, there was a consistent low level contamination from the three elements (Cu, Mg, Si) for all three soots with the concentration in the PC9 soot lower for each element due to the far larger contribution of sulphur in this soot. As these three elements were common to all three soots and at a low

concentration, it is postulated that they derived mostly from the engine and fuel system metallurgy with some further addition from the fuels depending upon the concentration in the fuels. The available fuel compositional information, Appendix 1 (Table A1.1), was taken from fuel sample analysis results and does not provide sufficient information to uniquely attribute each low level soot inorganics contaminate so this is not done herein.

Importantly, although not specific to the soot inorganics discussion, Figure 5.3 confirms that the ceramic thimble material which was alumina oxide (Al_2O_3) (Section 3.5.1.1) showed no evidence of having contaminated the soot bulk element analysis as there was no aluminium detected in the exhaust manifold ceramic thimble samples. This was an important result as contamination by thimble material was an issue encountered previously by Lubrizol and it was found in this work that such an issue had been successfully avoided through a detailed validation of the soot collection method and careful handling of the brittle ceramic thimbles. Additionally, the selection of thimble used in this work was also important Section 3.5.1.1.

It is clearly evident from Figure 5.3 that the unique contribution of sulphur to the inorganics to the PC9 soot resulted in the other contaminates, particularly (Ca, Fe, Zn), appearing to mirror the observations of the EN590 and B100 soot but with a lower concentration in each case. To address this finding, it is therefore appropriate to repeat the wt %/total wt % calculation of Table 5.4 but to first negate sulphur for all three soots so as to enable the evaluation of whether the other bulk inorganics elements of the PC9 soot essentially followed the pattern of concentration of those elements for EN590 and B100 soots. The result of this calculation is presented in Table 5.5 and the data from which is illustrated in Figure 5.4.

		#1269 ICP: Bulk Inorganic Contaminants by Acid-digestion ICP (% of Total wt% Inorganics)												
Des	cription	%Ca	%Cu	%Fe	%Mg	%Mn	%Na	%P	%S	%Si	%Zn	%Al	%Cd	Total %
19.5:1 CT	, EN590	45.109	1.630	18.478	1.087	6.522	0.000	8.696	0.000	0.543	17.935	0.000	0.000	100.000
19.5:1	CT, PC9	48.148	1.235	26.543	1.235	3.704	0.000	1.235	0.000	0.617	17.284	0.000	0.000	100.000
19.5:1 0	T, B100	37.738	2.044	23.297	0.681	1.362	11.308	6.948	0.000	2.316	14.305	0.000	0.000	100.000

Table 5.5: 19.5:1 Exhaust Manifold Soot Bulk Elemental Composition with Sulphur

 Contribution Negated (% wt/total % wt) (ICP-MS, Corrected)

Figure 5.4 shows clearly that the individual element contributions (Ca, Cu, Fe, Mg, Zn) to the total soot sample inorganics were actually very similar across the three fuel soots when PC9 sulphur was neglected. Indeed, caparison with Figure

5.4

5.3 reveals just how significantly the sulphur content of the PC9 fuel biased the overall inorganic signature of the PC9 soot.



Figure 5.4: 19.5:1 Exhaust Manifold Bulk Inorganic Contaminants with Sulphur Contribution Negated (% wt/total % wt) (ICP-MS, Corrected)

Figure 5.4 also confirms that the elements (Mn, Na, P, Si) had quite different concentrations across the three soots, thereby strengthening the earlier postulation that these elements largely derived from the inorganic content of the fuels experimentally investigated.

There was a notable concentration of sodium in the B100 soot, Figure 5.4, and since one of the catalysts commonly used in the transesterification process for biodiesel is NaOH (sodium hydroxide), it is postulated that a residue of this compound remained in the B100 fuel and thereby sodium became entrained within the soot which was collected. As an example of the plausibility of this, Gangwar et al. [266] reported a similar finding when investigating the soot produced from a vegetable oil. Appendix 1 (Table A1.1) confirms that for this 19.5:1 compression soot sample, the B100 fuel investigated was reported to have 0.5 ppm sodium. (Note: the reader is advised to refer to Appendix 8, Section A8.2.1 to see that sodium was also originally found in the EN590 and PC9 soot samples discussed in this section but the concentration was so significant in both cases that the sodium was attributed to foreign contamination of the samples and was thus negated when correcting the results to prepare them for discussed in this section. Since the B100 sodium concentration was so much lower and attributable to the fuel, it was not corrected for and remains unchanged as discussed herein.)

Phosphorus was present in the fuels but at a very low concentration and was only reported for the biodiesel fuel where it was measured to be (<0.5 ppm), Appendix 1 (Table A1.1). Phosphorus was detected primarily in the EN590 and B100 soot samples, being higher in wt % concentration in the latter, Figure 5.2. However, referral to Figure 5.4 reveals that in respect to the concentration of phosphorous to the total inorganics in each sample; the phosphorous concentration in the EN590 and B100 soots was actually similar. The concentration of phosphorus was far lower in the PC9 soot sample by comparison even with sulphur negated, Figure 5.4. Indeed, this relatively low PC9 phosphorus concentration was one of the main distinctions between the three soots inorganics once fuel mass flow, lubricant consumption and exhaust soot concentration were accounted for.

In addition to the fuel, phosphorus can also originate from the lubricant, Appendix 2 (Table A2.1), as it is a component of the Zinc Dithiophosphate (ZDDP) compound used as an anti-wear additive. The cause for the much lower concentration in the PC9 soot could therefore simply be attributed to a lower lubricant consumption rate in this experiment. However, Table 4.10 Part A shows that the lubricant consumption rate for the PC9 experiment was the highest of the three 19.5:1 compression ratio experiments. Thus, the more likely cause for the lower concentration would be a relatively low concentration in the fuel but this is unfortunately unknown, Appendix 1 (Table A1.1). The underlying explanation for the lower concentration of phosphorus in the PC9 soot is therefore an important distinction in the soot samples.

It is postulated that the concentration of phosphorus is related in some way to the very high sulphur concentration in the PC9 soot. This derives from the work of Covitch et al. [138] and Ripple et al. [165] of Lubrizol (as a reference they utilised the ceramic thimble soot collection method which is applied in this work). They reported that fuel sulphur influenced significantly the surface acid functionality of soot and that this in turn resulted in large changes in the fraction of soot absorbed into the lubricant. This was because the higher concentration of sulphur acted to increase soot surface acidity leading to the soot being more oleophilic. Thus, it is postulated that the high concentration of sulphur in the PC9 soot could have acted to subtly change the interaction with the lubricant molecules (i.e. the physiochemical process) and this then limited the phosphorus which became entrained in the PC9 soot collected form the exhaust manifold.

Since lubricant-soot interaction is a potential source of inorganics for the soot which forms in the cylinder, it is sensible to consider the lubricant inorganic concentrations reported in Appendix 2 (Table A2.1) and compare against the change in inorganics presented earlier in Figure 5.4. This comparison is presented in Figure 5.5.



Figure 5.5: 19.5:1 Exhaust Manifold Bulk Inorganic Contaminants with Sulphur Contribution Negated and Including Lubricant Element Concentration (% wt/total % wt) (ICP-MS, Corrected)

Figure 5.5 reveals that three of the main lubricant inorganic elements are all present in the three fuel soots with the correlation between (Ca, Zn) being particularly strong. As detailed earlier, the phosphorous correlation is not consistent for all fuel soots and is an indication of the preferential or non-preferential entrainment of phosphorous. The most significant difference is the sulphur concentration; obviously in the case of the EN590 and B100 soots there was negligible sulphur present in the samples which contrasted with the >40% concentration in the lubricant (the PC9 fuel sulphur concentration was very high and makes it difficult to separate fuel and lubricant sulphur for this soot so it is ignored here). It thus appears that the similar and yet gross differences between the concentrations of (Ca, P, S, Zn) in the soot and lubricant indicated that the entrainment of lubricant inorganics into the soot is a somewhat complex process.

The specific cause for the apparently low entrainment of lubricant sulphur into the soots could not be attributed with the information available but it is postulated that the findings of Covitch et al. [138] and Ripple et al. [165] as highlighted previously could be contributing to the mechanism behind this.

Note: the reader is encouraged to refer to Appendix 8 (Section A8.2.3) at this point as sulphur was detected in the exhaust manifold B100 soot at 19.5:1. However, the concentration was so significant that it was attributed to foreign contamination of the sample and the result was negated to produce the corrected ICP-MS data discussed herein.

Figure 5.5 illustrates that the concentration of iron ranged from 18-27% and it is believed that the iron originated principally from the engine metallurgy. Thus, two points can be developed from this. Firstly, the contribution of iron from the engine metallurgy to total soot inorganics at the exhaust manifold was important. Secondly, between the three fuel soots examined, iron appeared to contribute roughly equally to each suggesting that in-cylinder, the processes governing the entrainment of metals from the engine metallurgy into the soot were insensitive to the fuel used for the conditions investigated.

The negating of PC9 sulphur discussed earlier assisted with the assessment of the individual element contributions to the soot inorganics and it is appropriate to reassess the summation of total wt % of inorganics with sulphur negated to understand the non-sulphur inorganics total concentration for the three soots, this result is presented in Figure 5.6.



Figure 5.6: 19.5:1 Exhaust Manifold Bulk Total % Weight Inorganics with Sulphur Negated (% weight) (ICP-MS, Corrected)

Figure 5.6 compared with Figure 5.1, clearly shows that the negating of sulphur results in the contribution of total inorganics for the EN590 and PC9 soots appearing very similar. However, it is observed that in the case of the B100 soot, the wt % of inorganics was greater by a factor of 4.2 than observed for the

two mineral soots and it is postulated that this is because of the relationship of total inorganics to fuel rate, engine metallurgy and lubricant consumption rate. Each of these is postulated to contribute to the overall inorganic content of the soot with the exhaust soot concentration then determining the ratio of inorganics to the carbonaceous soot part.

The greater concentration of inorganics in the B100 soot in comparison to the mineral soots, as indicated in Figure 5.6, is potentially important in regard to soot porosity and oxidation potential. Boehm [118] states that the presence of foreign elements in the surface of the soot most likely increases the concentration of surface irregularities in the crystalline structure of the soot, with such irregularities having the potential to increase soot porosity. Later in Section 5.5.2 it will be shown that the B100 soot was observed to have quite distinct morphological characteristics and these could therefore certainly have been influenced by the somewhat greater extent of inorganic contamination of the B100 soot.

It is postulated in this work that the contribution of the fuel and lubricant to the concentration of inorganics in the soot should be relative to the respective differences in fuel consumption and lubricant consumption rates between experiments. For example, the density of the B100 fuel was approximately 6% greater than the densities of the two mineral diesel fuels and thus from Table 4.10 Part A the mass flow rate for the B100 rated power experiments was on average 7.6% greater. Thus, during the B100 combustion the simplifying assumption is that there was ~7.6% more fuel derived inorganics present in the cylinder during each cycle relative to the experiments with the other two fuels (the individual relative concentrations of the twelve ICP-MS inorganics in each fuel would have had an influence on this but is not accounted for due to insufficient information on the fuel inorganic composition). In respect to the lubricant consumption also reported in Table 4.10 Part A; the simplifying assumption is that the higher the lubricant consumption, the greater the concentration of total inorganics in the soot. The engine was refilled with an identical mass of fresh lubricant from the same batch for each experiment (Section 3.1.5.3) to minimise variances between the experiments and the implementation of this procedure strengths the above assumption.

Table 4.10 Part A reports that there was a very significant difference in AVL 415 (mg/m³) exhaust soot concentration (Refer to Section 3.2.2.5 for details concerning the exhaust smoke measurement) and it is assumed in the work reported herein that that since the AVL 415 provides a measure of the

5.4

concentration of just the carbonaceous soot concentration [194]; then the concentration of ICP-MS total inorganics should scale in proportion to the exhaust soot concentration reported by the AVL 415 since the carbonaceous fraction of soot is typically the most significant at 50-80% or more of the bulk, Section 2.4.1.2.

Thus, with these combined assumptions, a process was undertaken to scale the ICP-MS wt % concentration data presented in Table 5.3 to account for the relative differences in fuel rate, exhaust soot concentration and lubricant consumption. The first step in this process is to use the normalised Fuel Soot Factor (FSF) defined in Section 4.3.2 to scale the ICP-MS data for each soot sample to account for the differences in fuel mass flow rate and exhaust soot concentration and to this end the normalised FSF for the 19.5:1 compression ratio experiments detailed in Table 4.14 has been applied to the results presented earlier in Figure 5.6 to produce the result in Figure 5.7.





Before the result in Figure 5.7 is considered in detail, it is important to reflect on two points regarding the data analysis methodology from which the result derives. Firstly, since the AVL 415 smoke meter sample probe was not located in close proximity to the soot sample positions used in this work (Section 3.2.2.5); the simple approach of multiplying the bulk inorganics by the FSF factor was used rather than a more precise quantitative approach. A more precise approach would have required the measurement of carbonaceous soot fraction at the point where the soot was sampled from the exhaust to remove any effects from the

loss of carbonaceous soot fraction as the soots evolved in the exhaust (Chapter 7). However, this was not technically feasible in this work.

Secondly, the same normalised FSF scaling value has been applied to each element in the individual soot sample ICP-MS results as there was insufficient information and knowledge concerning the contribution of individual elements from the fuel and the lubricant to the soot inorganics to scale elements uniquely. i.e. if the normalised FSF was 0.5, then the wt % each element in a given soot sample was multiplied by 0.5 to adjust the overall inorganics to account for the FSF reported scaling between experiments.

Figure 5.7 illustrates that when the % wt of total inorganics is scaled by the normalised FSF, the accounting of exhaust soot concentration and fuel flow rate results in scaled total wt % of inorganics for the two mineral fuel soots being comparatively close. However, it is also observed that the B100 total inorganics concentration was actually lower than for the two mineral fuel soot and therefore opposite to the indication given by the original ICP-MS results, Figure 5.6. This significant shift for the B100 soot was largely a consequence of the ~80% lower exhaust soot carbonaceous fraction for the B100 fuel compared to the two mineral diesel fuels.

The alignment between the scaled ICP-MS results for the two mineral diesel soots in Figure 5.7 implies that with PC9 sulphur neglected, the two mineral fuels produced soot with roughly equal concentrations of non-sulphur inorganics at the same engine operating condition. Thus, for both fuels the processes that result in the entrainment of inorganics into the soot must have been quite similar. For the B100 soot, by contrast, it would appear that the processes regulating the entrainment of inorganics were somewhat distinct from those occurring for to the mineral soots.

However, the result presented in Figure 5.7 does not account for the aforementioned assumed contribution from the lubricant and referral to Table 4.10 Part A shows that rather interestingly the lubricant consumption rate in the 19.5:1 B100 soot collection experiment was somewhat lower than for the two equivalent mineral fuel experiments and this is illustrated in Figure 5.8.




Multiplication of the FSF scaled wt % data from Figure 5.7 with the respective lubricant consumption factor from Table 5.6 leads to the result presented in Figure 5.9.

Table 5.6: Normalised Lubricant Consumption Factors for the Rated Engine Power

 Exhaust Soot Collection Experiments

Experiment	Lubricant Consumption	Lubricant
	(g/h)	Consumption Factor
19.5:1 EN590	27.9	0.49
19.5:1 PC9	28.8	0.46
19.5:1 B100	16.8	0.79
16.5:1 EN590	24.6	0.54
16.5:1 PC9	37.8	0.35
16.5:1 B100	13.3	1

The result derived and then presented in Figure 5.9 is very useful as it shows that at the exhaust manifold in the experiments reported in this work; the wt % inorganics were found to be roughly proportional to the fuel consumption rate, the oil consumption rate and the concentration of carbonaceous soot in the exhaust gas. Thus, this result supports the aforementioned postulation for this relationship. From this it is therefore possible to conclude that for the rated engine power experiments at 19.5:1 compression, the effective contribution of inorganics (with PC9 sulphur neglected) to the bulk soot composition was close across the three fuels investigated once known uncontrolled contributing factors had been accounted for.





Thus, it can be asserted that from the results and analysis presented herein that the bulk inorganic content of diesel engine soot is sensitive to the concentration of the same inorganics in the fuel and lubricant, thus an elevation in an element in the fuel or lubricant will lead to an elevation of the concentration of that element in the soot bulk (i.e. PC9 fuel sulphur). Therefore, this work has shown that a large change in the concentration of a single element in the fuel or lubricant (i.e. sulphur) can also markedly change the bulk chemistry of the soot and thus possibly influence the oxidation and surface chemistry of the soot.

5.5 Soot Morphology

Presented in Table 5.7 are the complete morphological results for the soot collected at 16.5:1 at the exhaust manifold for the three fuels investigated. For reference: 1 Å = 0.1 nm, thus 256.73 Å = 25.673 nm i.e. mesopores, Section 2.4.2.2.

	BET Method		BJH Adsorption	N2 Pycnometry		Primary Particle Diameter
Description	Suface area (S _{BET}) (m ² /g)	Error	Average pore diameter (Å)	Density (ρ) (g/cm ³)	Error	Dpp = $6/(\rho S_{BET})$ (nm)
16.5:1 CT, EN590	262.4843	1.3344	116.156	1.9902	0.0117	11.486
16.5:1 CT, PC9	335.8769	1.9077	140.194	2.0011	0.018	8.927
16.5:1 CT, B100	35.6094	0.1757	256.73	2.8907	0.0243	58.289

Table 5.7: 16.5:1 Exhaust Manifold Soot Morphological Characteristics

5 5.5

Soot Morphology

5.5.1 Surface Area

The surface area data in Table 5.7 details how the mineral diesel fuel soots were broadly similar with the surface area of the biodiesel fuel soot being distinctly lower. The range of the surface area measurements was large because of the very low relative surface area measured for the B100 soot. This distinction in the physical attributes of the B100 soot extended across all the soot morphological parameters considered. Proposing an explanation for this observation therefore requires the other morphological results to be considered.

5.5.2 Porosity

Similar to the surface area measurements, the porosity measurements found similarity between the mineral diesel fuel soots but the B100 soot had an average pore diameter roughly double that of the mineral soots.

This B100 porosity distinction combined with the very low surface area could simply be explained by the B100 soot having had significant levels of absorbed HCs which intuitively would act to increase the size of the individual soots and possibly encourage larger agglomerate structures, each of which would act to reduce the surface area and porosity - thus neatly fitting the general B100 soot morphology observations. The plausibility of this hypothesis is supported by the very significant levels of HC emissions observed for the B100 fuel combustion which were reported in Table 4.10 Part C.

One issue with this hypothesis was that the engine exhaust gas temperatures were in excess of 500°C, Table 4.10 Part B, and thus it could be argued that the adsorption of SOF onto the soot surface would be unlikely as any SOF would remain in the vapour phase. Though this was the case, when the soot was collected at the exhaust manifold, the temperature in the sample line from the exhaust manifold reduced to typically 150°C, Table 4.10 Part B, at the ceramic thimble so the condensation of HCs onto soot either prior to or in the ceramic thimble was highly likely. Direct supporting evidence for the actual adsorption of greater SOF onto B100 soot comes from the observation of a greater proportion of lighter compounds released in the low temperature segment of the thermogravimetrical analysis of the B100 soot compared to the two mineral fuel derived soots (refer to Section 5.8).

So it is probable that the B100 soot therefore had greater adsorbed SOF but the sample preparation for the N2 adsorption tests should have removed any

<u>5</u>

condensed molecules. Due to there being no data to verify if all SOF was removed, there remains a possibility SOF could have influenced the B100 soot N2 based morphology examinations. Therefore, two scenarios are proposed that must be considered when interpreting the soot morphological results herein:

Scenario 1: All adsorbed SOF was successfully removed from the soot samples prior to the N2 adsorption measurements through sample pre-treatment and thus the findings reported herein represent the true *dry soot* morphological characteristics and can therefore be used to infer the structural differentiation between the soots.

Scenario 2: The measured adsorbed SOF actually persisted on the surface of the soot samples and influenced the N2 adsorption measurements, particularly in the case of the B100 soot samples, therefore causing some of the apparent fundamental differences in the soot morphology results.

Ascribing the distinct B100 soot morphological characteristics to SOF adsorption alone as per scenario 2, though a possibility, it is considered to be unlikely given the findings from literature which describe a fundamentally different morphology for B100 soot e.g. Song eta al. [16]. Additionally, this adsorbed SOF assignation fails to align with the physiochemical findings reported in later chapters which collectively point to the B100 soot being distinct from the mineral fuel soots in respect to surface and bulk compositions (e.g. Section 7.5). The B100 soots are therefore considered to have been genuinely morphologically district as per scenario 1. Explanations for the morphological findings assuming dry soot are therefore discussed in the following section when the differences in soot density are also included.

As a consequence of the concerns raised about the risk of impact on results from adsorbed SOF, it is recommended that in future work where the N2 adsorption techniques are used; the preparation methodology of exhaust soot samples also needs to be included as an additional factor to ensure isolation of any possible confounding between adsorbed SOF (which is almost certainly going to be present on engine exhaust soot) and N2 adsorption based morphological results.

5.5.3 Density

Measurements for the soot density reported in Table 5.7 revealed that the density of the two mineral diesel soots were very close, differing by 0.0109 g/cm³

or 0.6% of the EN590 soot density. This result is at the very upper end of the 1.7-1.8 g/cm³ range found in Section 2.4.2.3 to be frequently reported in literature for soot. The B100 soot was observed to have an even higher density which was indicative of either a somewhat different soot structure and or bulk elemental content.

Considering first the soot structure; the substantially different surface area and porosity of the B100 soots when considered using Equation 3.6 (Section 3.6.4.2) (pore volume is proportional to BET surface area and average pore diameter); point to the B100 soots as having a much smaller pore volume relative to the two mineral fuel soots. This could be indicative of the B100 soot having less open voids accessible from the surface due to much higher soot oxidation and also potentially an overall lower incidence of trapped internal voids. A reduced number of trapped internal voids would likely lead to a higher soot primary particle density.

This postulation is intriguing when compared to findings in literature from Song et al. [16] which describe B100 soot as having a hollowed out internal core with an intact outer shell. Such a characteristic should in principle lead to a high primary particle density if it is assumed that the oxidation of the soot had acted to reduce trapped internal voids through hollowing of the soot core (assuming that the N2 molecules used in the N2 adsorption measurement could permeate through the outer shell into the hollowed core).

Considering the impact of the bulk composition of the soot, it was shown in Section 5.4 that the distribution of inorganic elements was quite similar to the EN590 soot (Figure 5.3) though the total concentration in the soot of all reported inorganics was somewhat greater for the B100 soot, Figure 5.1. Consequently, it is appropriate to consider in greater detail the potential influence of the bulk inorganics on soot density. Table 5.8 presents the elemental density for each of the twelve ICP-MS reported elements and additionally the elemental density for carbon and oxygen.

The ICP-MS element densities in Table 5.8 are left aligned for elements with densities below that of elemental carbon and right aligned for element densities above. Comparison of Table 5.8 with Figure 5.2 reveals that for the elements (Ca, Fe, Zn), which were the highest concentration elements, calcium has a slightly lower density than carbon whilst iron and zinc are somewhat higher in density. Thus, depending upon the distribution of inorganic contaminates and the

5.5

total contribution to the soot mass, in principle the bulk inorganics would influence the soot density. Since Table 5.3 shows that the corrected ICP-MS results report a total mass of inorganics from just 0.185 to 0.734 wt % for the three fuel soots, then the potential contribution of inorganics to soot density is actually small. This would appear to be reflected in the fact that Table 5.7 shows a range of soot density from 1.9902 to 2.8907 g/cm3 which has a median of 2.44 g/cm³ and Table 5.8 which reveals elemental carbon has a density of 2.267 g/cm³. i.e. the measured soot densities were relatively close to that of pure carbon.

Element	Density (g/cm^3)
Calcium	1.54
Copper	8.933
Iron	7.874
Magnesium	1.738
Manganese	7.44
Sodium	0.971
Phosphorus	1.82
Sulphur	2.067
Silicon	2.3296
Zinc	7.134
Aluminium	2.698
Cadmium	8.69
Carbon	2.267
Oxygen	0.001429
Hydrogen	0.00008988

Table 5.8: Elemental Density for ICP-MS Reported Soot Inorganics⁹

However, the lowest measured density was for the EN590 soot which correlated to the lowest concentration of inorganics and the highest density soot was the B100 soot which had the greatest concentration of inorganics. Together therefore, the ICP-MS inorganics and N2 pycnometry derived density appear to provide broadly supportive evidence that the inorganic content of soot is an important forcing factor behind soot density though there is insufficient information to quantify the effect precisely.

In the absence of any evidence that residual SOF was present on the surface of the soots when the N2 adsorption measurements were performed; it is more likely that the higher B100 soot density derived from both soot bulk inorganic differences and actual soot structural differences. It is postulated that the bulk inorganic differences don't explain all variation in density due to the small

⁹ Measured at standard temperature and pressure (100.00 kPa and 0°C).

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contribution of inorganics to total soot sample weight and thus soot structure and hence voids are very important.

To recap; the review of literature revealed that in the case of biodiesel soot oxidation, observations have been reported which show via TEM that biodiesel soot oxidises in some situations completely differently to mineral soot. For example, Song et al [16] (Section 2.4.2.2) described how biodiesel soot appeared to oxidise - not from the loss of graphene planes from the surface but from a hollowing of the soot core. This was attributed partly to the more amorphous core structure of the B100 soot (compared to soots produced from Fischer-Tropsch fuel) which enabled oxidation conceivably via oxygen present in the soot core which originated from the fuel.

Thus, from the reported morphological data, several possibilities in terms of models to explain the soot morphological differentiation can be proposed, two of the more likely include:

B100 Soot Model 1: The B100 soots had undergone far more oxidation than the mineral soots when sampled due to an inherent higher rate of oxidation for the B100 soots (supported by findings presented in Chapter 7) and that this oxidation had opened up the small surface pores and internal voids in the soot thus creating a soot similar to that described by Song et al. [16] with internal voids that were connected to the surface allowing the N2 molecules to enter. Thus, the B100 soot had very few trapped voids thereby giving rise to the relatively high density measurement. Since the pores were opened up, the total pore volume and soot surface area would be low as was observed. However, the soot reported in Table 5.7 was sampled from the exhaust manifold so such extensive oxidation and physical transformation could be argued against as the soot was 'young'.

B100 Soot Model 2: Alternatively, the B100 soot primary particles could have had a far more regular graphene plane internal arrangement with fewer isolated internal voids than was the case for the mineral fuel derived soot. This was then combined with a low surface porosity which also resulted from the highly regular arrangement of the graphene planes. This would in principle give rise to soots with small surface area, low pore volume and higher density as observed but if this is how the B100 soots were structured physically, then it is opposite to the description derived from TEM micrographs by Song et al. [16].

Clearly, these are two almost opposite models for the B100 soot structure which attempt to explain the observed results and each are not ideal. However, a quite different explanation can also be devised in which the B100 soot at the exhaust manifold can be assumed to have been highly agglomerated due to the earlier proposed high SOF fraction acting to bind the primary soot particles together. Several sources in literature report that biodiesel fuels produce a higher SOF fraction compared to conventional mineral diesel fuels [266, 296, 306] and Song et al. [17] suggest that higher SOF may result in a much tighter aggregate soot structure which would also act to reduce the isotherm-BET determined surface area, so this postulation is also feasible.

For example, when the soots were examined using the N2 adsorption techniques, the highly agglomerated primary particles presented a low surface area and porosity as significant areas of the primary particles were touching and could not be exposed to the N2 gas. In this way, tightly packed primary particles would have acted like a much larger singular particle which may explain why the estimated particle size was so large, Table 5.7. Then as these B100 soots oxidised in the exhaust and passed through the oxidation catalyst the SOF was removed and the tight aggregate structure broke apart increasing the exposed surface area and then the physical oxidation processes of soot model one proceeded to open up the surface pores thus reducing the pore volume.

One issue with this proposal is the very high exhaust temperatures at the confluence point of the exhaust manifold where the soot samples were sampled from. Table 4.10 Part B details how the exhaust temperatures were in excess of 530°C during the rated engine condition soot collection experiments and thus at such a temperature the presence of absorbed volatiles would have been negligible if not non-existent as shown by Ishiguro et al. [131]. However it is possible that as the soot was transported from the exhaust manifold down the sample line to the ceramic thimble, volatiles were able to condense and then adsorb onto the soot surface. This is possible because the average ceramic thimble temperature when the soot was collected was 153.5°C for these experiments; 'CT Temp' in Table 4.10 Part B.

Thus, although the available morphological descriptions are very informative, they allow for quite different soot primary particle structure models and alternative non-structural explanations for the morphological distinctions between the soots. It can be concluded therefore that there is insufficient information to be completely confident of the correct model etc. to describe the B100 soot structure

Soot Surface Acid Functionality

observed in this work. More information is therefore required to investigate the morphological findings and possibly the most applicable method in this regard would be the use of TEM which would in principle provide more information on the internal graphene plane arrangement (i.e. core soot structure) in addition to giving a direct measure of soot primary particle size [16, 17].

5.5.4 Primary Particle Diameter

Primary particle diameter was calculated as described in Section 3.6.4.4 from the measured soot surface area and density and unsurprisingly the two mineral diesel soots were determined to have very similar primary particle diameters with the B100 soot primary particle diameter being estimated as much larger. The estimated diameters for the mineral diesel soots were smaller than the diameters reported in literature (15-30 nm) from direct measurement, as detailed in Section 2.4.2.4, and this was evidence of the limitations of the simplified assumptions of the calculation method which assumed a non-porous spherical particle. With both large surface areas and small average pore diameters, these soots almost certainly had significant porosity which caused the underestimation. Furthermore, the fact that the measured soot density aligned to the reported soot density in literature (Section 2.4.2.3), adds weight to this finding.

The large 58.3 nm estimation for the B100 soots (large for the exhaust manifold, Section 2.4.2.4) were more difficult to judge in terms of relevancy as the surface area was much smaller due most likely to the much lower observed soot porosity. The primary particle diameter estimates have therefore proven to be less reliable than hoped, pointing to the need to combine the estimate in this work with a direct measurement method such as TEM to achieve a fuller picture.

5.6 Soot Surface Acid Functionality

The results from the surface acidic functionality measurements are presented in Table 5.9 and are defined for both the total and carboxylic acid concentrations. The surface acidity could not be determined for the B100 fuel because the significant -80% reduction (Table 4.10 Part A) in exhaust soot concentration greatly reduced the total soot mass that could be collected for this fuel (also refer to Section 3.5.1.2).

	Boehm Titration									
	Total surface	stdev								
Description	acids (mmol/g)	(mmol/g)	acids (mmol/g)	(mmol/g)						
19.5:1 CT, EN590	0.621	0.083	0.181	0.008						
19.5:1 CT, PC9	1.163	0.010	0.749	0.001						
19.5:1 CT, B100	NA	NA	NA	NA						

Table 5.9: 19.5:1 Exhaust Manifold Soot Surface Acid Functionali	y	(Boehm titration)	ļ
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Table 5.9 shows that the surface acidity of the PC9 soot was more concentrated for both carboxylic and total acidity. It can also be observed that the ratios of carboxylic to total acidity were 29.1% for EN590 and 64.4% for the PC9 fuel soot. The greater ratio of carboxylic acidity for PC9 soot indicated a probable link with the higher surface sulphur and oxygen concentration for the PC9 soot since both were somewhat higher for the PC9 soot relative to EN590, Table 5.2.

This sulphur observation is supportive of the findings from literature such as Kittelson et al. [24] which state that the surface acid concentration is proportional to the fuel sulphur. The agreement with the higher oxygen content is supported by the findings of Studebaker [163] which describes a proportional relationship between soot surface oxygen concentration and surface acidity. Generally speaking, the data presented in Table 5.9 is suggestive of a link between the proportion of carboxylic component and the total surface acidity. This link has also been observed for other experiments reported later in Chapter 6 and Chapter 8 and is discussed in far more detail in Chapter 9 which considers all the soot surface acidity findings of this work in greater detail.

It is worth considering that the results reported in Table 5.9 are for soots sampled from the exhaust manifold and with the engine operating at maximum power with low AFR, Table 4.10 Part A. Since the preceding observations indicate that the surface acidity is strongly coupled to surface oxygen concentration, it would be assumed that the low AFR combined with the soots being relatively young would have limited the potential chemisorption of oxygen such that the surface acid concentration for these soots would be low. However, referral to Table 2.8 reveals that the mean concentration observed in literature is around 0.89 mmol/g so the soots did not have an especially low acidity as they had surface acidity between 0.621-1.163 mmol/g. It is therefore possible that the high temperatures and pressures of the engine operating condition encouraged large concentrations of NO_x (which is reported in Table 4.10 Part C) and it was this which reacted with the soot to form the surface functional groups [116].

Indeed, it is reported by Boehm that it is the surface oxides that are created at high temperatures that tend to be acidic in nature [118]. Therefore it is postulated that a combination of processes related to the high combustion temperatures for the engine operating condition used to collect these soot samples, resulted in the soots having sufficient surface oxygen content (Table 5.2) such as to drive the levels of surface acidity observed even though the engine was operating at a very low AFR of typically 19:1 to 20:1, Table 4.10 Part A.

The surface acidity of the soot reported in Table 5.9 was higher than the typical acidity Lubrizol had observed for lubricant drain soot (<0.5mmol/g). The lubricant from the engine soot collection experiments reported in this work was sampled (Section 3.1.5.3) but the concentration of soot in the end-of-test samples was too low to permit analysis of the soot suspended in the lubricant. It is postulated that the lower surface acidity of the soot suspended in the lubricant as indicated by Lubrizol, is likely due to the soot being drawn into the engine lubricant (through thermophoretic deposition and turbulent deposition) inside the cylinder and consequentially the soot has had less time to oxidise and absorb oxygen molecules onto the surface; especially if it becomes entrained in the lubricant during combustion thus sealing the soot surface to further reactions. These observations therefore indicate that a comparison of soot surface acidity between soot from the lubricant and the engine exhaust manifold from the same engine test; could be an interesting future study to test the surface O/C ratio and surface acidity relation indicated in Table 5.9 and discussed in greater detail in Chapter 9.

5.7 Soot Polycyclic Aromatic Hydrocarbon Profile

A total of sixteen PAH were investigated in the soot samples and the results are presented across Table 5.10 and Table 5.11.

 Table 5.10:
 19.5:1 Exhaust Manifold Soot Polycyclic Aromatic Hydrocarbon Profile

 (Naphthalene to Fluoranthene) (GC-MS)

PAH (µg PAH/g) Description	Naphthalene	1- methylnapht halene	2- methylnaphth alene	Acenaphthylene or biphenylene	Acenaph thene	Phenanthrene	Anthracene	Fluoranthene
19.5:1 CT, EN590	2.990	0.297	0.104	0.048	0.022	1.659	0.000	0.045
19.5:1 CT, PC9	0.031	0.005	0.003	0.000	0.002	0.096	0.000	0.010
19.5:1 CT, B100	0.000	0.000	0.000	0.000	0.002	0.010	0.000	0.003

Table 5.11: 19.5:1 Exhaust Manifold Soot Polycyclic Aromatic Hydrocarbon Profile(Pyrene to Benzo-perylene) (GC-MS)

PAH (μg PAH/g)	Pyrene	Benz(a)anth	Chrysene	Benzo(b)fluorant	Benzo(k) fluoranth	Indeno(1,2,3-	Dibenz(a,h)a	Benzo(g,l,h)	total
Description	racene			nene	ene	cu)pyrene	nunacene	peryrene	
19.5:1 CT, EN590	0.000	0.014	0.006	0.000	0.027	0.000	0.000	0.000	5.212
19.5:1 CT, PC9	0.001	0.013	0.000	0.000	0.000	0.000	0.000	0.000	0.161
19.5:1 CT, B100	0.003	0.003	0.000	0.000	0.000	0.000	0.000	0.000	0.021

The PAH results for the soot samples from the exhaust manifold for the 19.5:1 experiments (Table 5.10 and Table 5.11) proved to be the most valuable set of PAH results as they encompassed all three fuels and sufficient PAHs were recovered from the soots to enable a comparison of the individual PAH concentrations in the soot. The first observation was that when the individual PAH concentrations were summed for each fuel, there was a very large range across the fuels as illustrated in Figure 5.10.



Figure 5.10: 19.5:1 Exhaust Manifold Soot Total PAH for EN590, PC9 and B100 fuels (GC-MS)

The EN590 total PAH was a factor 32.4 times that of the PC9 soot and the PC9 soot PAH was a factor 7.7 times that of B100. Referral to Appendix 1 (Table A1.1) shows that the total aromatic content of the EN590 fuel was 19.25 vol % and for PC9 fuel it was 32.6 vol %; whilst for the B100 fuel, aromatics were not detected which is postulated to be the reason why the B100 PAH concentration was so low. Thus, the EN590 and PC9 soot measured PAH concentrations were opposite to the relative concentrations of PAH in the original fuels. To summarise from Section 2.4.4: PAH are largely concentrated on the surface of soot as they condense from the exhaust matter [25]. PAH derive from the original fuel and pyrosynthetic reactions during combustion [173, 175, 178] and also the lubricant [23, 28, 176, 177]. Thus, there may be several potential explanations for the

Soot Polycyclic Aromatic Hydrocarbon Profile

observed PAH concentrations for the EN590 and PC9 soots contradicting the original PAH concentration in the fuels.

It is postulated that the somewhat higher concentration of PAH for the EN590 soot is indicative of a physical process having either limited the pyrolysis of PAH for the PC9 fuel during combustion or alternatively had constrained the adsorption of PAH onto the PC9 soot surface. At this point it is important to note that the relative concentration of PAH increased somewhat for the PC9 soot as it evolved in the exhaust to the extent that it exceed the EN590 total concentration in the DPF soot samples, Section 7.7. As this correlated with changes in the surface sulphur concentration for the PC9 fuel, it is argued in Section 6.6 and Section 7.7 that these changes in total PAH reflected the differences in the physical processes that lead to the adsorption of the PAH on the soot surfaces. These physical processes, both in-cylinder and in the exhaust, appeared to be sensitive to fuel sulphur content. Thus, it is believed that the relative PAH concentrations in Table 5.11, being opposite to the relative PAH concentrations in the fuels, derived from the greater sulphur content of the PC9 fuel influencing the PAH adsorption onto the soot surface.

It could be argued however that the EN590 and PC9 PAH observations may have been the result of different PAH profiles for the two mineral fuels that resulted in the EN590 and PC9 discrepancy. i.e. an initially different PAH profile for each fuel lead to different pyrosynthetic reaction pathways leading to different total PAH concentrations. As will be shown in the second part of this section, the PAH profiles for both EN590 and PC9 soot were dissimilar in some specific respects suggesting that the pyrosynthetic reaction pathways and/or original fuel PAH profiles, did potentially contribute to the differences total PAH concentration in the soots.

As result of this significant difference in the total PAH, it is necessary to take the data in Table 5.10 and Table 5.11 and calculate the individual PAH as a percentage of respective soot sample total PAH and this result is presented in Figure 5.11 for Table 5.10 data and Figure 5.12 for Table 5.11.

Together Figure 5.11 and Figure 5.12 reveal that the PAH profiles for all three fuel soots were different although the general shape of the two mineral fuel soots profiles did agree. Naphthalene, a relatively low molar mass PAH and which is the PAH generally observed when PAH are present in fuel [175], was found to be high for the two mineral fuel soots but was not present for the B100 soot and

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therefore indicated that for the B100 soot the PAH must have formed through pyrosynthetic reactions rather than originating from the fuel [173, 175, 178].









Phenanthrene was observed consistently as one of the high relative concentration PAHs for the three fuels with Benz(a)anthracene being the other. The PAH molar mass range of the mineral fuel soot was greater than observed for the B100 soot with the B100 soot PAH mostly concentrated between Acenaphthene and Chrysene. This limited range of PAH in the B100 soot likely resulted from the lack of PAH in the B100 fuel such that the pyrosynthetic reactions were less complex compared to those for the two mineral fuels.

To help study the PAH profile for the three fuels more comprehensively, two additional approaches of data analysis were utilised. The first was to group the

PAH concentrations by the number of carbon and hydrogen atoms and then sum any like PAHs together. This was then used to create a plot of hydrogen verses carbon to produce a 'staircase' type pattern as described by Dobbins [25]. Each point on the plot was then scaled in size to represent the concentration of that PAH group in the sample. The result of this for the 19.5:1 exhaust manifold soot sample is presented in Figure 5.13.





Figure 5.13 shows there were some key differences between the PAH content of the two mineral and the biodiesel soots. The two mineral soots had high concentrations of PAH at $C_{10}H_8$ and $C_{14}H_{10}$ with concentrations generally much lower across a series of other PAH with 11 to 20 carbon atoms and 8-12 hydrogen atoms with the PC9 soot PAH encompassing a slightly narrower range.

For the B100 soot the distribution of PAH was different in that it was largely limited to PAH of 10 and 12 hydrogen atoms with the bulk of the PAH having 10 hydrogen atoms. The B100 PAH distribution also appeared less concentrated with a more even distribution across fewer PAH than for the mineral fuels. Interestingly, the B100 PAHs were low in concentration at $C_{10}H_8$ in comparison to the mineral diesel soots. From Figure 5.13 it can also be observed that there was a clear favoured concentration of PAH with 10 hydrogen atoms for all three fuels whereas there was no similar carbon atom number preference. There were also preferences for 8 and 12 hydrogen atoms but these were less significant.

The second method to assist with characterising the PAH profile was to group PAH by molar mass and then sum the PAH concentrations for like molar mass and then plot the result against molar mass. The final determined concentrations

Soot Polycyclic Aromatic Hydrocarbon Profile

for each PAH by molar mass are presented in Figure 5.14. Frequently in literature this result is presented as the raw mass spectrum from a sample so the result illustrated in Figure 5.14 can be readily compared to results from literature.



Figure 5.14: 19.5:1 Exhaust Manifold PAH Molar Mass Profile (GC-MS)

Figure 5.14 expands on what was presented in the carbon and hydrogen 'staircase' presentation of Figure 5.13 with the two mineral fuel soots having high concentrations of PAH at low molar mass 128 and a second high concentration at a medium molar mass of 178. In contrast, the majority of the B100 PAHs were between molar masses 154 to 228 with the similar peak concentration at 178.

This very strong concentration of PAH of molecular mass 178 (Phenanthrene) for all three fuel soots is a very interesting observation. Indeed, this result is repeated throughout the results of this work, see Section 6.6, Section 7.7 and Section 8.8. Phenanthrene is believed to be what is called a 'stabilomer specie' (Section 2.4.4), that is a PAH which has been shown to be very stable at temperatures typical of hydrocarbon flames [25, 180]. The review by Dobbins [181] specifically identifies alkylated phenanthrenes as a dominant PAH for hydrocarbon flames. This work herein therefore indicates that Phenanthrene is a stabilomer specie for both mineral diesel and biodiesel fuel combustion.

The low mass zone 128-142 depicted in Figure 5.14 is the signature of 2-3 ring PAH components (naphthalene, 1-methylnaphthalene, 2-methylnaphthalene) which from fuel analysis results reported in literature are the common original fuel borne PAH [25, 178] and this observation was therefore in agreement with this as the B100 had no aromatics whereas the EN590 and PC9 fuels both contained

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16.9% and 32.6% volume aromatics respectively, Appendix 1 (Table A1.1). This result implied these were PAH which survived combustion whereas the other PAH observed derived from pyrosynthesis during combustion.

Curiously, the low mass PAH concentrations of the mineral diesel soots were opposite in relative concentration to the original fuel aromatics with the PC9 soot PAH also having a higher overall concentration of medium molar mass, Figure 5.14. This is a strong indication that the pyrosynthetic reactions for these two fuels were indeed somewhat different, possibly due to different original PAH profiles in the fuels. It could therefore be argued that these potential differences in the pyrosynthetic reactions singularly account for the large difference in total PAH concentration, Figure 5.10. However, knowledge of the significant increase in PC9 soot total PAH concentration i.e. it exceeded that of the EN590 soot with reduced compression and exhaust evolution (Section 6.6 and Section 7.7); suggests that the earlier postulated sulphur related processes must also have been involved as the profile differences in Figure 5.14 are not thought to be significant enough to explain all the PAH results reported herein.

A similar set of PAH molar masses to those illustrated in Figure 5.14 were reported by Moldonova et al. [327] in the hot exhaust of a large diesel ship engine. Moldonova et al. also reported a concentration at 302 molar mass whereas the analysis in this work only extends to 276. Therefore there may have been additional PAH at molar masses which were not investigated herein and therefore it is important to note that the total concentration of PAH reported in Table 5.11 may not be the complete picture for this fuel comparison.

Lubrizol stated in a private communication that overall PAH concentrations reported in this work were very low in comparison to those the company had previously observed in carbon black and diesel soot drains. Lubrizol also commented that pyrene was a common PAH found in lubricant absorbed soot and that the soot sampled in this work was observed to have a relatively low pyrene component by comparison.

It is thought that the generally very low PAH concentration for the PAH samples discussed in Chapters 5, 6 and 7 result from the engine conditions and sample location. The engine was operated at rated power with exhaust manifold temperatures of 530-650°C at the point where the soot was sampled. Since PAH are largely concentrated on the surface of soot through condensation of exhaust matter [25] (Section 2.4.4); the conditions would have constrained the amount of

Thermogravimetrical Analysis

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PAH that could have condensed onto the soot as the sample cooled down in the sample line between the exhaust manifold and the thimble, Figure 3.24. This is also a possible indication that the soot surface SOF concentration for the soot sampled at the exhaust manifold in this work was also generally low, which strengths the earlier discussion of this topic in Section 5.5.3.

5.8 Thermogravimetrical Analysis

Presented in Table 5.12 are the thermogravimetrical results for the 16.5:1 DPF sampled soot where 'DPF' denotes the origin of these samples. Note: the limited soot sample mass for the exhaust manifold samples meant it was infeasible to undertake the thermogravimetrical analysis on these samples.

	RT to 300 °C	300 to 400 °C	400 to 700 °C	700 to 1000 °C	Residue at 1000 °C
Description	Oil Residue & Lighter Ends	Polymers & 'Sludge'	Mostly Traditional 'Soot'	Additional Carbonaceous Content	Non-combustible 'Ash'
16.5:1 DPF, EN590	1	0.5	84.1	0.4	14
16.5:1 DPF, PC9	1	0.6	85.4	0.2	12.8
16.5:1 DPF, B100	3.1	1.9	49.9	3.6	41.5

Thermogravimetrical analysis of the DPF collected soot detailed in Table 5.12 shows that the two mineral fuels were very similar across the 300-1000°C temperature range being composed of around 85% soot. The biodiesel soot by contrast was composed of 50% soot and 41.5% ash, Figure 5.15.





A contributing factor was the very low soot concentration in the exhaust gas for the biodiesel fuel which necessitated a collection period of 2 hours vs. the 20 min for both mineral fuels. Thus, the proportions of inorganic matter to momogravimotrical v maryolo

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carbonaceous matter in the B100 soot would be inherently high as was discussed previously in Section 5.4.

Table 5.12 also reveals that for temperatures up to 300°C the percentage of mass lost for the B100 soot was over three times that of the two mineral fuel soot samples which indicated the B100 soot had a higher proportion of lighter SOF. This finding supported the prior reasoning in Section 5.5.2 where condensed HCs were identified as a potential cause for the large disparity in the soot morphology observed at the exhaust manifold between the mineral and B100 soots. The conclusions in Section 4.4 attribute the higher B100 HC emissions to physical fuel properties such as density and viscosity which were quite different to the two mineral fuels, Appendix 1 (Table A1.1). This finding of a greater biodiesel fuel SOF fraction is reported in studies in literature which compare mineral and biodiesel soot SOF [306].

Interestingly, it is also reported in literature that biodiesel based fuels result in exhaust volatiles with higher molecular weights and higher boiling points than for mineral fuels [326] for which there is potential evidence in Figure 5.15. Therefore it is possible that more of the B100 fuel volatiles condensed onto the soot earlier in the sampling system sample line than occurred for the mineral fuels, thus further increasing the B100 soot fraction of volatiles at the ceramic thimble and DPF. Additionally, the reduced B100 carbonaceous soot mass would almost certainly have encouraged greater SOF adsorption on individual particles subject to the temperature and saturation conditions in the sampling system [6, 24].

Referral back to the soot total bulk inorganics with the sulphur negated, Figure 5.6; shows an overall distribution of the relative non-sulphur bulk inorganics across the three soots which correlate closely with that of the residue at 1000°C in Figure 5.15 i.e. the ash or non-combustible component of the soot. This is to be expected as the samples described in Figure 5.15 were collected using a DPF located in the exhaust approximately 5m downstream (Section 3.5.2) of a diesel oxidation catalyst and thus PC9 soot sulphur would have been greatly reduced through reactions which transformed the sulphur into sulphur compounds (H_2SO_4). This finding is considered in more detail throughout Chapter 7 where soot evolution in the exhaust is discussed.

Concluding Remarks

5.9

5.9 Concluding Remarks

The XPS surface elemental composition analysis revealed that the three fuels produced soot with markedly similar surface elemental composition with the dominant element being carbon followed by oxygen. Sulphur was detected only on the surface of the PC9 fuel soots and correlated with the 497ppm fuel sulphur content. Sulphur on the surface of the PC9 fuel soot appeared to increase the surface O/C ratio and this correlated with a higher carboxylic and total surface acidity suggesting a strong link between soot surface oxidation and surface acidity which is modulated through adsorption of sulphur from the fuel.

The ICP bulk elemental composition results revealed a similar total percentage weight of inorganics in the samples once the effects of fuel rate, lubricant consumption rate and exhaust soot concentration were accounted for. This indicated a strong sensitivity to each of these factors. The main contaminating inorganic elements in all three samples were (Ca, Fe, Na, S, Zn) in order of concentration indicating fuel, lubricant and engine metallurgy as sources.

Commonality between the mineral soot morphological characteristics contrasted with the distinct B100 soot morphology. A structural model was proposed describing B100 soot with a partially hollowed out core in which internal voids and pores are opened through more aggressive oxidation to produce a low surface area, high pore volume and high density. These morphological distinctions are postulated to be strongly linked to the higher XPS surface O/C ratio of the B100 soot and greater concentration of inorganic elements.

6 Soot Physiochemical Properties for High and Low Compression Ratio

6.1 Introduction

This chapter presents the results and analysis for soot produced with three different fuels at rated engine power. The aim of this chapter is *to* understand how the reduction in geometric compression ratio from 19.5:1 to 16.5:1 affected the soot physiochemical properties across the three fuels investigated. The samples were collected during the experiments described in Section 3.1.5.3 and samples from both the exhaust manifold with the ceramic thimble sampling system Section 3.5.1 and the DPF Section 3.5.2 are utilised in this chapter.

6.2 Data Selection and Grouping

The data selection for the analysis of compression ratio influence on exhaust soot was complicated by the constraint of having to distribute all nine soot analysis methods across both the high and low compression ratio soot samples at the exhaust manifold. The isolated comparison of compression ratio for the exhaust manifold soot therefore was limited to the surface and bulk element results. For a more broader consideration of the effect of compression ratio, the 16.5:1 DPF soot sample surface acidity and PAH results are also considered but this comparison was complicated by the soot evolution in the exhaust which is discussed in Chapter 7. Consequently, the results discussed in this chapter are grouped as detailed in Table 6.1.

Soot Characteristic	19.5	16.5	Section
Surface Elemental	19.5:1 Exhaust Manifold	16.5:1 Exhaust Manifold	6.3
Bulk Elemental	19.5:1 Exhaust Manifold	16.5:1 Exhaust Manifold	6.4
Surface Acid Functionality	19.5:1 Exhaust Manifold	16.5:1 DPF	6.5
Polycyclic Aromatic Hydrocarbon Profile	19.5:1 Exhaust Manifold	16.5:1 DPF	6.6

Table 6.1: Compression Ratio and Soot Analysis, Data Selection and Grouping

Soot Surface Elemental Composition

6.3 Soot Surface Elemental Composition

Table 6.2 summarises the soot surface carbon, oxygen, sulphur and chlorine as well as the ratios of surface oxygen/carbon and sulphur/carbon for the three fuels investigated. All soot samples were collected at the exhaust manifold with the Ceramic Thimble (CT) apparatus, Section 3.5.1.

 Table 6.2: 19.5:1 and 16.5:1 Exhaust Manifold Soot Surface Elemental Composition (XPS)

	wt%C	wt% O	wt% S	wt% Cl	O/C		S/C	
Description					ratio	precision	ratio	precision
19.5:1 CT, EN590	92.5	7.5			0.0805	0.0118		
19.5:1 CT, PC9	88.3	9.9	1.545	0.3	0.1121	0.0127	0.018	0.0059
19.5:1 CT, B100	92.0	8.0			0.0865	0.0119		
16.5:1 CT, EN590	94.1	5.9			0.0627	0.0114		
16.5:1 CT, PC9	91.6	8.4	0.050		0.0917	0.0120	0.001	0.0055
16.5:1 CT, B100	92.4	7.6			0.0823	0.0118		

Note: The estimated error for the surface elemental analysis was (+/-0.5%) for each element and this must be considered when the changes in the measured surface elemental composition with compression ratio fall within this boundary, the error is included in the figures in this section as a reference.

Figure 6.1 details the change in surface carbon content with the reduction in compression ratio and clearly the surface carbon concentration increased for all soots, with the increases in the two mineral fuel soots being the greatest.



Figure 6.1: 19.5:1 to 16.5:1 Soot Surface Carbon Change for EN590, PC9 and B100 fuels (XPS)

Figure 6.1 illustrates that the increase in the B100 soot surface carbon concentration only just exceeded the error bounds and therefore the change in the surface composition of the B100 soot to the reduction in compression ratio was somewhat less relative to that observed for the mineral fuel soots.

Soot Surface Elemental Composition

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Figure 6.2 presents the associated change in surface oxygen concentration with the reduction in compression ratio and illustrates that there was a consistent reduction observed for all soots. Interestingly, whereas the increase in carbon was somewhat higher for the PC9 soot compared to the EN590 soot, the reduction in oxygen was observed to be very similar. For this to occur clearly other surface element concentrations also had to change, these were sulphur and chlorine and are discussed later.





The surface carbon and oxygen changes presented in Figure 6.1 and Figure 6.2 resulted in a general reduction in the surface O/C ratio for all soots in response to the reduction in compression ratio and this is captured in Figure 6.3. With the exception of the mineral PC9 fuel for the 19.5:1 experiment, there was little or no sulphur or chlorine found in the soot surface. Thus, the change in the surface O/C ratio for all the other experiments reflected directly the change in the carbon/oxygen ratio alone.

Figure 6.3 details how the surface O/C reductions observed for the two mineral diesel fuels were similar with the EN590 fuel surface O/C reducing 22.1% and in the case of the PC9 fuel the O/C ratio reduced 18.2%; the biodiesel soot by contrast showed a reduction of only 4.9%. For the B100 soot the reduction was within the measurement error and thus the observation was less certain for this soot. The reduction in the soot surface O/C ratio was the inverse of the change in the AFR for these experiments which Table 4.11 Part A detailed as having increased by 4.1% for EN590, 5.4% for PC9 and 1.2% for the B100 experiments.



Figure 6.3: 19.5:1 to 16.5:1 Soot Surface O/C Ratio Change for EN590, PC9 and B100 fuels (XPS)

Additionally, the exhaust O_2 measurements for these experiments showed increases of 14.9, 14.0 and 21.4% for EN590, PC9 and B100 fuels respectively and reductions in NO_x of 23.1, 26.9 and 17% respectively. Consequently, the surface O/C reduction for all soots with the compression ratio reduction was opposite to the exhaust O_2 concentration change but did align with the reduction in NO_x. The exhaust soot were all sampled at the exhaust manifold and therefore the residence time of the soot in the exhaust gas as it exited the cylinder was very short and thus the effects from surface oxidation processes as soot evolves in the exhaust (Chapter 7) would have been small for these samples. These findings indicated that the concentration of exhaust O_2 was not the primary factor governing the soot surface O/C ratio for the young soot sampled at the exhaust manifold. Rather, it indicated that another factor likely relating to the conditions in-cylinder and therefore associated with the compression ratio reduction was responsible. This was most probably the aligned reduction in NO_x.

Consequently, it is useful at this point to refer back to Section 5.6 where it was recognised that the fairly high acidity of the 19.5:1 exhaust manifold soot was related to the also high surface O/C ratio for this soot. This however failed to align with the low AFR of ~ 19:1 for the experiments and the fact that the soot was relatively young, thus limiting the time for surface oxidation to occur. It was therefore postulated that the high temperatures of the operating condition had caused very high concentrations of NO_x and it was the NO_x which was reacting with the soot surface. The high cylinder temperatures were thought to be acting

such as to increase the rate of the NO_x -soot reaction to form the surface functional groups.

If this postulation is valid, then the reduction in compression ratio must have acted to reduce the in-cylinder peak temperatures. Consequentially, closed cycle thermodynamic analysis of the cylinder pressure data (Section 3.3.5) was conducted and the results are presented in Figure 6.4. This shows the relative peak cycle temperature estimates for the six soot collection experiments.

The results presented in Figure 6.4 confirm that the in-cylinder peak temperatures indeed reduced with the reduction in compression ratio (the reader is also encouraged to review the average closed cycle temperatures presented in Table 4.15). It is therefore postulated that the reduction in compression ratio acted to reduce the peak and average in-cylinder temperature and this in turn both reduced the formation of NO_x (-23.1, -26.9 and -17% for EN590, PC9, B100 respectively) and also reduced therefore the reaction rate between the NO_x and the soot; thereby resulting in the observed lower surface O/C ratio in the 16.5:1 compression soot samples Figure 6.3.



Figure 6.4: Cylinder Pressure Closed Cycle Analysis Estimated Peak Cylinder Temperature

Additionally, Figure 6.4 illustrates that the reduction in estimated in-cylinder peak temperature was greatest for the two mineral diesel fuels with the reduction in compression ratio with the reduction for the B100 fuel being far lower (the reduction was less significant due to a higher initial IMAT for the B100 16.5:1 experiment compared to the IMAT used in the two 16.5:1 mineral fuel

Soot Surface Elemental Composition

experiments, Table 4.10 Part B). Thus, the change in estimated in-cylinder temperature correlates to the reductions in surface O/C ratio for the three soots as indicated in Figure 6.3, therefore strengthening the postulation of the compression ratio induced change in the in-cylinder peak temperature being the primary factor responsible. It is likely therefore that this smaller reduction in in-cylinder temperature for the B100 fuel contributed to the smaller reduction in B100 NO_x and soot surface O/C ratio, Figure 6.3. However, it is postulated that since the reduction in the B100 soot O/C ratio was far less significant compared to the equivalent mineral soots, that additional factors such as the soot morphology also contributed to this result (such as surface area and soot structure).

It is worth noting that in Section 4.3.3 it was determined that the compression ratio reduction resulted in a 17.5% average reduction in peak cylinder pressure and only a 2.6% average reduction in average cylinder temperature, Table 4.15. Thus, the forgoing analysis indicates that the smaller scale change in the incylinder temperatures was in fact the most significant factor in the changes to the soot surface composition.

Thus, to summarise; it is postulated that a reduction in compression ratio will act to reduce cylinder temperature and NO_x formation and this in turn will result in soots with a lower surface oxygen concentration at like-for-like engine operating conditions – somewhat regardless of the AFR change. Following from the earlier discussion in Section 5.6; soots from lower temperature combustion will also have reduced surface acid functionality which from literature is reported by Covitch et al. [138] and Ripple et al. [165] to make soot more oleophilic i.e. potentially more soot will be absorbed into the oil and or interact with the oil during combustion.

In addition to the aforementioned O/C ratio findings, sulphur and chlorine were also observed on the surface and both changed with the engine compression ratio. Sulphur was observed on the surface of the PC9 soot alone and appeared therefore to be related directly to the sulphur content of the PC9 fuel which was 497 ppm relative to 6 ppm for the mineral EN590 fuel and < 10 ppm for the biodiesel fuel, Appendix 1 (Table A1.1). Significantly, the concentration of surface sulphur for the mineral PC9 soot was observed to fall by 96.8% with the reduction in compression ratio.

Soot Surface Elemental Composition

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This significant reduction in surface sulphur concentration aligned with the O/C ratio reduction and therefore suggested it was coupled to the same temperature based processes that were reducing the adsorption of oxygen molecules on the soot surface. Referring to Figure 6.1 and Figure 6.2, it is clear that the carbon content of the PC9 soot surface grew significantly with the reduction in compression ratio to offset the reduction in surface sulphur; with surface oxygen concentration reducing approximately equally to the reduction seen for the EN590 soot. Thus, it appeared that the reduction in sulphur for the PC9 soot did not result in the loss of additional oxygen.

This is an important observation as it was postulated in Section 5.3 that the PC9 surface sulphur alone was acting to inflate the surface oxygen concentration of the 19.5:1 soot. The substantial reduction in sulphur at 16.5:1 however does not appear to have resulted in a more significant reduction in surface oxygen for the PC9 soot with compression ratio change, Figure 6.2, and thus the sulphur-oxygen proportionality relation advised in Section 5.3 would appear to be more complex. As sulphur adsorbed onto the soot surface is typically in the form of sulphates [24], it would appear that the same temperature driven processes that reduced the soot surface oxygen concentration also acted to reduce the sulphur adsorption, likely due to the processes being linked chemically.

There is however a further possibility which relates to the observation of the measured concentration of HCs in the exhaust with the PC9 fuel at 16.5:1 compression being roughly half of what was observed at 19.5:1, Table 4.10 Part C. With a lower concentration of volatiles in the exhaust, it was possible that there was a reduced concentration of these volatiles condensing onto the soot in the sample line at the lower compression ratio and this therefore potentially reduced the sulphur surface deposition. However, as the reduction was only 50% compared to the 96.8% for the surface sulphur, this is thought not to be a full explanation on its own. Importantly, referral to Table 6.3 in the following section shows that sulphur comprised 1% of the PC9 soot bulk inorganics at the 16.5:1 compression ratio but the surface concentration was just 0.05%, Table 6.2. Such a discrepancy is better explained by the earlier in-cylinder processes postulation rather than a simple reduction in adsorbed SOF. Consequently, the hypothesis for in-cylinder temperature driven processes being responsible, is the more likely scenario.

Finally, chlorine was detected on the surface of the 19.5:1 PC9 soot at 0.3% weight but at 16.5:1 no chlorine was detected. As detailed in Section 5.3 this

6.4

observation of chlorine was not repeated in any of the other soot samples so its origin and cause were not clear though it was concluded to most likely have been the result of sample contamination during sample handling after the engine experiment. It was also postulated in Section 5.3 that the chlorine simply acted to reduce equally the surface concentrations of carbon, oxygen and sulphur. In light of the aforementioned sulphur and O/C ratio observations (i.e. no significant O/C reduction even though sulphur reduced significantly) with the reduction in compression ratio, it is possible however that the chlorine acted to positively bias the oxygen concentration in the 19.5:1 PC9 soot sample rather than sulphur but there is no way to know this for certain with the available information.

In conclusion, the compression ratio reduction effected important changes in soot surface chemistry, these were largely through what is postulated to be temperature driven physiochemical processes that occur in-cylinder during soot formation and oxidation.

6.4 Soot Bulk Elemental Composition

Table 6.3 presents the percentage weight of inorganics for the bulk composition of the sampled exhaust soot for both high and low compression ratio; this data has been converted to the percentage contribution of each element to the total sample inorganics and this result is presented in Table 6.4.

	#1269 ICP: Bulk Inorganic Contaminants by Acid-digestion ICP (wt%)												
Description	%Ca	%Cu	%Fe	%Mg	%Mn	%Na	%Р	%S	%Si	%Zn	%AI	%Cd	Total wt%
19.5:1 CT, EN590	0.083	0.003	0.034	0.002	0.012	0.000	0.016	0.001	0.001	0.033	0.000	0.000	0.185
19.5:1 CT, PC9	0.078	0.002	0.043	0.002	0.006	0.000	0.002	0.282	0.001	0.028	0.000	0.000	0.444
19.5:1 CT, B100	0.277	0.015	0.171	0.005	0.010	0.083	0.051	0.000	0.017	0.105	0.000	0.000	0.734
16.5:1 CT, EN590	0.250	0.000	0.066	0.023	0.000	0.000	0.043	0.000	0.000	0.056	0.000	0.000	0.438
16.5:1 CT, PC9	0.320	0.000	0.110	0.021	0.000	0.000	0.072	1.060	0.000	0.077	0.000	0.000	1.660
16.5:1 CT, B100	2.880	0.000	1.080	0.350	0.000	0.450	1.030	0.014	0.000	0.560	0.000	0.000	6.364

Table 6.3: 19.5:1 and 16.5:1 Exhaust Manifold Soot Bulk Elemental Composition (% weight) (ICP-MS, Corrected)¹⁰

Table 6.4: 19.5:1 and 16.5:1 Exhaust Manifold Soot Bulk Elemental Composition (%weight/total % weight) (ICP-MS, Corrected)

	#1269 ICP: Bulk Inorganic Contaminants by Acid-digestion ICP (% of Total wt% Inorganics)									-			
Description	%Ca	%Cu	%Fe	%Mg	%Mn	%Na	%Р	%S	%Si	%Zn	%AI	%Cd	Total %
19.5:1 CT, EN590	44.865	1.622	18.378	1.081	6.486	0.000	8.649	0.541	0.541	17.838	0.000	0.000	100.000
19.5:1 CT, PC9	17.568	0.450	9.685	0.450	1.351	0.000	0.450	63.514	0.225	6.306	0.000	0.000	100.000
19.5:1 CT, B100	37.738	2.044	23.297	0.681	1.362	11.308	6.948	0.000	2.316	14.305	0.000	0.000	100.000
16.5:1 CT, EN590	57.078	0.000	15.068	5.251	0.000	0.000	9.817	0.000	0.000	12.785	0.000	0.000	100.000
16.5:1 CT, PC9	19.277	0.000	6.627	1.265	0.000	0.000	4.337	63.855	0.000	4.639	0.000	0.000	100.000
16.5:1 CT, B100	45.255	0.000	16.970	5.500	0.000	7.071	16.185	0.220	0.000	8.799	0.000	0.000	100.000

¹⁰ Table 6.3 and Table 6.4 present corrected ICP-MS results; this involved negating foreign element contamination which was identified in some samples (Refer to Appendix 8).

The total percentage weight of inorganics was observed to change with the reduction in compression ratio and this is detailed in Figure 6.5 for the six experiments defined in Table 6.3. The relative total inorganics between the different fuel soots was quite different at the two compression ratios, with the relative difference between the two mineral soots increasing at reduced compression.



Figure 6.5: 19.5:1 and 16.5:1 Exhaust Manifold Soot Total % Weight Inorganics (ICP-MS, Corrected)

The most dramatic change however was the increase in the B100 soot total inorganics and this is illustrated in addition to the factor change in inorganics in Figure 6.6.





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Figure 6.6 also describes how in the case of the mineral EN590 and PC9 soot, the total inorganics increased by factors of 2.4 and 3.7 respectively with the reduction in compression ratio. Relative to this, the biodiesel soot sample total inorganics increased by a factor of 8.7, thus twice that observed for the two mineral fuel derived soots.

Further analysis of Table 6.3 reveals that at 19.5:1 compression, the PC9 soot total inorganics were a factor 2.4 greater than those of the EN590 soot and at 16.5:1 compression this factor increased to 3.8. The difference in the mineral soot total inorganics at 19.5:1 compression was identified in Section 5.4 to be principally related to the sulphur from the PC9 fuel. With the reduction in compression it also appears that again PC9 fuel sulphur is largely responsible for the differentiation between the EN590 and PC9 soot. The effects of the engine compression ratio reduction are best illustrated through the calculation of the change in contribution of each element to the total sample inorganics. This is computed from Table 6.3 by simply subtracting the individual element wt % concentration at 19.5:1 from the value at 16.5:1 i.e. for EN590 Ca (0.250-0.083 = 0.167 wt %). These processed results are presented in Figure 6.7.

Figure 6.7 clearly illustrates that the B100 soot experienced by far the most significant change across all principle soot inorganic elements and that the observed increases for each element appeared to mirror the individual element increases for EN590 and PC9 soots with approximately the same scaling factor for each element i.e. no one particular element appeared to be responsible for the significant increase in total soot inorganics for the B100 soot.





To be more precise concerning how the individual element concentrations for each soot changed with compression ratio reduction, it is necessary to calculate the individual elemental wt % change as a percentage of the total change in inorganics in the sample i.e. for Ca in the EN590 samples from Table 6.3; (0.250-

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0.083/(0.438-0.185) x 100 = 66%. This calculation therefore qualifies the extent to which the change in concentration of each element with the reduction in compression contributed to the total inorganic change for that fuel. The results for all three fuel soots are presented in Figure 6.8.



Figure 6.8: Change in Soot Inorganic Elements (% wt/total % wt) at the Exhaust Manifold Between 19.5:1 to 16.5:1 for EN590, PC9 and B100 fuels (ICP-MS, Corrected)

Figure 6.8 illustrates that for both the EN590 and B100 soots, the increase in total inorganic fraction of the soot samples was composed of increases in (Ca, Fe, P, Mg, Zn) in order of significance and that the increases in the individual elements were similar in magnitude for both fuels, implying a related mechanism was behind both. For the PC9 soot, the increase in soot bulk sulphur was by far the biggest component of the change in inorganics for this soot and acted to reduce the relative contribution from the other elements; thereby making comparison with the EN590 and B100 bulk elemental change difficult without first negating the sulphur influence for the PC9 soot. Since PC9 fuel sulphur was approximately 100 times higher at (497 ppm) versus (<10 ppm) concentration in the other two fuels, Appendix 1 (Table A1.1); attributing PC9 soot sulphur to the high concentration in the fuel was logical.

From Table 6.4 it is observed that the contribution of sulphur to the PC9 soot total inorganics at 19.5:1 was 63.5% and then this increased slightly to 63.9%

with the reduction in compression ratio. This contrasted with the 96.8% reduction in surface sulphur discussed previously in Section 6.3. Indeed, from Table 6.3 it is clear that at 19.5:1 compression the PC9 soot sulphur was roughly 0.28% of the soot bulk compared with 1.5% concentration at the surface. In contrast at 16.5:1 compression, the sulphur was 1% of the soot bulk and yet the surface concentration was 0.05%. These contrasting observations are somewhat difficult to reconcile as they clearly point to complex processes occurring during soot inception, formation and oxidation in the cylinder.

A postulation that potentially explains these observations is as follows: the reduction in compression ratio acted to increase the entrainment of inorganics (as indicated in Figure 6.5) early in the soot formation process (possibly due to the lower reaction temperature and pressure and thus impaired fuel atomisation and fuel mixing). This then resulted in the subsequent reduction in free sulphur in the cylinder later in the soot formation oxidation process. i.e. at the lower compression ratio the fuel derived sulphur remained bound to the HCs of the fuel and/or the other inorganic matter and hence less well distributed in the cylinder. This therefore meant there was a greater probability the fuel sulphur was localised to the soot precursors (possibly even acting as precursor molecules) and then remained chemically bound to these soot precursors as they developed thus entraining the majority of the fuel borne sulphur into the soot bulk. As the combustion proceeded there was then far less sulphur free within the cylinder and the temperatures of the reactions were also lower so the chemisorption of sulphates onto the soot was reduced leading to the lower soot surface sulphur and oxygen concentration and the higher carbon concentration, Section 6.3.

Additionally, the monitored exhaust temperatures (Table 4.10 Part B) failed to exhibit any consistent change with compression reduction and therefore there was unlikely to have been any significant change in the condensation of volatiles onto the soot in the sample line with the compression ratio reduction; thus supporting the above hypothesis that the changes in PC9 soot sulphur must have occurred in-cylinder.

Therefore with the available information the proceeding hypothesis seems a valid explanation and suggests that lower engine compression can be used as a tool to influence soot surface reactivity through management of the temperature based reactions and also any fuel borne sulphur. Indeed, these are some of the most interesting findings from the compression ratio investigation and point to a potentially interesting avenue for further future research.

There were two metal elements in the soot bulk inorganics which appeared to have very specific responses to the compression ratio reduction for all three fuels; these were (Cu, Mn) Figure 6.8. For both elements the reduction in compression appeared to result in the concentrations of these elements decreasing to the point that they went below the detection threshold of the ICP-MS measurement, Table 6.3. It is likely therefore that this was because these two elements did not increase in concentration like the other elements with the compression ratio reduction but instead they remained unchanged in concentration and thus became far less significant in the soot samples. It is postulated that these two metals may therefore have come from the fuel system as firstly the fuel rate did not change significantly across the experiments, Table 4.10 Part A, and secondly the elements which increased in concentration appeared to derive from the lubricant and engine cylinder metallurgy (as discussed later in this section); so (Cu, Mn) must have derived from elsewhere.

To confirm if PC9 soot behaviour followed that of the EN590 and B100 soots, the PC9 data presented in Figure 6.8 was re-evaluated with the sulphur component negated in both the 19.5:1 and 16.5:1 sample groups and the results from this analysis are presented in Figure 6.9. With sulphur isolated, Figure 6.9 indicates that the individual elemental contribution to the increase in inorganic content in the soot was actually broadly similar across the three fuels investigated.



Figure 6.9: Change in Soot Inorganic Elements (% wt/total % wt) (with Sulphur Negated) at the Exhaust Manifold Between 19.5:1 to 16.5:1 for EN590, PC9 and B100 fuels (ICP-MS, Corrected)

Although the result in Figure 6.9 is therefore very useful, it does not account for the large differences in the total inorganics concentration following engine compression ratio reduction as was illustrated earlier in Figure 6.5. Rather, the result of Figure 6.9 implies that this broad increase in organics resulted from approximately equal contributions in each element across the spectrum of elements analysed.

It was shown previously in Section 5.4 that differences in fuel consumption, exhaust soot concentration and lubricant consumption could be used to explain the different concentrations of the total inorganics in the three fuel soots at 19.5:1 compression. Indeed, a methodology was presented that detailed how the total inorganics of each sample could be scaled in proportion to the differences in these factors across the 19.5:1 experiments to result in almost equalisation of the sample total wt % of inorganics. Thus, following the same methodology; referral to Table 4.11 Part A reveals that the fuel rate, exhaust soot concentration and lubricant consumption rate all changed with compression ratio reduction and that the changes observed were not consistent across the three fuels and compression ratio reduction. The implication of this is that the initial result presented in Figure 6.5 is masking information about the actual mechanisms behind the changes in soot total inorganics with compression ratio reduction. To confirm this, data processing like that utilised in Section 5.4 is required.

The first step is to consider the differences between fuel consumption and exhaust soot concentration; this is captured in Table 4.14 as the normalised FSF for each experiment. These normalised FSF factors have been applied to the data in Table 6.3 (summarised in Figure 6.5) to scale the ICP-MS results to find the estimated change in total inorganics following the reduction in compression ratio with the effects of fuel rate and exhaust soot concentration negated, Figure 6.10.

Before the result in Figure 6.10 is considered in detail, it is important to reflect on two points regarding the data analysis methodology from which the result derives (for consistency this is repeated from Section 5.4). Firstly, since the AVL 415 smoke meter sample probe was not located in close proximity to the soot sample positions used in this work (Section 3.2.2.5); the simple approach of multiplying the bulk inorganics by the FSF factor was used rather than a more precise quantitative approach. A more precise approach would have required the measurement of carbonaceous soot fraction at the point where the soot was sampled from the exhaust to remove any effects from the loss of carbonaceous

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soot fraction as the soots evolved in the exhaust (Chapter 7). However, this was not technically feasible in this work.

Secondly, the same normalised FSF scaling value has been applied to each element in the individual soot sample ICP-MS results as there was insufficient information and knowledge concerning the contribution of individual elements from the fuel and the lubricant to the soot inorganics to scale elements uniquely. i.e. if the normalised FSF was 0.5, then the wt % each element in a given soot sample was multiplied by 0.5 to adjust the overall inorganics to account for the FSF reported scaling between experiment.



Figure 6.10: 19.5:1 and 16.5:1 Exhaust Manifold Soot Total % Weight Inorganics x Normalised FSF (ICP-MS, Corrected)

The comparison of Figure 6.10 to Figure 6.5 leads to two fundamental observations for the compression ratio reduction influence on soot inorganics:

- There was a step increase in the total wt % of inorganics in all soot samples with the reduction in compression ratio that was independent of the fuel rate change and exhaust soot concentration change.
- 2) The PC9 fuel had by far the greatest concentration of inorganics at both the compression ratios investigated and from Table 6.4 the major inorganics contaminate in the high and low compression PC9 soot samples was sulphur (65.5 and 63.9% of total inorganics at 19.5:1 and 16.5:1 respectively).

Thus, repeating the calculation steps which yielded Figure 6.10 but with sulphur isolated was the next logical step prior to considering the effect of lubricant consumption. This result is presented in Figure 6.11 and illustrates that with sulphur negated, the EN590 and PC9 soot total inorganics at 19.5:1

compression were effectively very similar but at 16.5:1 they remained quite distinct. The total inorganics for the B100 soot also remained distinct at both compression ratios, so there were clearly additional factors that needed to be accounted for.



Figure 6.11: 19.5:1 and 16.5:1 Exhaust Manifold Soot Total % Weight Inorganics (with Sulphur Negated) x Normalised FSF (ICP-MS, Corrected)

It was found in Section 5.4 that the inclusion of oil consumption in the scaling of ICP-MS data resulted in the total concentration of the scaled inorganics at 19.5:1 for the three soots being almost identical, Figure 5.9. Thus it is important to also include oil consumption here to confirm that the apparent step increase in concentration of inorganics with reduced compression ratio, which is implied from the result presented in Figure 6.11, is not solely attributable to a change in oil consumption rate. Lubricant consumption rate was found to be influenced by the reduction in compression ratio and for clarity Table 6.5 and Figure 6.12 present and illustrate the lubricant consumption data taken from Table 4.10 Part A.

 Table 6.5: 19.5:1 and 16.5:1 Soot Collection Experiment Lubricant Consumption

 Summary

Experiment	Lubricant Consumption (g/h)	Lubricant Consumption Factor
19.5:1 EN590	27.9	0.49
19.5:1 PC9	28.8	0.46
19.5:1 B100	16.8	0.79
16.5:1 EN590	24.6	0.54
16.5:1 PC9	37.8	0.35
16.5:1 B100	13.3	1

Table 6.5 includes a normalised non-dimensional factor 'Lubricant Consumption Factor' to represent the difference between the least to greatest
lubricant consumption rate across the six soot collection experiments. It is calculated for each experiment by equating the factor to 1 for the lowest lubricant consumption rate, i.e. 13.3 g/h for the 16.5:1 B100 experiment, and then dividing 13.3 by the lubricant consumption for each of the other experiments in turn.



Figure 6.12: 19.5:1 and 16.5:1 Soot Collection Experiment Measured Lubricant Consumption Rate

It is therefore assumed (as originally discussed in Section 5.4) that the greater the measured rate of lubricant consumption, the greater the concentration of lubricant derived inorganics in the soot. Thus, multiplying the 'Lubricant Consumption Factor' from Table 6.5 with the normalised FSF and total wt % product result presented earlier in Figure 6.11; leads to the result presented in Figure 6.13.





Thus, Figure 6.13 repeats the finding from Section 5.4 (Figure 5.9) for the 19.5:1 compression ratio, specifically that equating for all suspected sources of inorganics and the soot carbonaceous fraction leads to equalisation of the total inorganics in the samples, thus providing further confidence in these postulated relationships and the methodology used to account for them in the ICP-MS data. However, at the lower 16.5:1 compression, it is observed that although the total inorganics of the EN590 and PC9 soots are similar, the scaled B100 soot total inorganics concentration is more than double by comparison.

The commonality illustrated in Figure 6.13 between the total inorganics in the two mineral fuel soots at each compression ratio gives confidence that there was indeed a step increase in inorganic concentration in the soot that resulted from the reduction in compression ratio - as was suspected earlier from the interim result Figure 6.11. Therefore, this finding suggests that there must remain an additional factor or mechanism not accounted for in the proceeding analysis which when combined with the reduction in compression caused the observed increase in soot inorganic concentration. Further, this factor or mechanism was clearly far more significant for the B100 soot suggesting that something associated with the B100 fuel amplified the effect.

The factor 2 higher 16.5:1 B100 total sample inorganics following ICP-MS result scaling is postulated to have several possible root causes:

- There was an error in one of the factors (most likely lubricant consumption rate since fuel rate and exhaust soot concentration were averaged for the entire experiment).
- 2) The B100 fuel and the soot at 16.5:1 compression behaved somewhat differently in response to the compression ratio reduction through some mechanism not applicable to the mineral fuel soots.
- 3) There was a combination of 1 and 2.

It is believed that scenario 3 is the most likely and that a specific set of circumstances occurred for this experiment which stemmed ultimately from the physical properties of the fuel.

Firstly, the B100 fuel used in this work was ~6% more dense and had double the viscosity of the mineral fuels, Appendix 1 (Table A1.1). Thus there was a higher mass of fuel in the cylinder in each combustion cycle and combined with the higher viscosity likely meant there was greater fuel penetration and thus likely fuel impingement on the cylinder walls. This could then have resulted in fuel

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dilution of the lubricant, which if sufficiently excessive could then have masked any actual increase in lubricant consumption.

To recount, lubricant consumption rate in this work was measured by regularly checking the engine lubricant level and then adding fresh lubricant to maintain the level, the lubricant added was then used to compute the consumption rate. Consequently, the very low lubricant consumption rate for the 16.5:1 B100 experiment, Figure 6.12, was a strong indicator for excessive fuel dilution of the lubricant. It is therefore possible that when using the factor of 1 for the 'Lubricant Consumption Factor' for the 16.5:1 B100 experiment, Table 6.5, that the true factor was somewhat lower, therefore explaining the much higher apparent concentration of total inorganics relative to the other samples as described by Figure 6.13. Further, the additional 16.5:1 B100 experiment observations: 1) the extremely high 600ppm HC emissions (Table 4.10 Part C) and 2) the extreme injector coking for this experiment, Appendix 9; add supporting evidence to the postulation that this experiment observed significant wall wetting and thus likely fuel dilution of the lubricant and other possible mitigating factors that could contribute to the result of Figure 6.12 and Figure 6.13.

It is useful therefore to now consider whether there is any additional information in the individual element contributions to the total inorganics which might assist the understanding of the preceding 16.5:1 B100 experiment finding. Referring again to the distribution of elements that comprise the total inorganics in the soot samples in Table 6.3; it is possible to re-calculate from this table the contribution of each element to the total soot sample inorganics for each sample but with sulphur negated to enable the comparison across the three fuels at each compression ratio without the masking effect of sulphur. This result is presented in Figure 6.14 for 19.5:1 compression and Figure 6.15 for 16.5:1. Figure 6.14 and Figure 6.15 also incorporate the equivalent wt % of the lubricant inorganic component; taken from Appendix 2 (Table A2.1) to assist the result interpretation.

Comparison of Figure 6.14 and Figure 6.15 reveals that at both compression ratios, the contribution of individual elements to the total wt % inorganics was quite similar in terms of the broad pattern. Indeed, there was no specific element or series of elements which explain the relatively higher concentration of inorganics in the 16.5:1 B100 sample. Rather, it is observed that the concentration of elements matches closely the general pattern across the six experiments. It is also observed that the concentration of primary soot inorganics

(Ca, P, Zn) match fairly closely to the relative concentration of these elements in the lubricant.



Figure 6.14: 19.5:1 Exhaust Manifold Bulk Inorganic Contaminants with Sulphur Contribution Negated and Including Lubricant Element Concentration (% wt/total % wt) (ICP-MS, Corrected)



Figure 6.15: 16.5:1 Exhaust Manifold Bulk Inorganic Contaminants with Sulphur Contribution Negated and Including Lubricant Element Concentration (% wt/total % wt) (ICP-MS, Corrected)

If the change in the concentration of each element in the total inorganics of each sample is now considered between 19.5:1 and 16.5:1 compression i.e. the data in Figure 6.14 is subtracted from the data in Figure 6.15 for each element in turn, then this leads to Figure 6.16. Figure 6.16 shows that across all six soot samples, the compression ratio reduction acted to increase the relative

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concentration of (Ca, Mg, P) in the 16.5:1 soots and reduce the relative concentrations of (Cu, Fe, Mn, Na, Zn).¹¹



Figure 6.16: 19.5:1 to 16.5:1: Change in Exhaust Manifold Bulk Inorganic Contaminants with Sulphur Contribution Negated and Including Lubricant Element Concentration (% wt/total % wt) (ICP-MS, Corrected)

Taken together, Figure 6.16, Figure 6.13 and the earlier Figure 6.9; explain that the reduction in compression ratio resulted in an increase in the overall concentration of inorganics for all soot, Figure 6.13, and that this increase was driven by the further addition of (Ca, Fe, Mg, Na, P, Zn) with the small loss of (Cu, Mn) Figure 6.9; irrespective of the fuel.

The addition of increased Ca was the most significant change followed by approximately equal addition of (Fe, P) and then slightly lower addition of (Zn, Mg), Figure 6.9. These changes which occurred through the reduction in compression ratio then changed the pattern of distribution of elements in the soot samples according to Figure 6.16 with (Ca, P) increasing in proportion to the other inorganics and (Fe, Mn, Zn) reducing in proportion. However, these changes importantly did not grossly change the distribution of elements in the soot inorganics, Figure 6.14 and Figure 6.15.

Thus, as the increase in the concentration of soot inorganics was found to be predominantly forced by the addition of more Ca and then (Fe, P, Zn), Figure 6.9; it is postulated that the reduction in compression ratio primarily increased the relative entrainment of the lubricant derived inorganic contaminates (Ca, P, Zn) into the soot which then resulted in a proportionally smaller increase in metals

¹¹ The small reduction in Si is ignored here as this derives from the contamination issues outlined in Appendix 8, Section A8.2.2.

from the engine metallurgy (Fe, Mg). Secondly, these increases occurred even after factoring in the changes in lubricant consumption so the mechanism was not governed by lubricant consumption rate but by the mechanisms of the sootlubricant interaction occurring at lower compression during combustion.

The postulation of increased soot-lubricant (hence cylinder wall) interaction at the lower compression was supported by several other additional observations. Firstly, the lower measured peak cylinder pressure, Figure 6.17 (a), which details the observed lower in-cylinder charge density which would have caused increased fuel spray tip penetration due to a much weaker 'wall' of gas phase molecules for the fuel molecules to diffuse through. Increased fuel spray penetration would in principle result in the soot forming regions of the spray to be generally closer in proximity to the cylinder wall. Lower cylinder gas pressure would also have reduced the piston ring force and thereby possibly increased the level of residual lubricant on the cylinder walls on the expansion stroke.

A further consideration is that the reduced gas ring pressure would also likely have resulted in increased blowby and on the engine used in this study the crankcase breather returned to the engine air intake so increased blowby could have caused increased mixing of lubricant molecules into the combustion thereby further amplifying the postulated soot-lubricant interaction at the lower compression ratio.





The longer duration of combustion, Figure 6.17 (b), could also have increased the residence time of any developing/evolving soot in the region of the cylinder wall during combustion. This increased soot-lubricant interaction could then have resulted in the increase in proportion of both lubricant and engine metallurgy

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derived inorganic contaminates in the soot, to concentrations greater than observed at the higher 19.5:1 compression ratio.

In respect of the factor 2 higher scaled total inorganics result presented in Figure 6.13 for the 16.5:1 B100 soot; it would appear that this proposed increase in soot-lubricant interaction must have been somewhat more extensive than that which occurred for the two mineral fuels at 16.5:1. This conclusion is supported by the observation of extreme HC emissions for this specific experiment, Table 4.10 Part C, and also it is thought, the significant injector coking that is reported in Appendix 9. A compelling additional observation was the evidence of significant wall wetting from unburned fuel on the inside of the exhaust manifold for the B100 fuel at 16.5:1 compression (Figure A9.4); so it is possible this unburned fuel acted to exacerbate the entrainment of inorganics into the soot.

The specific facets of the B100 combustion at 16.5:1 compression are captured via the following conjecture; firstly it can be postulated that there was impaired B100 fuel atomisation which stemmed from the reduction in compression which reduced the in-cylinder charge density which in turn when coupled to the factor 2 higher viscosity of the B100 fuel and 6% high density, caused increased mass of fuel contacting the lubricant film on the cylinder wall [87]. This then reduced the fuel conversion efficiency which caused a reduction in the soot carbonaceous concentration relative to the B100 19.5:1 experiment. The increased fuel dilution of the lubricant then encouraged more lubricant to combust in the cylinder which increased the concentration of lubricant contaminants (Ca, P, Zn, S) in the cylinder which were then in turn entrained in the soot as it formed. (The soot collection experiment summary presented in Table 4.10, details the measured parameters that support this conjecture).

This postulated increase in lubricant-soot interaction is therefore believed to have been the outline mechanism behind the general increase in concentration of soot bulk inorganics for all soots with the reduction in compression ratio. The details of this mechanism are however harder to define as accounting for the change in lubricant consumption in particular failed to explain the inorganics concentration change which is illustrated in Figure 6.13.

Additionally, there was a distinct lack of sulphur present in the EN590 and B100 soot when sulphur was the element of greatest concentration in the lubricant, Appendix 2 (Table A2.1). Thus, a further finding from this work is a highly likely preferential entrainment into the soot of specific elements from the

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fuel and lubricant and possibly even the engine metallurgy; though the mechanisms governing this remain unknown due to insufficient information.

Consequently, a full description of the fundamentals of the mechanisms occurring within the postulated greater soot-lubricant interaction with lower compression ratio cannot be proposed in this work as this requires more information about the fuel, lubricant and soot interaction at the cylinder wall. This would therefore be a suitable investigation for future research.

6.5 Soot Surface Acid Functionality

The results from surface acidic functionality measurements are presented in Table 6.6 and are defined for both the total and carboxylic acid concentrations. The data for this analysis is drawn from across the exhaust manifold and the DPF soot samples as there was insufficient soot mass to determine the soot surface acidity for the 16.5:1 exhaust manifold soot samples. Consequently, it is necessary in this discussion to separate out the change in acidity caused by the reduction in compression ratio from the change caused by the soot evolution in the exhaust which is discussed in Chapter 7. Additionally, as stated in Section 5.6, the B100 surface acidity data was unavailable for the 19.5:1 exhaust manifold soot sample.

	Boehm Titration										
	Total surface	stdev	Surface carboxylic	stdev							
Description	acids (mmol/g)	(mmol/g)	acids (mmol/g)	(mmol/g)							
19.5:1 CT, EN590	0.621	0.083	0.181	0.008							
19.5:1 CT, PC9	1.163	0.010	0.749	0.001							
19.5:1 CT, B100	NA	NA	NA	NA							
16.5:1 DPF, EN590	0.601	0.045	0.169	0.004							
16.5:1 DPF, PC9	0.575	0.004	0.207	0.004							
16.5:1 DPF, B100	0.850	0.005	0.311	0.016							

Table 6.6: 19.5:1 and 16.5:1 Exhaust Manifold and DPF Soot Surface AcidFunctionality (Boehm titration)

The results detailed in Table 6.6 indicate that in the case of EN590 soot the surface acidity reduced in both carboxylic and total acidity by only 3.2% and 6.6% which contrasted with the significant 50.6% and 72.4% reductions in both carboxylic and total acidity for the PC9 soot. Thus, the percentage of carboxylic/total acidity for EN590 and PC9 soot changed from 29.1% and 64.4% at 19.5:1; to 28% and 36% at 16.5:1, thus becoming closer. Interestingly, the percentage of carboxylic/total acidity for the 16.5:1 compression B100 soot was 37% and thus similar to that observed for the PC9 soot at the same conditions.

This indicates that both soot surface O/C ratio and surface sulphur contribute to soot surface acidity rather than O/C ratio alone, as the two O/C ratios for these soots were quite different, Section 6.3.

These observations imply that soot surface acidity reflects to a degree the O/C ratio and sulphur changes in the soot surface elemental composition between these two sets of soot samples. Therefore this supports the earlier findings of Chapter 5 and also the findings discussed in the next chapter for the soot evolution in the exhaust. Consequently, the change in surface acidity detailed in Table 6.6 appear to be indirectly linked to both compression ratio and soot evolution in the exhaust by the more fundamental driving physiochemical changes such as O/C ratio and surface sulphur concentration. For example:

- The reduction in the in-cylinder temperature for the compression ratio change was postulated to have effected changes in the O/C ratio, Section 6.3.
- The oxidation catalyst reactions in the exhaust are postulated to have resulted in physiochemical changes as indicated by the surface compositional change (Section 7.3) and soot morphological change (Section 7.5); specifically in regard to PC9 soot surface sulphur concentration.

For the B100 soot it was only possible to compare the surface acidity with the other two soots at 16.5:1 compression; however it was possible to use the already established relationship between surface O/C ratio to infer the likely B100 surface acidity at 19.5:1 compression. For example; it can be assumed that the total surface acidity for all soots reduced with the reduction in compression ratio due to the reduction in surface O/C ratio for all three soots, Section 6.3. Since the reduction in surface O/C ratio was more pronounced for the two mineral soots, it can also be assumed that the reduction in surface acidity for the B100 soot.

The results reported in Table 6.6 support this conjecture as both the mineral soots had lower surface acidity at 16.5:1 compression at the DPF. Referral to Figure 7.1 in the following chapter shows that the change in the O/C ratio for both the mineral soots as they evolved in the exhaust was small relative to the B100 soot for which the O/C ratio increased significantly. Consequently it can be assumed that the surface acidity of the B100 soot at 16.5:1 compression, Table

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6.6, was the highest due to the extensive oxidation of this soot in the exhaust rather than it being caused by the reduction in compression ratio.

From this postulation it can be surmised that the soot surface acidity for the B100 soot at 19.5:1 compression reduced slightly with the reduction in compression due to the small reduction in O/C ratio and it then increased somewhat as the soot evolved in the exhaust. Therefore, the B100 soot surface acidity at 19.5:1 compression was most probably less than 0.850 mmol/g and likely just slightly greater than the EN590 soots acidity of 0.621 mmol/g due to the slightly higher surface O/C ratio of the B100 soot at the same conditions, Table 6.2. This consequently defines a relatively small range of 0.621<0.850mmol/g for the B100 soot surface acidy at 19.5:1 compression at the exhaust manifold.

The above reasoning, which is based upon the assumption of a strong proportional relationship between the soot surface O/C ratio and surface acidity and also surface sulphur and surface acidity, is very important. It is shown later in Chapter 9 that this reasoning is based upon fundamental relationships which confirm how the above reasoning is a robust prediction of the behaviour of surface acidity with the reduction in engine compression ratio.

6.6 Soot Polycyclic Aromatic Hydrocarbon Profile

A total of sixteen PAH were investigated in the soot samples and the results are presented across Table 6.7 and Table 6.8. These results are similar to the surface acidity results in that they are for soots taken from both the exhaust manifold 19.5:1 compression ratio samples and the DPF 16.5:1 compression ratio samples. Consequently, it is necessary in this discussion to separate out the change in PAH caused by the reduction in compression ratio and the change caused by the soot evolution in the exhaust as discussed in Chapter 7.

Table 6.7: 19.5:1 and 16.5:1 Exhaust Manifold and DPF Soot Polycyclic AromaticHydrocarbon Profile (Naphthalene to Fluoranthene) (GC-MS)

PAH (µg PAH/g)	Naphthalene	1- methylnapht	2- methylnaphth	Acenaphthylene or biphenylene	Acenaph thene	Phenanthrene	Anthracene	Fluoranthene
Description		naiene	alene					
19.5:1 CT, EN590	2.990	0.297	0.104	0.048	0.022	1.659	0.000	0.045
19.5:1 CT, PC9	0.031	0.005	0.003	0.000	0.002	0.096	0.000	0.010
19.5:1 CT, B100	0.000	0.000	0.000	0.000	0.002	0.010	0.000	0.003
16.5:1 DPF, EN590	0.000	0.000	0.000	0.770	2.800	1.330	0.000	0.000
16.5:1 DPF, PC9	0.000	1.990	1.440	0.520	1.960	1.870	0.000	0.000
16.5:1 DPF, B100	NA	NA	NA	NA	NA	NA	NA	NA

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Soot Polycyclic Aromatic Hydrocarbon Profile

Table 6.8: 19.5:1 and 16.5:1 Exhaust Manifold and DPF Soot Polycyclic AromaticHydrocarbon Profile (Pyrene to Benzo-perylene) (GC-MS)

PAH (µg PAH/g)	Pyrene	Benz(a)anth racene	Chrysene	Benzo(b)fluorant hene	Benzo(k) fluoranth ene	Indeno(1,2,3- cd)pyrene	Dibenz(a,h)a nthracene	Benzo(g,l,h) perylene	total
19.5:1 CT. EN590	0.000	0.014	0.006	0.000	0.027	0.000	0.000	0.000	5.212
19.5:1 CT, PC9	0.001	0.013	0.000	0.000	0.000	0.000	0.000	0.000	0.161
19.5:1 CT, B100	0.003	0.003	0.000	0.000	0.000	0.000	0.000	0.000	0.021
16.5:1 DPF, EN590	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	4.900
16.5:1 DPF, PC9	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	7.780
16.5:1 DPF, B100	NA	NA	NA	NA	NA	NA	NA	NA	NA

Figure 6.18 outlines the total PAH concentration (µg PAH/g) from Table 6.8 for the six soot samples. The absent result for the B100 soot at 16.5:1 is due to sample mass limitations and thus it is not possible to be certain of the relationship of B100 PAH relative to the mineral fuel soots with the reduction in compression ratio. However, the 19.5:1 B100 soot PAH results suggest that the concentrations of PAHs in the B100 soot were generally very low by comparison; so relative to the EN590 and PC9 soots, any effects would have been very small. As reported in Section 5.7, the B100 total PAH concentration is attributed to there being no aromatic content in the original fuel, Appendix 1 (Table A1.1).



Figure 6.18: Total PAH for 19.5:1 Exhaust Manifold and 16.5:1 DPF Soot for EN590, PC9 and B100 Fuels (GC-MS)

Figure 6.18 clearly illustrates how the total PAH concentrations observed for the EN590 soot varied little with compression ratio and soot exhaust evolution, contrasting with the total PAH for the PC9 soot which increased significantly. At 19.5:1 compression at the exhaust manifold the total PAH for the mineral EN590 fuel was measured to be a factor of 32.4 greater than observed for the mineral PC9 fuel but at the lower compression at the DPF, the PC9 fuel soot total PAH was greater by a factor of 1.59. Therefore there was a 6% reduction in the total Soot Physiochemical Properties for High and Low Compression Ratio Soot Polycyclic Aromatic Hydrocarbon Profile

PAH for the EN590 fuel soot and a 4732% increase in the total PC9 soot PAH content.

Since the PAH originated from the base fuel and pyrosynthesis during combustion (Section 2.4.4), the increased DPF PC9 soot PAH concentration suggests this was the result of the compression ratio reduction and/or a significant change in non-PAH related components in the soot as the soot evolved in the exhaust. In Section 7.4, analysis of the PC9 bulk inorganics reveals a significant reduction occurred in the PC9 soot bulk sulphur content between the exhaust manifold and DPF due to oxidation in the oxidation catalyst. The sulphur which was released from the bulk of the soot was observed to increase the concentration of sulphur on the soot surface, Section 7.3, indicating that sulphur released from the soot bulk then partially condensed onto the soot surface between the oxidation catalyst and DPF. It is therefore postulated that part of the 4732% increase in PAH for the PC9 soot in Figure 6.18 is attributable to the condensation/adsorption of material released in the oxidation catalyst reactions in the exhaust system.

To ascribe all of the increase in PC9 soot total PAH to the soots evolution in the exhaust however cannot be valid as the other feature of the results presented in Figure 6.18 is that, relative to the EN590 soot at 19.5:1 compression at the exhaust manifold, the PC9 soot had an extremely low PAH content. In the previous discussion in Section 6.3 it was postulated that the reduction in compression ratio changed the processes by which the PC9 fuel sulphur was entrained within the soot and adsorbed onto the surface as the surface sulphur reduced 96.8% with the reduction in compression ratio. Therefore, it is intuitive to assume that a further linked process also acted to do the opposite and constrain the adsorption of PAH onto the soot surface at 19.5:1 compression.

The low PAH concentration for the PC9 soot at 19.5:1 compression ratio at the exhaust manifold was opposite to the high surface sulphur content, then at the DPF the situation reversed with the surface sulphur concentration lower, Section 7.3, and the PAH concentration significantly increased. It is therefore postulated that either the processes which changed the sulphur adsorption on the PC9 soot surface also regulated the PAH adsorption or alternatively the sulphur itself when adsorbed at sufficient concentration on the soot surface acted to inhibit the adsorption of PAH. Soot Polycyclic Aromatic Hydrocarbon Profile

Therefore in summary; it is very likely that the reduction in compression ratio, due to its associated reduction in PC9 soot surface sulphur concentration, also resulted in an increase in the surface PAH adsorption. It is also believed that this PC9 soot PAH concentration was further increased as the PC9 soot then evolved in the exhaust leading to the very significant increase in total PAH concentration as measured in the DPF soot sample, Figure 6.18.

The forgoing hypothesis of the related sulphur and PAH behaviour for the PC9 soot is supported by the relatively stable EN590 soot PAH concentration between the 19.5:1 exhaust manifold soot sample and the 16.5:1 DPF soot sample, Figure 6.18, and the fact that sulphur was not detected on the EN590 soot surface.

The significant change in the total PAH concentration for the PC9 mineral fuel soot leads to the direct comparison of individual PAH components (μ g PAH/g) (Table 6.7 and Table 6.8) being difficult. It is therefore appropriate to look at the individual soot PAH profile with the PAH concentration calculated as a percentage of total sample PAH for each sample and these results are presented in Figure 6.19 for the 19.5:1 compression ratio and Figure 6.20 for 16.5:1.

Figure 6.19 and Figure 6.20 indicate that the PAH profiles of the two mineral fuel soots changed markedly with both the compression ratio reduction and evolution of the soots in the exhaust. At high engine compression ratio the normalised concentrations of PAH for the two mineral fuels were similar and distributed largely between Naphthalene to Phenanthrene. By contrast the B100 PAHs were concentrated in the group Acenaphthene to Chrysene. In Section 5.7 it is argued that the limited range of PAH in the B100 soot indicated that the lack of PAH in the B100 fuel possibly resulted in less complex pyrosynthetic reactions by comparison to the two mineral fuels.

At the lower engine compression ratio for the DPF soot, both the mineral fuels presented a much narrower distribution of the detected soot PAH, focussed between 1-methylnaphthalene and Phenanthrene. Thus, there was a distinct absence of Naphthalene in these low compression DPF soots. Naphthalene is a common PAH reported in fuels and its presence at relatively high concentration at the exhaust manifold then contrasting with no Naphthalene being detected in the DPF sample, provides a clear illustration of the significant effects compression ratio, or perhaps more likely the soot evolution, had on the soot PAH profile.



Figure 6.19: 19.5:1 Exhaust Manifold Soot PAH for EN590, PC9 and B100 fuels (GC-MS)



Figure 6.20: 16.5:1 DPF Soot PAH for EN590, PC9 fuels (GC-MS)

The very similar total concentration of PAH for the EN590 soot but the significant change in PAH distribution was very interesting in that the mechanism driving the considerable change in PAH profile for this soot appeared to not change the overall concentration in the soot. For the PC9 soot this was not the case and yet the change in distribution was not dissimilar therefore supporting the earlier suggestion that the PC9 soot PAH total concentration increased because some other significant soot contaminate reduced in concentration i.e. sulphur.

Concluding Remarks

What was not clear however was the precise mechanism and therefore factor (i.e. compression ratio/evolution in the exhaust) driving the PAH profile change for the mineral soots for these samples though it was more likely to be the result of the soot evolution in the exhaust (possibly oxidation in the catalyst) than the compression ratio reduction as the PC9 PAH concentration increase was so significant and appeared to relate well to the sulphur concentration reduction observed in the exhaust which was driven by soot oxidation in the catalyst.

Thus in summary; it is postulated that the change in PC9 PAH concentration was effected by the same processes and factors governing surface sulphur concentration change i.e. both compression ratio reduction and soot evolution. The significant PAH profile change however is postulated to be primarily the result of the evolution and hence oxidation catalyst reactions experienced by the soot in the exhaust. This significant change in PAH distribution illustrated between Figure 6.19 and Figure 6.20 would be a very interesting area to study in future work.

6.7 Concluding Remarks

This chapter has considered the influence the reduction of engine geometric compression ratio had on the soot physiochemical properties for three different fuels. One of the most significant observations was that there was a general reduction in the soot surface O/C ratio, regardless of fuel, in response to the compression ratio reduction and appeared to be the inverse of the change in the AFR. The change in O/C ratio for all soots was also opposite to the exhaust O₂ concentration change but did align with a reduction in NO_x. It is postulated that the reduction in compression ratio acted to reduce the peak and average incylinder temperature and this in turn both reduced the formation of NO_x and also therefore the reaction rate between the NO_x and the soot in the formation of surface functional groups. The O/C ratio reduction was more significant for both mineral fuel soots and this is thought to be the consequence of significant morphological distinction of the B100 soot in terms of it gross graphitic/amorphous nature and therefore the availability and distribution of the surface functional groups which chemisorb O₂.

The compression ratio reduction was associated with a 97% reduction in PC9 soot surface sulphur concentration at the exhaust manifold which in turn saw the surface total acidity reduce by 50%. This reduction in PC9 soot surface sulphur did not appear to amplify the reduction in surface oxygen when compared to the

Concluding Remarks

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EN590 soot and thus the sulphur-oxygen proportionality relation previously advocated in Section 5.3 could be somewhat more complex.

Together, the soot surface O/C ratio and sulphur concentration findings implied that lower engine compression can be used as a tool to influence soot surface reactivity through influence on the in-cylinder temperature based soot formation and oxidation processes.

The reduction in compression ratio was suspected of causing an increase in lubricant consumption for all rated engine power soot collection experiments and this was most likely because of increased blowby. This increase in lubricant consumption was believed to be a contributing factor to the clear step increase in the fraction of bulk inorganic contaminate in all soots. However, it is also postulated that the reduction in compression ratio also affected the soot-lubricant interaction mechanism by increasing the relative entrainment into the soot of the lubricant derived inorganic contaminates (Ca, P, Zn) in comparison to the metals from the engine metallurgy (Fe, Mg).

There was a small change in the concentration of total PAH in the EN590 soot samples between the exhaust manifold at 19.5:1 and the DPF at 16.5:1; however in the case of the PC9 soot there was a significant increase of 4732% in the total concentration of PAH. It is thought likely that the reduction in compression ratio which caused a significant reduction of PC9 soot surface sulphur concentration also resulted in an increase in the PC9 soot surface PAH adsorption with further increases then occurring as the soot evolved in the exhaust with condensation/adsorption of material released in the oxidation catalyst reactions. The PAH profiles of the two mineral fuel soots changed markedly with both the compression ratio reduction and exhaust evolution with a much narrower distribution of PAH. It was concluded that the soot evolution was more significant in the change in PAH distribution than compression ratio.

7 Soot Evolution between the Exhaust Manifold and DPF

7.1 Introduction

This chapter presents the results and analysis for the soot sampled from both the engine exhaust manifold and the DPF in the exhaust at 16.5:1 compression ratio with the engine fuelled with a total of three different fuels at rated engine power. The aim of this chapter is to understand the processes of evolution of the soot in the exhaust through the changes in soot physiochemical properties and isolating the differences in this evolution across the three fuels. The samples were collected during the experiments described in Section 3.1.5.3.

7.2 Data Selection and Grouping

It was infeasible to undertake all soot physiochemical analysis procedures on either of the 19.5:1 or 16.5:1 compression ratio exhaust manifold soot samples due to limited sample mass, Section 3.6.8. Thus, both the 19.5:1 and 16.5:1 exhaust manifold soot sample results are required for the analysis in this chapter and Table 7.1 summarises the soot sample result grouping used. The main point to note is the need to use the 19.5:1 exhaust manifold soot sample results for the investigation of the soot surface acidity and PAH evolution in the exhaust and thus in these two cases there is also the change in compression ratio to factor into the analysis.

Soot Characteristic	Exhaust Manifold	DPF	Section
Surface Elemental Composition	16.5:1 Exhaust Manifold	16.5:1 DPF	7.3
Bulk Elemental Composition	16.5:1 Exhaust Manifold	16.5:1 DPF	7.4
Morphology	16.5:1 Exhaust Manifold	16.5:1 DPF	7.5
Surface Acid Functionality	19.5:1 Exhaust Manifold	16.5:1 DPF	7.6
Polycyclic Aromatic Hydrocarbon Profile	19.5:1 Exhaust Manifold	16.5:1 DPF	7.7

Table 7.1: Exhaust Soot Evolution Analysis; Data Selection and Grouping

Soot Surface Elemental Composition

7.3 Soot Surface Elemental Composition

Table 7.2 summarises the soot surface carbon, oxygen, sulphur and chlorine as well as the ratios of surface oxygen/carbon and sulphur/carbon for the three fuels investigated at the 16.5:1 compression ratio at both the exhaust manifold and the DPF. In this table CT denotes the soot sample was collected with a ceramic thimble and DPF denotes the soot was collected with a DPF, this notation is used throughout this work in the results presentation.

 Table 7.2: 16.5:1 Exhaust Manifold and DPF Soot Surface Elemental Composition

 Comparison (XPS)

	wt% C	wt% O	wt% S	wt% Cl	O/C		S/C	
Description					ratio	precision	ratio	precision
16.5:1 CT, EN590	94.1	5.9			0.0627	0.0114		
16.5:1 CT, PC9	91.6	8.4	0.050		0.0917	0.0120	0.001	0.0055
16.5:1 CT, B100	92.4	7.6			0.0823	0.0118		
16.5:1 DPF, EN590	92.8	7.2			0.0776	0.0117		
16.5:1 DPF, PC9	92.0	8.0	0.300		0.0870	0.0119	0.003	0.0055
16.5:1 DPF, B100	84.2	15.8	0.050		0.1876	0.0143	0.001	0.0060

Table 7.2 is divided into two parts with the upper half detailing the surface elemental results for the exhaust manifold soot samples (Section 3.5.1) and the lower half detailing the results for the soot sampled approximately 5m down the exhaust at the DPF after the diesel oxidation catalyst (Section 3.5.2).

The PC9 fuel soot had a higher surface concentration of oxygen and a higher O/C ratio than the EN590 fuel soot, both at the exhaust manifold and further down the exhaust at the DPF. The PC9 soot was also observed to have a lower surface carbon concentration than the EN590 fuel, again at both locations in the exhaust. The AFR for the 16.5:1 EN590 and PC9 experiments were close, measured at 20.7 and 20.5 respectively (Table 4.10 Part A), and thus the difference observed in the soot O/C at the exhaust manifold and the change in the exhaust was not directly linked to the AFR difference between these experiments but more closely linked to the sulphur adsorbed on the surface of the PC9 soot.

This AFR and soot O/C ratio conclusion is strengthened when the surface oxygen concentration of the B100 soot is also considered. At the exhaust manifold the O/C ratio for B100 soot was higher than observed for EN590 soot and closer to that observed for the PC9 soot even though the 16.5:1 B100 experiment AFR was 7.2% lower (Table 4.10 Part A) than for the EN590 fuel test. However, when the B100 soot had reached the DPF, the surface oxygen

Soot Surface Elemental Composition

7 7.3

concentration had increased to 15.8% and the O/C had increased 128%. This dramatic increase in the surface oxygen content of the B100 soot indicated that the B100 soot underwent far more significant transformation in the exhaust than experienced for either of the two mineral diesel fuel soots. These changes in the O/C ratio are illustrated in Figure 7.1 with the estimated error included.

The review of literature in Chapter 2 reported that there has been observed an increased rate of oxidisation for biodiesel soot with it being attributed to nanoscale crystalline structural differences in the soot [18] (graphitic/amorphous soot nucleolus and outer shell) or alternatively to the surface oxidative activity [17]. Lamharess et al. [112] concluded that the initial morphology of B100 soot is not sufficient to explain the oxidation characteristics and that the surface concentration and type of oxygen groups are also important.



Figure 7.1: 16.5:1 Soot Surface (O/C) Change from the Exhaust Manifold to DPF for EN590, PC9 and B100 Fuels (XPS)

Figure 7.1 illustrates that for the EN590 and B100 soot, the evolution of the surface of the soot in the exhaust included an increase in the O/C ratio but for the PC9 fuel it was observed to reduce although the change fell within the error bounds of the measurement. This suggests that the oxidative process was similar for the EN590 and B100 soot but a factor 1.8 times greater (based on O/C ratio change) in the case of the latter, implying that the B100 soot had a far higher rate of oxidation. Such a result is supported by many similar observations reported in literature [16, 17, 111, 319, 320, 321].

For the PC9 soot the reduction in O/C ratio occurred due to an increase in the surface carbon concentration and a reduction in the surface oxygen which

Soot Surface Elemental Composition

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proceeded in parallel with an increase in sulphur from 0.05 to 0.3, a factor 6 increase or 500%. Thus, it was logical to assume that sulphur was the causative factor for the disagreement in the O/C behaviour relative to the other soots as they evolved in the exhaust. However, if a simple model is assumed in which oxygenated sulphur compounds (e.g. H_2SO_4) produced in the oxidation catalyst reactions are then subsequently adsorbed on the soot surface, then an increase in the soot surface oxygen therefore indicates a more complex process occurred and it is postulated that this process was also responsible for the substantially reduced surface acidity of the PC9 soot at the DPF, Section 7.6 (i.e. potential for increased basic surface sites).

A potential explanation for the fall in PC9 soot surface oxygen was that sulphur migrated (possibly through pores in the soot) to the surface of the soot and then oxidised with surface oxygen and free oxygen in the exhaust in the oxidation catalyst and then finally volatilised. Such a mechanism would cause the reduction in bulk sulphur (as per the observations discussed in the proceeding section) and also the reduction in surface oxygen which was observed. It would be possible to test this in future studies by sampling both before and directly after the diesel oxidation catalyst over a wider range of exhaust temperatures. Clearly therefore, the PC9 soot surface sulphur and also bulk sulphur (as is discussed in the proceeding section) were central to the evolution of the PC9 soot being distinct from the evolution of the other mineral fuel EN590 soot.

The sulphur concentration was also observed to increase on the surface of the B100 soot as it was conveyed down the exhaust with the concentration increasing from zero sulphur at the exhaust manifold to a very low 0.050% weight concentration at the DPF. Sulphur was not detected on the surface of the EN590 soot across all experiments and since both the EN590 and B100 fuels had (<10 ppm) sulphur content, Appendix 1 (Table A1.1), the sulphur on the B100 soot surface at the DPF appeared to originate from a source other than the fuel itself. It was therefore likely that this sulphur was contamination derived from the exhaust system or the DPF. Since it only occurred for the B100 soot, it is postulated that it may be a consequence of the very high B100 HC emissions (Table 4.10 Part C) which possibly encouraged the entrapment of foreign contaminates from the exhaust system onto the soot.

For all the 16.5:1 soot samples, chlorine was not detected though it was observed at 19.5:1 for the PC9 fuel soot as detailed in Section 5.3 where is was

proposed the chlorine was a possible external contaminate of the sample during post experimental sample handling and processing.

In summary, the surface elemental analysis comparison between the exhaust manifold soot and soot from 5 meters down the exhaust at the DPF revealed a significant change in the soot surface composition with the evolutionary pathway being strongly dependent on the original fuel. These observations and findings are therefore of potential practical interest to diesel engine aftertreatment development, especially when a mineral and biodiesel fuel mix needs to be considered.

7.4 Soot Bulk Elemental Composition

Table 7.3 presents the percentage weight of inorganics for the bulk composition of the exhaust manifold and DPF sampled exhaust soot at 16.5:1 compression ratio; this data has been converted to the percentage contribution of each element to the total sample inorganics, Table 7.4. All elements with a wt % > 0.001% (10ppm) are reported.

Table 7.3: 16.5:1 Exhaust Manifold and DPF Soot Bulk Elemental Composition (% weight) (ICP-MS, Corrected)¹²

	#1269 ICP: Bulk Inorganic Contaminants by Acid-digestion ICP (wt%)												
Description	%Ca	%Cu	%Fe	%Mg	%Mn	%Na	%P	%S	%Si	%Zn	%AI	%Cd	Total wt%
16.5:1 CT, EN590	0.250	0.000	0.066	0.023	0.000	0.000	0.043	0.000	0.000	0.056	0.000	0.000	0.438
16.5:1 CT, PC9	0.320	0.000	0.110	0.021	0.000	0.000	0.072	1.060	0.000	0.077	0.000	0.000	1.660
16.5:1 CT, B100	2.880	0.000	1.080	0.350	0.000	0.450	1.030	0.014	0.000	0.560	0.000	0.000	6.364
16.5:1 DPF, EN590	0.990	0.080	3.420	0.064	< 0.001	0.060	0.690	0.250	0.000	2.870	0.130	0.060	8.614
16.5:1 DPF, PC9	0.990	0.080	4.680	0.068	< 0.001	0.080	0.510	0.320	0.000	2.250	0.130	0.060	9.168
16.5:1 DPF, B100	5.250	0.840	9.620	0.730	< 0.001	0.890	2.300	1.500	0.000	5.300	0.210	1.230	27.870

Table 7.4: 16.5:1 Exhaust Manifold and DPF Soot Bulk Elemental Composition (% weight/total % weight) (ICP-MS, Corrected)

		#1269 ICP: Bulk Inorganic Contaminants by Acid-digestion ICP (% of Total wt% Inorganics)												
Description	%Ca	%Cu	%Fe	%Mg	%Mn	%Na	%P	%S	%Si	%Zn	%AI	%Cd	Total %	
16.5:1 CT, EN590	57.078	0.000	15.068	5.251	0.000	0.000	9.817	0.000	0.000	12.785	0.000	0.000	100.000	
16.5:1 CT, PC9	19.277	0.000	6.627	1.265	0.000	0.000	4.337	63.855	0.000	4.639	0.000	0.000	100.000	
16.5:1 CT, B100	45.255	0.000	16.970	5.500	0.000	7.071	16.185	0.220	0.000	8.799	0.000	0.000	100.000	
16.5:1 DPF, EN590	11.493	0.929	39.703	0.743	0.000	0.697	8.010	2.902	0.000	33.318	1.509	0.697	100.000	
16.5:1 DPF, PC9	10.798	0.873	51.047	0.742	0.000	0.873	5.563	3.490	0.000	24.542	1.418	0.654	100.000	
16.5:1 DPF, B100	18.837	3.014	34.517	2.619	0.000	3.193	8.253	5.382	0.000	19.017	0.753	4.413	100.000	

The re-representation of the data in Table 7.3 to the elemental percentage weight/total percentage weight presented in Table 7.4 greatly assists the analysis of the soot transformation in the exhaust as the most significant change in total inorganics which was observed in the work reported herein occurred when soot transited between the exhaust manifold and DPF.

¹² Table 7.3 and Table 7.4 present corrected ICP-MS results; this involved negating foreign element contamination which was identified in some samples (Refer to Appendix 8).

The total percentage weight of inorganics in each of the six soot samples from Table 7.3 is presented in Figure 7.2 and indicates that the total inorganic contaminant in the B100 soot was clearly higher than observed for the mineral soots at both sample locations in the exhaust. The factor difference between the B100 soot total inorganic contaminant to the average of the two mineral soots was 6.1 at the exhaust manifold and 3.1 at the DPF; this indicated that the two mineral fuel soots evolved to have a greater relative inorganic content compared to the B100 soot as they travelled through the exhaust in addition to the substantial increase in inorganics observed in each soot.



Figure 7.2: 16.5:1 Exhaust Manifold and DPF Soot Total % Weight Inorganics (ICP-MS, Corrected)

It is useful to revisit the earlier findings from Section 6.4 to understand why the B100 soot inherently had such a higher concentration of inorganic content at the exhaust manifold: To recount, it was postulated to have been caused by the physical properties of the B100 fuel encouraging the soot forming regions in the cylinder to interact in a more significant way with the lubricant film on the cylinder wall; this being the result of increased fuel spry penetration into the cylinder which arose due to the higher density and viscosity of the B100 fuel, Appendix 1 (Table A1.1).

It is postulated that this greater soot-lubricant interaction acted to increase the entrainment of lubricant derived inorganics in the soot, however this entrainment process appeared to favour some lubricant inorganics elements more than others i.e. there was evidence of high concentrations of (Ca, P, Zn) but little or no sulphur and yet sulphur was the most dominant of the ICP-MS analysed inorganics present in the lubricant, Appendix 2 (Table A2.1). Thus, upon initial

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analysis of the total inorganics in the DPF samples for the same experiments; it was clear that this higher concentration of inorganics in the B100 sample persisted as the soot travelled the exhaust to the DPF, Figure 7.2.

Previously in both Section 5.4 and Section 6.4, a technique was used to analyse the soot bulk elemental composition analytically to evaluate the removal of the effects of any potential differences in fuel consumption rate, exhaust soot concentration and lubricant consumption rate between experiments. This involved multiplication of the ICP-MS results of Table 7.4 with the FSF (Section 4.3.2) and a lubricant consumption factor. However, this methodology has not been adopted in the discussion in this section as will be explained.

It was shown earlier in the analysis of the O/C ratio in Section 7.3 that there was a 1.8x greater increase in B100 soot O/C ratio compared to the mineral diesel soots indicating that there was increased oxidation and potentially loss of carbonaceous material as the soots evolved in the exhaust. This finding was then considered against the position in the exhaust where the AVL 415 smoke meter measured the exhaust soot concentration, since the AVL 415 measures simply the carbonaceous soot part. For the soot collection tests at rated engine conditions, the AVL 415 sample probe was located approximately 5 meters upstream of the DPF, Section 3.5.2.1, and in fact only 2 meters from the exhaust manifold. Thus, if there was any significant oxidation and loss of carbonaceous soot part between the AVL 415 sample location and the DPF, then using the AVL 415 smoke meter measurement in the FSF calculation to adjust the DPF ICP-MS results would lead misleading observations. On account of the likelihood of this being an issue, the FSF methodology has not been applied to the ICP-MS results analysis in this section.

To understand how the soot total inorganics changed in the exhaust for the three fuels, the change in total weight of inorganics (Table 7.3) for individual fuel soots between the exhaust manifold and DPF was calculated and was also expressed as a factor and the results from this analysis are presented in Figure 7.3.



Figure 7.3: 16.5:1 Soot Total % Weight Inorganics Change between the Exhaust Manifold and the DPF (ICP-MS, Corrected)

Figure 7.3 reveals that the change in the total wt % of inorganics for the two mineral diesel soots was quite similar with the change observed for the B100 soot being significantly higher. However, due to the initially lower concentration of inorganics in the EN590 soot compared to the PC9 soot, the increase in wt % inorganics constituted a factor 19.7 increase for EN590 soot whereas for PC9 soot the factor increase was 5.5 and was closer to the factor increase observed for the B100 soot. Thus, there was potentially an important difference in the evolution of the two mineral soots between the exhaust manifold and DPF which is analysed later in this section.

To understand these observed changes in the soot overall inorganic content, the changes in the individual inorganic elements of the soots between sample locations need to be considered. Figure 7.4 presents the change in the wt % between the exhaust manifold and DPF for each element (Table 7.3) for the three different soots. Figure 7.4 illustrates that the percentage change in the individual elements was generally positive for all elements apart from the PC9 soot sulphur and also that the B100 soot elemental increase was generally greater for all elements in respect to the changes observed for the two mineral fuel soots. Apart from the PC9 sulphur, the two mineral soots were observed to experience increases in concentration at a similar overall level for all elements with only subtle differences.



Figure 7.4: Change in Soot (% Weight) Inorganics between the Exhaust Manifold and DPF at 16.5:1 for EN590, PC9 and B100 fuels (ICP-MS, Corrected)

The B100 fuel specification, Appendix 1 (Figure A1.1), details that the most significant inorganic contaminants of the B100 fuel were in the order of highest to lowest: sodium, calcium, phosphorus and magnesium. For all four of these elements, increases were observed for the B100 soot. Assuming that in the exhaust system the increase in soot inorganics concentration should only arise from materials from which the exhaust was made e.g. iron; these increases in original fuel borne elements suggest the soot was evolving to loose mass other than the inorganics analysed i.e. increases in the concentration of sodium, calcium, phosphorus and magnesium through addition of these elements in the exhaust system was very unlikely with there being no source. This hinted very strongly that the increases in the concentration of soot bulk inorganics occurred mostly as the result of the loss of the carbonaceous fraction of the soot and that this process occurred for all the soots but was more significant in the case of the B100 soot.

The observed changes in surface O/C ratio reported in Section 7.3 and attributed to soot oxidation provide indirect evidence to support this conclusion. As the changes in the bulk inorganics were observed to be far more significant for the B100 soot and thus similar to the surface O/C change, the observed increase in B100 soot inorganic concentration added further evidence in support for the postulation that there was an increased rate of B100 soot oxidation between the exhaust manifold and DPF relative to the mineral fuel soot.

Due to the much higher overall increase in inorganics in the B100 soot, it is not possible from Figure 7.4 to ascertain how the postulated oxidation process influenced the individual elemental contribution to the soot inorganics. To determine this, the changes in element wt % presented in Figure 7.4 were calculated as a percentage of the change in total inorganics in each sample i.e. for EN590 Ca: ((0.990-0.250)/(8.614-0.438))x100 = 9.05%. The results from this analysis are presented in Figure 7.5.



Figure 7.5: Change in Soot (% wt/total % wt) Inorganics between the Exhaust Manifold and DPF at 16.5:1 for EN590, PC9 and B100 fuels (ICP-MS, Corrected)

From Figure 7.5 it can be observed that the three soots evolved in the exhaust somewhat differently to how the soots responded to the reduction in compression ratio, Section 6.4. First, the two most significant elemental increases in the soot inorganics for all soots were (Fe, Zn) and the increases in these elements were roughly in the same proportion to the overall inorganics increase for all soots but with the PC9 soot observed to have the largest increase in iron. This initial result indicates that there were additional processes occurring in parallel to the earlier postulated soot oxidation (i.e. carbonaceous part reduction).

Since the bulk inorganic ICP-MS measurement was performed on the collected soot samples as a whole, there was a high probability that the sample could contain elements that derived from the environment in which the soot transformed in the exhaust. An example of this was the iron, zinc, aluminium and to a lesser extent cadmium highlighted in Figure 7.5. The iron and the zinc were present at (<20%) of total inorganics for all soots at the exhaust manifold, Figure 7.6, whilst at the DPF, both iron and zinc increased in their contribution to total inorganics to be over 30% for iron and over 15% for zinc for all soots, Figure 7.7.



Figure 7.6: 16.5:1 Exhaust Manifold Soot Bulk Elemental Composition (% weight/total % weight) (ICP-MS, Corrected)



Figure 7.7: 16.5:1 DPF Soot Bulk Elemental Composition (% weight/total % weight) (ICP-MS, Corrected)

The extent of the increases in concentration of iron and the zinc suggests that these elements must have been added to the soot as it evolved in the exhaust and must therefore have originated from the exhaust material. The iron can be attributed to the steel in the exhaust and the zinc was from the galvanised surface coating of the exhaust pipe extension which was required to reduce the temperatures at the DPF to limit soot regeneration, Figure 3.31. The other source of iron was the DPF which was made of cordierite (Mg,Fe)₂Al₄Si₅O₁₈. The DPF material could therefore also be responsible for the increase in aluminium in the DPF soot samples as illustrated in Figure 7.7.

Comparing Figure 7.6 and Figure 7.7, it is clear that for the majority of elements other than iron and zinc, the relative contribution of calcium and magnesium to total weight of inorganics reduced as the soot travelled the exhaust thus illustrating the significance of the contamination from the exhaust system.

The zinc contamination in the exhaust manifold samples, Figure 7.6, likely derived from the lubrication as described in Section 5.4 and Section 6.4. The lubricant was also an additional source of calcium and phosphorous. The fact that calcium could come from both the fuel and the lubricant was the likely reason why the contribution of calcium to the soot total inorganic elements was so significant for the exhaust manifold soot (Figure 7.6) and then reduced in concentration sharply as the soots gained principally iron and zinc from the exhaust metallurgy as the soot evolved in the exhaust, Figure 7.7.

The contribution of phosphorous to total inorganics for both sample positions can be seen from Figure 7.6 and Figure 7.7 to remain similar with a general overall loss in the concentration of phosphorous in respect to total inorganics as the soots evolved. There was however a larger reduction in phosphorous for the B100 fuel and is it believed this occurred as there was an overall greater increase in (Ca, Cu, Mg, Na, Cd) for the B100 soot which is discussed later in this section.

Interestingly, from comparison of Figure 7.6 and Figure 7.7 it is observed that the calcium reduced more significantly for the EN590 soot than for the PC9 soot. This change was not caused by a significant difference in the actual amount of calcium in these soots but was due to the very high percentage of sulphur in the PC9 soot at the exhaust manifold which then decreased significantly as the soot passed through the oxidation catalyst. The significance of this reduction in PC9 soot bulk sulphur is illustrated in Figure 7.8.

Figure 7.8 depicts how the PC9 soot bulk sulphur reduced from 63.9 wt % at the exhaust manifold to 3.5 wt % at the DPF, a 95% reduction. This reduction in sulphur is postulated to have been caused by the oxidation catalyst reducing sulphate or SOF prior to the DPF. This change in PC9 soot sulphur was the principle observation which separated the transformational behaviour of the mineral fuel EN590 and PC9 soots in the exhaust and also affected the relative elemental changes between the two types of soot as observed for calcium and magnesium in Figure 7.6 and Figure 7.7.

This change in PC9 soot bulk sulphur correlated with the change reported earlier in Section 7.3 for the surface sulphur concentration where it was observed to increase 500% as the soot evolved in the exhaust between the exhaust manifold and DPF. Taken together, it is postulated that these contrasting bulk and surface sulphur findings resulted from either sulphur which migrated from the interior of the soot or oxidised sulphur compounds (H_2SO_4) which were condensing onto the surface of the soot downstream of the oxidation catalyst.



Figure 7.8: 16.5:1 Exhaust Manifold and DPF Soot Sulphur Content (wt %/total wt %) (ICP-MS, Corrected)

The concentration of sulphur in the EN590 and B100 soot at the DPF suggests that both soots had been exposed to additional sulphur when transiting the exhaust as the concentration in both soots at the exhaust manifold was originally negligible, Figure 7.8. Therefore the earlier postulated reduction in soot carbonaceous fraction through oxidation was likely not the sole cause these bulk sulphur increases. The increase in bulk sulphur for the EN590 soot however does not correlate with the surface sulphur data in Table 7.2 which shows that no surface sulphur was detected for either the exhaust manifold of DPF EN590 soot. For the B100 soot, the surface and bulk sulphur changes in the exhaust are in agreement.

It is postulated that the sulphur behaviour for the EN590 soot is explained by there being some very small almost negligible sulphur contamination from the engine cylinder when the soot formed which then increased in proportion of the soot bulk inorganics by the oxidation of the soot and carbonaceous part reduction as the EN590 soot moved down the exhaust. For the B100 soot, it is thought that

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> the same process occurred but additional sulphur was also adsorbed onto the surface of the soot as a result of contamination from the exhaust system. Appendix 9 (Table A9.1) shows that in terms of test sequencing, the 16.5:1 B100 experiment occurred before the EN590 experiment so there was increased likelihood of a gradual flushing of the exhaust system of sulphur compounds as these rated engine power 16.5:1 tests progressed. The sulphur contamination having had originated from the earlier 19.5:1 compression ratio PC9 experiment.

> So significant was the reduction in the bulk concentration of sulphur in the PC9 soot as it travelled the exhaust it is important to re-consider the contribution this made to the earlier analysis of the change in total soot inorganics presented in Figure 7.3. Thus, presented in Figure 7.9 is the change in total wt % inorganics of the soots and the associated factor increase this represents for each fuel with sulphur negated.





From Figure 7.9 it is clear that the change in soot total inorganics for both mineral fuels were actually closer than initially indicated with sulphur ignored, Figure 7.3. This suggests that these two soots actually followed a similar evolutionary process in respect to the majority of ICP-MS inorganics, other than sulphur, but the marginally greater factor increase for EN590 soot suggested that there was some differentiation such as a potentially higher rate of oxidation.

Due to the similarities between the EN590 and PC9 soot total inorganics evolution (other than the PC9 sulphur), it was appropriate to review these two soots side-by-side in more detail to help provide further insight into the sulphur

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increase in EN590. With sulphur negated, Figure 7.9 illustrates that there remained a proportionally larger factor increase in the non-sulphur inorganics in the EN590 soot relative to the PC9 soot. It was postulated that the greater increase in non-sulphur inorganics in the EN590 soot sample had several possible explanations:

- The reduction of the carbon component of the EN590 soot in the exhaust was greater than for the PC9 soot
- The EN590 soot through some process became entrained with relatively more metals from the exhaust system metallurgy
- Unburned lubricant was present in the exhaust due to a small leak from the turbocharger oil seals (there were several turbocharger failures over the course of the work reported herein due to the extended operation at maximum engine power and elevated IMAT in the soot collection experiments)

The analysis earlier in Section 7.3 of the change in surface O/C ratio found that the O/C ratio for the EN590 soot had increased and the for the PC9 soot it had decreased so explanation 1 is likely. The individual element % wt change to total sample inorganics presented in Figure 7.5 has been re-calculated with sulphur negated leading to the result presented in Figure 7.10. From Figure 7.10 it can be observed that there is no consistent pattern of increase in % weight across all the elements for the EN590 soot relative to the PC9 soot implying that there was no significantly higher carbonaceous fraction loss for the EN590 soot.

Rather, Figure 7.10 reveals that there were increases in (Ca, P, Z) when comparing EN590 to PC9. Additionally, the % wt increase in metals (Cu, Mg, Al, Cd) were all very similar for both soots whilst (Fe, Zn) were quite different. It was thus postulated that the slightly higher increase in concentration of non-sulphur inorganics was most likely the result of the presence of lubricant in the exhaust.

To investigate this, the (PC9 sulphur negated) change in wt % of inorganics for both EN590 and PC9 from Figure 7.10 were compared in combination with the inorganics profile for the lubricant Figure 7.11.

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From Figure 7.11 it can be observed that there was a potential link between the differences in the change of inorganics, with the greater increase for the EN590 soot aligned to all four principal lubricant inorganic components. Thus, the difference in the wt % change of each element for both EN590 and PC9 was computed to understand how the differences scaled against the concentrations of the lubricant inorganics, this result is presented in Figure 7.12.



Figure 7.11: Change in Soot (% wt/total % wt) Inorganics between the Exhaust Manifold and DPF at 16.5:1 for EN590, PC9 fuels (with Sulphur Negated) vs. Lubricant Inorganics (% wt) (ICP-MS, Corrected)

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The result in Figure 7.12 confirms that the increases in (Ca, P, Zn) for the EN590 soot vs. PC9 soot comparison align well to the primary elements of the lubricant. Therefore, EN590 soot could certainly have been exposed to lubricant in the exhaust and that this exposure resulted in the differences in the non-sulphur inorganics evolutionary changes in the exhaust for the mineral fuel soots. However, the failure of the elemental increases in the EN590 vs. PC9 soot inorganics to match precisely the concentration of the elements in the lubricant, Figure 7.12, suggests that the lubricant had not simply been adsorbed by the soot but was a more complex process. A more complex process could be attributed to the oxidation catalyst reactions prior to the soots reaching the DPF.

Indeed, it is expected that the process of entrainment of elements from free lubricant in the exhaust is quite different to the soot-lubricant interaction occurring in the cylinder during combustion due to the different temperature and pressures and chemical processes. For example, revisiting the ICP-MS results discussion of Section 5.4 and Section 6.4 reveals that although (Ca, Zn) concentration in the exhaust manifold soots compared favourably to the lubricant concentrations, there was a distinct lack of sulphur (apart from high sulphur PC9 fuel soot) and inconsistent phosphorous concentrations. The DPF results comparison for EN590 vs. PC9 soot in Figure 7.12 clearly shows a different relationship to the lubricant element wt % concentrations.

¹³ In Figure 7.12 the difference in sulphur % change between EN590 and PC9 is represented as the increase in sulphur for EN590 between the exhaust manifold and DPF for clarity.

Thus, exhaust lubricant contamination appears to be part of the explanation for the sulphur increase for EN590, however the B100 soot was observed to have an even greater increase in sulphur concentration as it passed along the exhaust, Figure 7.5. To also attribute this to lubricant contamination of the exhaust is harder to prove due to the much greater change in inorganics relative the EN590 and PC9 soots, Figure 7.3. However it is suspected on the basis of the strong indication of the influence of lubricant on the EN590 soot and the turbocharger being the same unit for these experiments.

Comparison of Figure 7.10 (sulphur negated) and the earlier Figure 7.5 (sulphur inclusive), reveals that for the B100 soot there was a characteristic increase above that seen for EN590 and PC9 soots in the elements (Ca, Cu, Mg, Na, Cd) with very similar contributions of (Fe, Zn). Therefore, relative to the total inorganics for each soot, the elements (Ca, Cu, Mg, Na, Cd) all increased in the B100 soot more than was observed for the mineral fuel soots. Set against the quite similar, by comparison, increase in (Fe, Zn); these observations add important evidence that supports the general postulation that the B100 soot had a much greater loss of carbonaceous soot fraction than the mineral soots as the soots moved from the exhaust manifold to the DPF. Thus, the main constituents of the B100 soot at the exhaust manifold (Ca, Cu, Mg, Na, Cd) increased somewhat more in concentration as more carbonaceous material was lost but a similar proportion of (Fe, Zn) was gained from the exhaust metallurgy.

To provide quantification of this proposed increased rate of B100 soot oxidation and to more clearly illustrate the effect of this increased oxidation in the individual element concentrations; the change in wt % calculated from Table 7.3 for the transition from the exhaust manifold to DPF as shown in Figure 7.4 has been scaled by a factor 0.5 and this result is shown in Figure 7.13.

Figure 7.13 reveals that for roughly the equivalent increase in (Fe, Zn) contamination from the exhaust metallurgy; the B100 soot experienced proportionally greater increases in (Ca, Cu, Mg, Na, Cd), thus providing a simple form of illustration of the necessary increased rate of oxidation of this soot.

From the earlier Figure 7.5 where the computed change in wt % between the exhaust manifold and DPF is presented as a percentage of the total inorganics increase in each soot; it is possible to estimate the factor increase between the average of the EN590 and PC9 soot response and that of the B100 soot for the

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distinguishing elements (Ca, Cu, Mg, Cd); doing so leads to ratios of 1.2, 3.8, 3.1, 7.5 for (Ca, Cu, Mg, Cd) respectively.



Figure 7.13: Change in Soot (% weight) Inorganics between the Exhaust Manifold and DPF at 16.5:1 for EN590, PC9 and B100 fuels with B100 multiplied by 0.5 (ICP-MS, Corrected)

These ratios basically describe the factor by which the increases in these elements were more pronounced for the B100 soot vs. the mineral fuel soots. They therefore provide an estimate for the equivalent factor increase in the loss of carbonaceous soot fraction during exhaust evolution between the mineral and biodiesel soots and this therefore appears to be in the range 1.2 to 7.5 but likely to be somewhere in the middle i.e. around 3-4. This compares to the factor of 1.8 derived in Section 7.3 from analysis of the O/C ratio change. As both of these ratios derive from alternative physiochemical soot property analysis and therefore relate to difference physiochemical changes, disagreement in these estimates are to be expected but they are nonetheless broadly in agreement.

An interesting final observation comes from a comparison of the exhaust soot total inorganics for each soot at the DPF with the TGA reported ash for the same samples (the TGA results were discussed in Section 5.8, Table 5.12). This comparison is illustrated in Figure 7.14 and the first observation is that the relative proportions of the inorganics match favourably between the two measurement techniques. Indeed, the scale factors from the ICP-MS to TGA results for the two sets of data are 1.6, 1.4, 1.5 for EN590, PC9 and B100 respectively. Thus, the two result sets have favourable agreement in respect of the relative concentrations of total inorganics between the samples. The average factor of 1.5 higher concentration reported by TGA is explained by the TGA

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> analysis capturing all non-combustible components of the soot whereas the ICP-MS analysis is limited to the 12 elements reported in this study.



Figure 7.14: Comparison of 16.5:1 DPF Soot Sample ICP-MS Total % weight Inorganics with the TGA % weight of Ash

In summary, the much lower initial total percentage weight of inorganic contamination of the EN590 fuel soot relative the PC9 was due to the lower sulphur content from the fuel. The subsequent evolution of the PC9 soot in the exhaust saw the sulphur concentration fall significantly and these sulphur changes dominated the relative change in EN590 and PC9 soot total percentage weight of inorganics. The B100 soot was observed to have much more significant increase in the total weight of inorganics relative to the mineral soots as it evolved in the exhaust and this aligned with the higher rate of oxidation implied by the change in the O/C ratio. Thus, the total inorganics in the B100 soot fraction.

7.5 Soot Morphology

Presented in Table 7.5 are the complete morphological results for the soot collected during the 16.5:1 compression ratio experiments at the exhaust manifold and the DPF for the three fuels investigated.

	BET Method		BJH Adsorption	N2 Pycnometry		Primary Particle Diameter		
Description	Suface area (S _{BET}) (m ² /g)	Error	Average pore diameter (Å)	Density (p) (g/cm ³)	Error	Dpp = $6/(\rho S_{BET})$ (nm)		
16.5:1 CT, EN590	262.4843	1.3344	116.156	1.9902	0.0117	11.486		
16.5:1 CT, PC9	335.8769	1.9077	140.194	2.0011	0.018	8.927		
16.5:1 CT, B100	35.6094	0.1757	256.73	2.8907	0.0243	58.289		
16.5:1 DPF, EN590	353.4348	2.4715	140.95	2.0846	0.0082	8.144		
16.5:1 DPF, PC9	393.3226	2.3225	129.26	2.0623	0.0098	7.397		
16.5:1 DPF, B100	235.9619	1.4264	147.132	2.3607	0.0142	10.771		

 Table 7.5: 16.5:1 Exhaust Manifold and DPF Soot Morphological Characteristics
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7.5.1 Surface Area

The surface area data from Table 7.5 is presented in Figure 7.15 and shows that the measured surface area increased at the DPF for all three fuel soots.



Figure 7.15: 16.5:1 CT & DPF Soot Surface Area (S_{BET}) for EN590, PC9 and B100 (BET)

At the exhaust manifold the average surface area of the mineral diesel soot was 299.2 m²/g and the biodiesel soot was found to have a surface area 88.15% lower at 35.6 m²/g. At the DPF the average surface area of the mineral diesel fuel soots was 373.4 m²/g, an increase of 24.8% whilst the surface area of the biodiesel soot was 36.8% lower at 236 m²/g. Thus, the surface area of the B100 soots increased by a factor of 6.6 in the exhaust whilst the mineral soots surface areas increased by 1.3 for EN590 and 1.2 for PC9 fuel soots. These significant differences in the change of the observed surface area between the exhaust manifold and DPF, suggests that the biodiesel soot underwent far more significant physical transformation in the exhaust than the two mineral fuel soots. It is postulated that this is additional evidence of 'accelerated' oxidation of the carbonaceous fraction of the B100 soot as asserted earlier in Section 7.3 and Section 7.4.

The proceeding sections identified evidence for oxidation processes transforming the soot in the exhaust and it is hypothesised that these processes could have acted to reduce the primary particle size of the soot through removal of the ordered graphene planes that form the outer shell of the soot particles (i.e. the mineral diesel soots) and/or hollowing out of internal voids (i.e. the B100 soot models proposed in Section 5.5.3). These processes also potentially influenced

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the porosity by increasing the size of existing pores and creating new pores. The aggregate structure of the soot also likely transformed and all of these physical soot changes could have contributed to the change in the surface area. A combination of these processes likely resulted in the increase in the mineral fuel soot surface area in the exhaust as illustrated in Figure 7.15.

A further possible mechanism of soot surface transformation that needs to be considered was the possibility of absorbed HCs on the soot surface being removed as the soot passed through the oxidation catalyst. For example, Ishiguru et al. [131] reported a six fold increase in surface area (Table 2.3), which is very similar to the 6.6 increase shown in Figure 7.15 for the B100 soot, when soot samples were heated up to 550°C and this was attributed to the release of the volatile fraction absorbed on the surface of the soots. A similar finding was also reported in by Otto et al. [135] and others [130, 132, 133].

In the case of the N2 adsorption technique utilised for the BET surface area measurement, any residual adsorbed SOF would have filled the soot pores and therefore given rise to a low pore volume and surface area measurement as is reported for the 16.5:1 B100 soot. In Section 5.5.2 this possibility is discussed in detail and here it was concluded that the collective B100 soot physiochemical results reported in this work are indicative of a physical dry-soot explanation rather than SOF residues on the soot when the N2 adsorption experiments were performed.

Consequentially, the soot surface area increases illustrated in Figure 7.15 are postulated to be the result of surface oxidative action and therefore the results describe the increase in surface area of the dry largely carbonaceous soots as the oxidative processes, primarily in the oxidation catalyst, reduced the carbonaceous fraction of the soot. For both the mineral diesel soots this process appeared to be similar in terms of the physical changes that lead to the increase in surface area (likely overall primary particle diameter reduction) whereas for the B100 soot there was clearly an additional action which as is discussed in the next section was the change in porosity.

Clearly, the results in Figure 7.15 are indicative of quite different mineral and biodiesel soot morphological transformation in the exhaust and it is postulated that this stemmed from differences in the original structural form and surface state of the soots they it exited the cylinder.

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7.5.2 Porosity

Soot surface oxidative action was postulated in the forgoing section to explain the soot surface area transformation and as will be shown in this section, the changes which this describes were not universal. For example, the mineral diesel soot porosity change illustrated in Figure 7.16 shows that the porosity of the EN590 soot, measured by the average pore diameter, increased whilst porosity was observed to reduce for both the PC9 and B100 two fuel soots. This suggests that physical changes other than porosity also occurred to account for the surface area changes summarised in Figure 7.15.





The opposed change in porosity for the two mineral diesel soots illustrated in Figure 7.16 was the only notable divergence in the change in morphological characteristics for these soots as they evolved in the exhaust. Equation 3.6 shows that the average pore diameter is proportional to pore volume and inversely proportional to surface area. Therefore, the increase in pore diameter for the EN590 soot equated to a substantial increase in pore volume such that the pore volumes of the EN590 and PC9 soots were much closer at the DPF. This is interesting as it implies that the pore structures of these two soots evolved to become closer and it is possible this was coupled to the reduction in PC9 soot sulphur in the soot bulk and 500% increase in sulphur on the surface as described earlier in Section 7.4 and Section 7.3.

One of the most important observations from the porosity results outlined in Figure 7.16 was how the B100 soot porosity was much closer to the porosity

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observed for the two mineral diesel soots at the DPF compared to the exhaust manifold. This was also the case with the surface area illustrated earlier in Figure 7.15. Indeed, the porosity of the B100 soot at the exhaust manifold was a factor 1.25 greater than the two mineral soot porosity results. Together, these observations are indicative of the B100 soot surface being physically distinct from the surfaces of the two mineral fuel soots at the exhaust manifold. Then, as the B100 soot evolved in the exhaust to increase in both surface O/C concentration (Section 7.3) and bulk inorganics (Section 7.4), and in both cases much more significantly than the two mineral diesel soots; the B100 soot also evolved morphologically such that the differentiation from the mineral fuel soots observed at the exhaust manifold was somewhat reduced based on the morphological characteristics investigated in the work herein.

At this point it is appropriate to recall the discussion earlier in Chapter 5. In Section 5.8 it was stated that the 16.5:1 exhaust manifold B100 soot had a greater fraction of SOF which was characterised by a more significant loss of mass in the room temperature to 400°C segment of the thermogravimetrical examination and also greater HC emissions, Table 4.10 Part C. As a result, it was postulated in Section 5.5 that this increased SOF could have influenced the N2 adsorption based morphological examinations of the soot (surface area, porosity) and in so doing have been the principal cause of the significant morphological distinctions at the exhaust manifold. However, it was concluded in Section 5.5 that this could not be the sole cause of the B100 soot morphological distinction.

This conclusion drew upon the observations earlier in this chapter which include the increased in both O/C ratio and bulk inorganic concentration discussed in Section 7.3 and Section 7.4 respectively. This is because it is considered that these other non-morphological soot properties support there being a fundamentally different B100 transformation behaviour in the exhaust compared to the mineral fuel soots which is not simply the effect of increased SOF. It can therefore also be postulated that there must be underlying these observations, a B100 soot characteristic at the exhaust manifold that can account for these significant evolutionary distinctions of the B100 soot.

Clearly, the morphological distinctions of B100 soot surface area and porosity and also density at the exhaust manifold, rather than being an artefact in the measurements caused by potential SOF adsorption, must actually be the key to understanding the B100 soot distinction from the two mineral soots.

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Consequently, the changes in the B100 soot morphology in the exhaust are intriguing as they reveal insights into how the B100 soot physically transformed and therefore how the B100 soot physically compared to the mineral soots at the exhaust manifold and the DPF.

7.5.3 Density

Figure 7.17 reveals that in addition to the forgoing surface area and porosity distinctions of the B100 soot, the density behaviour between the exhaust manifold and the DPF was also unique. The opposite density change for the B100 soot is considered very important as it is believed that this provides insight into the differences in internal soot core structural transformation in the exhaust.





Summarising the results presented in Figure 7.17, it is observed that the skeletal density of the PC9 soot increased by 3.1% and this change was therefore similar to the 4.7% increase observed for the EN590 soot. However, referring back to Section 7.4, it was observed that the PC9 soot also experienced a 69.8% reduction in the bulk sulphur content set against an overall increase in soot bulk inorganics concentration. This contradictory change in PC9 soot sulphur is a possible indication that the PC9 core soot structure was originally distinct from that of the EN590 soot and then also evolved differently. This postulation is supported by the opposed change in pore diameter for the two soots, Figure 7.16. In contrast to the mineral soot density changes, the B100 soot density reduced by 18.3%.

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It is useful at this point to recount that it was highlighted in Section 2.4.2.3 that Park et al. [152] found the heating of soot to remove volatile components resulted in a higher soot density and generally more stable soot density measurements. Therefore it is a possibility that any changes in soot SOF fraction between the exhaust and the DPF could have influenced the density measurement.

The first step to understand the soot density findings depicted in Figure 7.17 is to consider the impact of the significant increase in soot bulk inorganics concentration that occurred for all three soots as they transited the exhaust, Section 7.4. Part of this was attributed to oxidation which acted to reduce the carbonaceous fraction and in turn increase the bulk inorganic concentration. This was then augmented by the aggregation of iron and zinc from the exhaust metallurgy and it was this later process which appeared to be of greater significance. Therefore the bulk inorganic fraction increased for all three soots and the elements which increased the most were iron and zinc which have a much greater elemental density than carbon.

Consequently, for all soots the loss of carbonaceous fraction and the growth of the inorganics fraction should in principle have acted to increase the soot density and indeed this is what is observed for the EN590 and PC9 soots. In contrast, the B100 soot density falls and yet it has by far the most significant increase in inorganics fraction. The only way to reconcile this is to conclude that trapped inter-particle voids [141] (Section 2.4.2.2) must have been forming in the B100 soot as the soot transited the exhaust (i.e. trapped voids would result in the N2 pycnometry method over-estimating the skeletal volume, Section 3.6.4.3, thereby giving a lower density measurement). Therefore, the B100 soot structure must have evolved such that the soot became more akin to the hollowed out soot core with intact outer shell in the form of that described by Song et al. [16].

Referring back again to Section 5.5.3, there were two B100 soot physical descriptions proposed to explain the differences in the B100 soot at the exhaust manifold, these are repeated here for convenience:

B100 Soot Model 1: The B100 soot had undergone far more oxidation than the mineral soots when sampled due to an inherent higher rate of oxidation for the B100 soots and that this oxidation had opened up the small surface pores and internal voids in the soot thus creating a soot similar to that described by Song et al. [16] with internal voids that were connected to the

surface allowing the N2 molecules to enter. Thus, the B100 soot had very few trapped voids thereby giving rise to the relatively high density measurement. Since the pores were opened up, the total pore volume and soot surface area would be low as was observed.

B100 Soot Model 2: Alternatively, the B100 soot primary particles could have had a far more regular graphene plane internal arrangement with fewer isolated internal voids than was the case for the mineral fuel derived soot. This was then combined with a low surface porosity which also resulted from the highly regular arrangement of the graphene planes. This would in principle give rise to soots with small surface area, low pore volume and higher density as observed but if this is how the B100 soots were structured physically, then it is opposite to the description derived from TEM micrographs by Song et al. [16].

It is possible to take both these models and to theorise what would happen to these soots as the oxidation processes continues as the soot transited the exhaust to the DPF. The main consideration is that the B100 soot density reduction demands the increase in trapped internal pore volume. Additionally, it is worth noting that Zerda et al. [137] studied the heating of soot to temperatures between 400-500°C and report that the decomposition of the soot causes the opening or more cavities. Consequently, it can be postulated:

For soot model 1; the soot is already well advanced in terms of the opening of pores and internal voids so for this model to be valid, the soot cannot be so significantly hollowed out at the exhaust manifold to enable trapped internal voids to further form in the soot.

For soot model 2; this model is more feasible in that the extensive oxidation of the B100 soot in the exhaust acted to create the internal voids in the highly regular soot core in addition to creating new pores on the surface thereby also increasing the surface area and pore volume.

Thus, in these two scenarios, model 2 soot is actually moving in the direction of the model 1 soot but it is doing so from a quite different initial soot structure which better conforms to the overall B100 soot findings. It is therefore postulated that model 2 is the more likely candidate for the B100 soot at the exhaust manifold and which also fits the observations for the B100 soot evolution.

However, a quite different explanation can also be devised in which the B100 soot at the exhaust manifold were highly agglomerated due to the known high

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SOF fraction acting to bind the primary soot particles together. Thus, when the soots were examined using the N2 adsorption techniques, the highly agglomerated primary particles presented a low surface area and porosity as significant areas of the primary particles were touching and could not be exposed to the N2 gas. In this way, tightly packed primary particles would have acted like a much larger singular particle which may explain why the estimated particle size was so large, Table 7.5. Then as these B100 soots oxidised in the exhaust and passed through the oxidation catalyst the SOF was removed and the tight aggregate structure broke apart increasing the exposed surface area and then the physical oxidation processes of soot model 1 proceeded to open up the surface pores thus reducing the pore volume.

One issue with this alternate proposal is the very high exhaust temperatures at the confluence point of the exhaust manifold where the soot samples were sampled from. Table 4.10 Part B details that the exhaust temperatures were in excess of 530°C for the rated engine condition of the soot collection experiments and thus at such a temperature the presence of absorbed volatiles would have been negligible or possibly non-existent as shown by Ishiguro et al. [131]. However it is possible that as the soot was then transported from the exhaust manifold down the sample line to the ceramic thimble, volatiles were able to condense and then adsorb onto the soot surface. This is possible because the average ceramic thimble temperature when the soot was collected was 153.5°C for these experiments; 'CT Temp' Table 4.10 Part B.

Several sources in literature report that biodiesel fuels produce a higher SOF fraction compared to conventional mineral diesel fuels [266, 296, 306] and Song et al. [17] suggest that higher SOF may result in a much tighter aggregate soot structure which would also act to reduce the isotherm-BET determined surface area, so this postulation is highly feasible. Interestingly, it is also reported that biodiesel based fuels lead to exhaust volatiles with higher molecular weights and higher boiling points than for mineral fuels [326] (which agrees with the TGA findings Section 5.8). Therefore it was possible that more of the B100 fuel volatiles condensed on the soot earlier in the sampling system sample line than occurred for the mineral fuels, thus further increasing the B100 soot fraction of volatiles at the ceramic thimble and DPF. Additionally, the reduced B100 carbonaceous soot mass would almost certainly have encouraged greater SOF adsorption on individual particles subject to the temperature and saturation conditions in the sampling system [6, 24].

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Thus in summary, there are several alternate models which can partly explain the B100 soot morphological distinctions in comparison to the EN590 and PC9 mineral fuel soots observed in the work herein. These alternate models arise as there is not enough information to rule out specific scenarios. It is therefore concluded that to more fully understand the actual physical structural differences between the B100 and mineral fuel soots, additional soot morphological examination methods such as TEM are necessary.

However, the results reported herein describe fundamental physical differences between B100 and mineral diesel soot which are present at the exhaust manifold and therefore instilled right from the initial B100 soot inception and formation processes in-cylinder. These differences then absolutely govern the behaviours of these soots as they evolve in the exhaust, particularly the greater reduction of the carbonaceous fraction in the B100 soot which would have in turn been a factor in the greater than 80% reduction in exhaust soot concentration relative to the mineral diesel fuels, Chapter 4. Therefore the findings of this section support the work reported by Boehman et al. [306] and Wal et al. [18] wherein they conclude that there exists a structure-property relationship between soot nanostructure and oxidation reactivity.

7.5.4 Primary Particle Diameter

As was described earlier, the soot observed at the DPF exhibited higher surface area than those at the exhaust manifold. Physically, this was indicative of the reduction in primary particle diameter and Figure 7.18 confirms that indeed the estimated mean particle diameters for the soots were seen to reduce between the exhaust manifold and DPF.

Again, the primary particle diameter estimations for the two mineral fuels were quite similar. In the case of the PC9 fuel these observations when combined with the generally increased exhaust soot concentration at the rated power condition (Table 4.10 Part A) implied that the total particle number count for the PC9 soots was higher than the other fuel soots at the rated power condition.

The factor 6.6 increase in B100 soot surface area in the exhaust system between the exhaust manifold and DPF and the factor 1.2 reduction in density, combined to reduce the B100 soot mean particle diameter estimation by a factor 5.4. Thus, at the DPF the morphological results for the three soots suggested that the B100 soot had evolved physically such as to be similar to the mineral

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diesel soots in regards to its morphological description. However, the B100 soot retained a distinctly lower surface area so the closer alignment in overall morphological results was not necessarily indicative of similar soot structure.



Figure 7.18: 16.5:1 CT & DPF Soot Primary Particle Diameters Est. for EN590, PC9 and B100 (spherical particle assumption)

In Section 2.4.2.4 it was identified that the quoted range in literature for primary soot diameters is 15-30 nm, therefore the estimates using the method outlined in Section 3.6.4.4 proved to be low at both the exhaust manifold and the DPF for the majority of the soots characterised. The primary particle estimation method (Equation 3.9) is based on the assumption of spherical non-porous particles and thus fails to consider the effects of porosity change and any aggregation of the particles.

As has been discussed through the course of this chapter and also Chapter 5 and Chapter 6, soot porosity is highly dynamic during oxidation and since porosity is not considered in Equation 3.9, the validity its application to estimate diesel engine soot particle size can be questioned. Based on the findings of the work reported herein, it is advised that Equation 3.9, which is also reported elsewhere for soot (e.g. Lapuerta et al. [136], Table 2.7), is not sufficiently reliable or accurate for application to diesel engine soot. It is recommended that direct measurement methods such as TEM be employed in engine soot research to measure soot primary particle diameter.

In summary, the morphological evolution of the two mineral fuel soots in the exhaust appeared to be quite similar with the exception of an increase in the average pore diameter for the EN590 soot which acted to align the total pore

volume of the mineral soots at the DPF. The B100 soot was in contrast very distinct at the exhaust manifold and then evolved such that its morphological characteristics became closer to the mineral soots but still remained distinct at the DPF. These observations are captured in the presentation of the combined morphological characteristics in Figure 7.19 for the three fuel soots. In Figure 7.19 the circular markers are scaled in diameter to represent surface area.



Figure 7.19: 16.5:1 CT & DPF Surface Area (S_{BET}), Soot Average Pore Diameter (Å) and Primary Particle Diameter for EN590, PC9 and B100

7.6 Soot Surface Acid Functionality

The data for the analysis of soot surface acidity with soot evolution in the exhaust is drawn from across the high compression ratio exhaust manifold soot samples and the low compression ratio DPF soot samples as there was insufficient soot mass to determine the soot surface acidity for the 16.5:1 exhaust manifold soot samples. Additionally, as stated previously in Chapters 5 and 6, for the same reason the B100 surface acidity data was unavailable for the 19.5:1 exhaust manifold soot sample. Consequently, it is necessary in this discussion to distinguish the change in acidity caused by the soot evolution in the exhaust from the change caused by the reduction in compression ratio, Section 6.5. The results from surface acidic functionality measurements are presented in Table 7.6 and are defined for both the total and carboxylic acid concentrations.

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Table 7.6: 19.5:1 and 16.5:1 Exhaust Manifold and DPF Soot Surface AcidFunctionality (Boehm titration)

		Boehm	n Titration	
	Total surface	stdev	Surface carboxylic	stdev
Description	acids (mmol/g)	(mmol/g)	acids (mmol/g)	(mmol/g)
19.5:1 CT, EN590	0.621	0.083	0.181	0.008
19.5:1 CT, PC9	1.163	0.010	0.749	0.001
19.5:1 CT, B100	NA	NA	NA	NA
16.5:1 DPF, EN590	0.601	0.045	0.169	0.004
16.5:1 DPF, PC9	0.575	0.004	0.207	0.004
16.5:1 DPF, B100	0.850	0.005	0.311	0.016

The results detailed in Table 7.6 indicate that in the case of EN590 soot the surface acidity reduced in both carboxylic and total acidity by only 3.2% and 6.6% respectively which contrasted with the significant 50.6% and 72.4% reductions in both carboxylic and total acidity for the PC9 soot. Thus, the percentage of carboxylic/total acidity for EN590 and PC9 soot changed from 29.1% and 64.4% respectively at the exhaust manifold to 28% and 36% at the DPF, thus becoming closer. Interestingly, the percentage of carboxylic/total acidity for the PC9 soot act the B100 soot at the DPF was 37% and thus similar to that observed for the PC9 soot at the same sample location. This indicated that both soot surface O/C ratio and sulphur contributed to soot surface acidity rather than O/C ratio alone as the two O/C ratios for these soots were quite different, Section 7.3.

Thus, as was postulated in Section 6.5, these observations implied that the surface acidity reflected to a degree the O/C ratio and sulphur changes in the soot surface elemental composition between these two sets of soot samples (Section 6.3 and Section 7.3). The change in soot surface acidity detailed in Table 7.6 appeared to therefore be indirectly linked to both compression ratio and soot evolution in the exhaust by these more fundamental driving physiochemical changes i.e. the reduction in the in-cylinder temperature for the compression ratio change, Section 6.3, and the physiochemical changes in the exhaust as indicated by the surface compositional (Section 7.3) and soot morphological (Section 7.5) changes.

In Section 6.5 is was postulated that the surface acidity for the exhaust manifold B100 soot in Table 7.6 was most probably less than 0.850 mmol/g (the B100 DPF soot surface acidity) and likely just slightly greater than the EN590 soots acidity of 0.621 mmol/g at the exhaust manifold due to the slightly higher surface O/C ratio of the B100 soot at the same conditions and also the low surface sulphur concentration of the B100 soot. This postulation was built upon

Soot Surface Acid Functionality

the proposed proportional relationship between surface O/C ratio and surface acidity which is expanded in far greater detail in Chapter 9.

The observations for the changes in the contribution of the carboxylic acid to the total acidity are very interesting. For the EN590 soot, the carboxylic acid fraction was 29.1% at the exhaust manifold and 28% at the DPF and the total acidity reduced from 0.621 to 0.601 mmol/g. So for this mineral fuel soot there was a small reduction in total acidy which hardly changed the relative contribution of carboxylic acid following both the reduction in compression ratio and soot evolution in the exhaust. This reflects the fact that for this soot there was no sulphur observed on the surface at either the exhaust manifold (Section 6.3) or DPF (Section 7.3) and that the surface O/C ratio reduced from 0.0805 to 0.0776 g/mol.

In contrast for the PC9 soot, the total acidity reduced from 1.163 to 0.575 mmol/g with the carboxylic fraction reducing from 64.4% to 36%. For this soot, the surface sulphur concentration reduced from 1.545 to 0.05 wt % and then increased again to 0.3 wt % with the reduction in compression ratio and the subsequent evolution in the exhaust. The surface O/C ratio also reduced from 0.1121 to 0.0870. Thus, for the PC9 soot the reduction in contribution of carboxylic acid to the total aligns with the reduction in surface sulphur concentration and it is postulated therefore that the carboxylic acid component is strongly influenced through the presence of sulphates on the soot surface. i.e. it is likely that increases in surface sulphur proportionally increase the carboxylic acid and thus the total acidity of the soot.

However, at the DPF the total acidity for the PC9 soot was lower than that of the EN590 soot even though the PC9 soot had a higher surface O/C ratio and a surface sulphur concentration of 0.3 wt %. For this soot the carboxylic acid fraction was 36% and thus higher than the 28% of the EN590 soot. Thus, for this PC9 DPF soot sample, the higher carboxylic acid content did not lead to a higher total acidity as was the case at the exhaust manifold. It is postulated that this was because the chemistry of the adsorbed sulphur in the PC9 DPF soot was different to that if the exhaust manifold soot, possibly being basic rather than acidic, which thus reduced the total acidity to below that which is seen with the EN590 soot with no surface sulphur present. Support for this postulation can be derived from the analysis of Section 7.3 in which it was observed that PC9 surface sulphur at the exhaust manifold appeared to increase the O/C ratio but at the DPF the surface sulphur appeared to reduce the O/C ratio.

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This different sulphur chemistry could be explained by the surface of the PC9 soot at the exhaust manifold having been produced in the high temperature incylinder reactions whereas the sulphur on the surface of the DPF soot is likely to be from sulphates released when the soot passed through the oxidation catalyst in the exhaust. Clearly, from these observations and hypothesis, the presence of sulphur in diesel fuel has the potential to significantly change the surface functional groups on the soot and that the effect of the sulphur could change with the conditions under which it is adsorbed onto the soot.

Therefore to summarise; the surface acidity changes from the exhaust manifold soot to the DPF soot detailed in Table 7.6 are postulated to be the culmination of the following processes:

- The compression ratio reduction (reduced peak in-cylinder temperature) and the resultant reduction of surface O/C ratio for all soots (Section 6.3) acted to reduce the surface acidity of all three soots in proportion to the reduction in surface O/C ratio (refer to Chapter 9 for the quantitative analysis which justifies this).
- 2. The compression ratio reduction also acted to reduce the PC9 soot surface sulphur concentration by 96.8% and this then caused a significant further reduction in surface acidity in addition to the reduction caused by process 1 outlined above. As the PC9 soot surface sulphur concentration became almost negligible; it is postulated that the PC9 soot surface acidity aligned to the acidity of the equivalent EN590 and B100 soot with the surface acidy therefore primarily controlled through the surface O/C ratio. From Table 6.2; the 16.5:1 PC9 exhaust manifold soot would therefore still have had the highest acidity due to it retaining the highest surface O/C ratio but it would have been much closer to the other two soots.
- 3. As these three soots evolved in the exhaust from the exhaust manifold to the DPF there would have been a process of chemisorption of oxygen to the soot surface, Figure 7.1. However, this process proceeded differently between the mineral and biodiesel soots with the B100 soot experiencing an increase in surface O/C ratio of approximately 1.8 times that of the mineral fuel soots. Consequently, the surface acidity of the B100 soot increased more significantly as the soots evolved in the exhaust and this appeared to be related to the significant B100 soot morphology changes in the exhaust (Section 7.5) which in turn were postulated to derive from a

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different structural composition of the B100 soot which was established during soot inception and formation during combustion.

The PC9 soot evolved in the exhaust to lose about 69.8% of its original bulk sulphur content (Section 7.4) whilst at the same time the surface sulphur concentration increased by 500% due it was postulated to oxidation reactions in the oxidation catalyst and the condensation of sulphates onto the soot surface between the catalyst and the DPF. Compared to the EN590 soot at the DPF, the PC9 soot had a slightly higher O/C ratio and the presence of this surface sulphur but the total surface acidity of the EN590 soot was higher and yet the carboxylic concentration lower. Thus, the sulphates adsorbed onto the PC9 soot in the exhaust did not result in the same significant increase in soot surface acidity which occurred when the sulphur was adsorbed into the soot surface in-cylinder during combustion. This indicates that the composition of the surface sulphur compounds and chemistry were different between the exhaust manifold and DPF soots, leading to increases and decreases in soot surface acidity respectively. The effect of the high concentration of sulphur was however by far the more significant.

The above reasoning, which is based upon the assumption of a strong proportional relationship between the soot surface O/C ratio and surface acidity and also surface sulphur and surface acidity, is very important and it is shown later in Chapter 9 that this reasoning is based upon fundamental quantifiable relationships derived through the work reported herein which detail how the above reasoning is a confident explanation of the behaviour of surface acidity with evolution of the soot in the exhaust.

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The PAH results related to exhaust soot evolution, like the surface acidity results, are for soot samples taken from both the exhaust manifold at high compression and from the DPF at low compression. Consequently, it is necessary in this discussion to separate out the change in PAH caused by the soot evolution in the exhaust from the change caused by the reduction in compression ratio (Section 6.6). A total of sixteen PAH were investigated in the soot samples and the results are presented across Table 7.7 and Table 7.8.

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Table 7.7: 19.5:1 and 16.5:1 Exhaust Manifold and DPF Soot Polycyclic Aromatic

Hydrocarbon Profile (Naphthalene to Fluoranthene) (GC-MS)

PAH (μg PAH/g)	Naphthalene	1- methylnapht	2- methylnaphth	Acenaphthylene	Acenaph	Phenanthrene	Anthracene	Fluoranthene
Description		halene	alene		linene			
19.5:1 CT, EN590	2.990	0.297	0.104	0.048	0.022	1.659	0.000	0.045
19.5:1 CT, PC9	0.031	0.005	0.003	0.000	0.002	0.096	0.000	0.010
19.5:1 CT, B100	0.000	0.000	0.000	0.000	0.002	0.010	0.000	0.003
16.5:1 DPF, EN590	0.000	0.000	0.000	0.770	2.800	1.330	0.000	0.000
16.5:1 DPF, PC9	0.000	1.990	1.440	0.520	1.960	1.870	0.000	0.000
16.5:1 DPF, B100	NA	NA	NA	NA	NA	NA	NA	NA

Table 7.8: 19.5:1 and 16.5:1 Exhaust Manifold and DPF Soot Polycyclic AromaticHydrocarbon Profile (Pyrene to Benzo-perylene) (GC-MS)

PAH (μg PAH/g)	Pyrene	Benz(a)anth	Chrysene	Benzo(b)fluorant	Benzo(k) fluoranth	Indeno(1,2,3-	Dibenz(a,h)a	Benzo(g,l,h)	total
Description		lacene		nene	ene	oupyrene	nandoone	peryrene	
19.5:1 CT, EN590	0.000	0.014	0.006	0.000	0.027	0.000	0.000	0.000	5.212
19.5:1 CT, PC9	0.001	0.013	0.000	0.000	0.000	0.000	0.000	0.000	0.161
19.5:1 CT, B100	0.003	0.003	0.000	0.000	0.000	0.000	0.000	0.000	0.021
16.5:1 DPF, EN590	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	4.900
16.5:1 DPF, PC9	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	7.780
16.5:1 DPF, B100	NA	NA	NA	NA	NA	NA	NA	NA	NA

The total PAH concentrations (μ g PAH/g) from Table 7.8 for the six soot samples are illustrated in Figure 7.20.



Figure 7.20: Total PAH for 19.5:1 Exhaust Manifold and 16.5:1 DPF Soot for EN590, PC9 and B100 Fuels (GC-MS)

The limited sample mass for the B100 16.5:1 soot sample precludes that the PAH for this sample could not be investigated so it is not possible to be certain of the relationship of B100 PAH relative to the mineral fuels soots with soot evolution in the exhaust. However, the three 19.5:1 exhaust manifold soot results indicate that the concentrations of PAHs in the B100 soot were generally very low

relative to the EN590 and PC9 soots; thus any change in B100 soot total PAH concentration with soot evolution are postulated to have been very small.

The B100 total PAH concentration was low due to there being no aromatic content in the original fuel, Appendix 1 (Table A1.1), as was discussed in previously in Section 5.7 and Section 6.6. The key observation from Figure 7.20 is that the total PAH concentration observed for the EN590 soot varied little with compression ratio and soot exhaust evolution, contrasting with the total PAH for the PC9 soot which increased significantly.

At 19.5:1 compression at the exhaust manifold, the total PAH for the mineral EN590 fuel was measured to be a factor of 32.4 greater than observed for the mineral PC9 fuel but at the lower compression at the DPF the PC9 fuel soot total PAH was greater by a factor of 1.59. Therefore there was a 6% reduction in the total PAH for the EN590 fuel soot and a 4732% increase in the total PC9 soot PAH content.

Since the PAH originated from the base fuel and pyrosynthesis during combustion (Section 2.4.4), the increased DPF PC9 soot PAH concentration suggests this was the result of the compression ratio reduction and/or a significant change in non-PAH related components in the soot as the soot evolved in the exhaust.

The analysis of the PC9 soot bulk inorganics in Section 7.4 revealed that there was a significant reduction in PC9 soot bulk sulphur concentration from 63.86% to 3.49% of the total wt % of inorganics in the two soot samples between the exhaust manifold and DPF at the same compression ratio and this was attributed to oxidation reactions in the oxidation catalyst. Parallel to this, in Section 7.3, it was shown that the PC9 soot surface sulphur concentration increased by 500% between the exhaust manifold and the DPF. It is postulated that this was sulphur released from the soot bulk which then partially condensed onto the soot surface between the oxidation catalyst and DPF. It is therefore postulated that part of the 4732% increase in PAH for the PC9 soot in Figure 7.20 is attributable to the condensation/adsorption of material released in the oxidation catalyst reactions in the exhaust system.

However, the assignation of all of the increase in the PC9 soot PAH illustrated in Figure 7.20 to these oxidation catalyst reactions alone is not the complete picture. As was previously detailed in Section 6.6, the PC9 soot at 19.5:1 compression ratio at the exhaust manifold had an extremely low PAH

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concentration relative to the EN590 soot and this finding was opposite to the relative concentration of aromatics in the EN590 and PC9 fuels, Appendix 1 (Table A1.1). Further, cross referencing the results depicted in Figure 7.20 with the results discussed in previously in Section 7.3; the low PAH concentration for the PC9 soot at the 19.5:1 compression ratio at the exhaust manifold was opposite to the high surface sulphur content; then at the DPF the situation reversed with the surface sulphur concentration lower and the PAH concentration significantly increased. In the result discussion in Section 6.3 it was postulated that the reduction in compression ratio from 19.5:1 to 16.5:1 changed the processes by which the PC9 fuel sulphur was entrained within the soot and adsorbed onto the surface.

Consequently, in Section 6.6 it was postulated that either the processes which changed the sulphur adsorption on the PC9 soot surface also regulated the PAH adsorption or alternatively the sulphur itself when adsorbed at sufficient concentration on the soot surface acted to inhibit the adsorption of PAH. It was therefore concluded in Section 6.6 that it was likely the reduction in compression ratio also resulted in an increase in the surface PAH adsorption. Thus, it is hypothesised that the significant increase in PC9 soot total PAH concentration depicted in Figure 7.20 occurred do the additive effects of the reduction in compression ratio and soot evolution in the exhaust and the respective PC9 soot surface and bulk sulphur changes which followed.

The forgoing hypothesis of the related PC9 soot sulphur and PAH behaviour is supported by the relatively stable EN590 mineral diesel fuel soot PAH concentration between the 19.5:1 exhaust manifold soot sample and the 16.5:1 DPF soot sample, Figure 7.20, and the fact that sulphur was not detected on the EN590 soot surface, Table 7.2.

As a result of the significant change in the total PAH concentration for the PC9 soots, Figure 7.20, the direct comparison of individual PAH components (µg PAH/g) reported in Table 7.7 and Table 7.8 is not particularly revealing. It is more useful to consider the individual soot PAH profile with the PAH concentration calculated as a percentage of total sample PAH for each sample and this data is presented in Figure 7.21 for the 19.5:1 compression ratio and Figure 7.22 for 16.5:1.



Figure 7.21: 19.5:1 Exhaust Manifold Soot PAH for EN590, PC9 and B100 fuels (GC-MS)





Comparison of Figure 7.21 and Figure 7.22 reveals that the PAH profiles of both mineral fuel soots changed markedly with both the compression ratio reduction and evolution of the soots in the exhaust. At the exhaust manifold the normalised concentrations of PAH for the two mineral fuels were similar and distributed largely between Naphthalene to Phenanthrene. In contrast, the B100 soot PAH were largely concentrated in the smaller centralised group of Acenaphthene to Chrysene. Previously in Section 5.7 it was argued that this narrower range of PAH in the B100 soot was the result of the original fuel having no aromatic content, Appendix 1 (Table A1.1); which in turn meant all the B100 soot PAH derived from pyrosynthetic reactions during combustion rather than

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from the fuel. Thus, concentrations of low molar mass PAH in the B100 soot, which are typically associated with the original fuel [173, 174, 179], were low or negligible.

Further down the exhaust at the DPF, the distribution of PAH in the EN590 and PC9 soot PAH profiles was found to be tightly focussed between 1methylnaphthalene and Phenanthrene, Figure 7.22. Thus, there was a distinct absence of Naphthalene in these low compression DPF soots. Since Naphthalene is a common PAH reported in fuels [181], the lack of any Naphthalene at the DPF is a clear indication that the evolution of the soot in the exhaust resulted in a significant change in the profile of the soot PAH and therefore the changes in PAH distribution between Figure 7.21 and Figure 7.22 were most likely the result of the reactions precipitated by the oxidation catalyst between the exhaust manifold and DPF rather than the compression ratio reduction.

The very similar total concentration of PAH for the EN590 soot but the significant change in PAH distribution was very interesting in that it implies the reactions driving the considerable change in PAH profile likely did not also significantly change the overall concentration of PAH in the soot. In the case of the significant change in PC9 soot PAH concentration, Figure 7.20, this indicates that the change in concentration must have been forced by some additional mechanism and therefore the earlier postulation of a mechanism linked to the parallel changes in surface sulphur concentration would appear to be the principal mechanism even though the PAH profile changed considerably.

It was discussed previously in Section 5.7 that the process of grouping PAH by molar mass and then summating the PAH concentrations for like molar mass was a fruitful methodology in the evaluation of the differences in the PAH for the three fuels. Since it is observed from Figure 7.21 and Figure 7.22 that the PAH profiles of the mineral diesel soot changed considerably as the soots evolved in the exhaust, it is useful to also consider what the same PAH analysis method might reveal about this evolutionary behaviour. Presented in Figure 7.23 is the result of the application of this PAH molar mass grouping to the PAH results for EN590 and PC9 soots at the exhaust manifold at 19.5:1 and at the DPF at 16.5:1. 7



Figure 7.23: Mineral Fuel 19.5:1 Exhaust Manifold and 16.5:1 DPF PAH Molar Mass Profile (GC-MS)

Figure 7.23 confirms that the DPF soot generally had a somewhat narrower molar mass distribution of PAH which was concentrated in the range of 142 to 178 molar masses. The EN590 soots at the DPF compared to the PC9 soots had a slightly narrower molar mass range 152-178 (vs. 142-178) and therefore a slightly higher central molar mass. Interestingly for the DPF soot, the PAH concentrations at 128 and 142 molar masses which were present at the exhaust manifold were not present for the EN590 soot and only atomic mass 142 was present for the PC9 fuel soot. These two PAH atomic masses are typical of the aromatics present in the fuel, Section 2.4.4, so the disappearance or transformation into higher atomic mass PAH illustrates the significant potential for PAH profile evolution in the exhaust as the soot matures. Therefore, it is conceivable that the soot evolutionary processes could also change the toxicity of the soot. Additionally, the compression ratio reduction which is postulated to have influenced the total PAH concentration for the sulphur rich PC9 fuel soot (discussed in Section 6.6 and alluded to earlier in this section), could therefore also influence the toxicity of the soot.

The final observation from Figure 7.23 reciprocates the finding discussed in Section 5.7 that there appears to be a preference for soot PAH of molar mass 178 g/mol (Phenanthrene). In Section 5.7 this was reported to be common observation across the three fuels and the result presented in Figure 7.23 extends this to also include the evolutionary changes in the exhaust. This reinforces the statement in Section 5.7 that Phenanthrene is believed to be what is called a 'stabilomer specie' (Section 2.4.4), that is a PAH which has been

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shown to be very stable at temperatures typical of hydrocarbon flames [25, 180]. The review by Dobbins [181] specifically identifies alkylated phenanthrenes as a dominant PAH for hydrocarbon flames. This work herein therefore indicates that Phenanthrene is a stabilomer specie for both mineral diesel and biodiesel fuel combustion and which also appears regardless of change in engine compression ratio and soot evolution in the exhaust through a diesel oxidation catalyst.

In summary; it is postulated that the change in PC9 PAH concentration was effected by the same processes and factors governing surface sulphur concentration change i.e. both compression ratio reduction and soot evolution. The significant PAH profile change however is postulated to be primarily the result of the evolution and hence oxidation catalyst reactions experienced by the soot in the exhaust. This significant change in PAH distribution illustrated between Figure 7.21 and Figure 7.22 would be a very interesting area to study in future work.

7.8 Concluding Remarks

It is clear from the result analysis and discussion presented in this chapter that the soot transformation in the exhaust is highly dependent on the original structural form and surface state of the soot as it exits the cylinder i.e. the specific physiochemical soot properties 'baked in' during combustion.

When the soots were sampled at the DPF the commonality observed between the EN590 and B100 soot surface composition at the exhaust manifold was no longer observed as the surface O/C ratio of the EN590 soot had increased 23.8% whereas for the B100 soot the increase was 128% and had also gained a very low level sulphur concentration. By contrast the PC9 soot surface O/C ratio had reduced 5.1% Thus, from this it was deduced that B100 soot must have undergone a much higher rate of oxidation than the other two soots, compared to the EN590 soot the B100 soot O/C ratio increased by a factor of 1.8. Additionally, the analysis of ICM-MS bulk inorganics concentration change as the soots evolved in the exhaust also suggested a relatively higher rate of carbonaceous fraction loss which was 3-4 times that of the mineral soots.

A 5% fall in PC9 soot surface oxygen in the exhaust is believed to have been caused by sulphur which migrated (possibly through pores in the soot) to the surface of the soot, oxidised with surface oxygen and free oxygen in the exhaust in the oxidation catalyst and was then volatilised. Such a mechanism would cause the reduction in bulk sulphur and reduction in surface oxygen as was

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> observed. Investigation of this process by sampling both before and directly after the diesel oxidation catalyst over a wider range of exhaust temperatures with similar medium sulphur fuels as utilised herein is proposed for future work.

> The multi-faceted, even opposed changes in morphological properties during the exhaust evolutionary process for all soots made it difficult to develop a full physical understanding of each individual soot transformation in the exhaust and several alternate models have been proposed in this chapter to explain the key observations. TEM is strongly advised as supportive soot morphological analysis method in future diesel soot work in combination with the methods utilised herein.

> A complex interplay was observed between PC9 soot surface sulphur and surface acidity as the soot evolved in the exhaust which indicated the relationship defined in earlier chapters that describes a proportional increase in surface acidity with sulphur concentration is incomplete. This relationship is likely sensitive to the environment in which the sulphur compounds are formed and adsorbed onto the surface of the soot. For example, soot surface sulphates at the exhaust manifold which are derived from high temperature in-cylinder reactions have a different influence on the soot surface functional groups compared to sulphates released and re-adsorbed when the soot passes through the oxidation catalyst in the exhaust.

> There was observed a significant PAH profile change as both the mineral fuel soots evolved in the exhaust and it is postulated that the oxidation catalyst reactions had the primary role. There was also a 4732% increase in the total PC9 soot PAH content which it is postulated was coupled to the same processes and factors governing surface sulphur concentration change. In support of findings from previous chapters, Phenanthrene (molar mass 178 g/mol) was found to be persistent in the PAH profile of all fuel soots even after oxidation catalyst reactions, therefore further increasing confidence that this is a PAH 'stabilomer specie'.

8 Soot Physiochemical Properties for High and Low EGR

8.1 Introduction

This chapter presents the results and analysis for the soot sampled from the engine exhaust system DPF (Section 3.5.2) with the engine fuelled with EN590 and B100 fuels and operated at a baseline condition of 1400 rpm and 12 bar BMEP for the EN590 low EGR condition. This aim of this chapter is to understand how the change from low to high EGR affected soot physiochemical properties for both the EN590 and B100 fuels. The samples were collected during the experiments described in Section 3.1.5.4.

8.2 EGR Experimental Test Parameters

The determination of the actual achieved EGR rate for each of the four EGR experiments was calculated with Equation 3.1 detailed in Section 3.1.5.4 using the measurements of the intake mass air flow, intake pressure and intake temperature without EGR and then with. Following this calculation it was determined that the low EGR rates for the EN590 and B100 fuel experiments were 10% and 12% respectively. At high EGR the stability of the EGR control available was improved and for both fuel experiments the EGR rate was estimated to be 55%. Consequently, in this chapter 'low EGR' is used collectively to describe 10-12% EGR rate and 'high EGR' is used to describe 55%.

Table 8.1 presents the averaged engine performance and emissions data for the four EGR experiments which were conducted according to the methodology in Section 3.1.5.4. It can be observed that the injection duration used for both fuels at like EGR conditions was equivalent and that this resulted in lower BMEP for the B100 fuel due to the lower heating value of the RME biodiesel. The fuel inlet temperature was very similar across all four experiments along with the pre-EGR valve IMAT and IMAP, ensuring there was good consistency across the experiments. The post-EGR valve IMAT saw a very significant increase in temperature with the high EGR as the engine was devoid of EGR cooling.

	Speed	Load	BMEP	IMAT Pre EGR	IMAT PostEGR	Exhaust Man	DPF Inlet	FuelIn	IMAP	Start of Inj.	Inj. Duration	DPF ΔP Max.
Description	(udu)	(jug	(bar)	(c)	(c)	(c)	(c)	(c)	(mbar)	("CA BTDC)	(CA)	(Pa)
EN590 55% EGR	1400	51.1	3.4	28.7	171.9	391,165	289.5	25	1076	4	8.2	12000
EN590 10% EGR	1400	181.3	12	26.2	51.7	593.2	449.4	27	1556	ξ	12.8	22000
B100 55% EGR	1400	48.2	3.2	25.5	185.9	415.1	295.9	26.8	1088	4	8.2	23000
B100 12% EGR	1400	172.1	11.5	28.6	54.9	548.6	398.9	29	1556	13	12.8	4000
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	MAF	Fuel Rate	AFR	AVL415	AVL415	AVL415 Mean	Soot	C02	8	02	NOX	нc
Description	(kg/h)	(kg/h)	•	(FSN)	(mg/m 3)	(m g/m3)	(4/B)	% Vol	mdd	% Vol	mqq	mqq
EN590 55% EGR	37.8	2.656	14.2	8.41 to 9.63	2506 to 10865	2018	216.6	11.92	0009	1.93	8	10000
EN590 10% EGR	113.76	6:059	18.8	3.13 to 4.33	126 to 275	183	17.0	10.81	822	5.91	885	64
B100 55% EGR	39.6	2.816	14.1	6.96 to 9.49	1196 to 6541	2655	85.8	12.8	2000	3.09	24	2686
B100 12% EGR	105.48	6.248	16.9	0.69 to 1.91	11 to 48	38	3.3	10.89	1060	7.42	917	8

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EGR Sample Collection Parameters

The second part of Table 8.1 defines the air and fuel measurements and also the emissions measurements for the EGR experiments. The fuel rate for the B100 experiments was higher than the equivalent EN590 fuel due to the higher density of the B100 fuel, Appendix 1 (Table A1.1). The controllability of the MAF was not of high precision and thus there was slight variation in the averaged MAF for the like EGR experiments. Very low AFR was observed in the two high EGR experiments and consequently the observed mean AVL 415 exhaust soot concentrations were extremely high for both fuels. The exhaust emissions measurements showed that the NO_x emissions were almost eliminated with the very high rate of EGR for both fuels and the HCs were significantly increased. The concentration of exhaust CO_2 increased with the high rate of EGR as the MAF and fuel rate reduced leading to a lower AFR.

Section 4.3.2 introduced the fuel-soot-factor parameter to provide a measure of the relative soot producing tendency of the fuels used in this investigation and when applied to the data in Table 8.1 yields the averaged FSF data presented in Table 8.2.

	Fuel Rate	MAF	AVL415 Mean	Soot	FSF	FSF	Normalised FSF
Description	(kg/h)	(kg/h)	(mg/m3)	(g/h)		(%)	
EN590 55% EGR	2.656	37.8	7018	216.6	0.081543	8.154	1.000
EN590 10% EGR	6.059	113.76	183	17.0	0.002805	0.281	0.034
B100 55% EGR	2.816	39.6	2655	85.8	0.030481	3.048	0.374
B100 12% EGR	6.248	105.48	38	3.3	0.000524	0.052	0.006

Table 8.2: 16.5:1 Low and High EGR Fuel-Soot-Factor (FSF)

From Table 8.2 it can be seen that the EN590 fuel at low EGR was observed to have an FSF which is a factor of x5.4 greater than that of the B100 fuel but at high EGR the relative difference between the fuels was reduced to x2.7. Thus, at high EGR the relative tendency of the B100 fuel to produce soot by this measure was higher than at low EGR. e.g. the factor increase in the FSF from low to high EGR was x29 and x58.2 for the EN590 and B100 fuels respectively. This was the combined effect of the very significant increase in EGR and the reduction in AFR detailed in Table 8.1.

8.3 EGR Sample Collection Parameters

Table 8.3 presents a summary of the soot collection for the EGR experiments and shows how the collection duration varied from just over nine minutes to over 190 minutes by virtue of the far higher exhaust soot concentration observed at high EGR and for the EN590 fuel.

Soot Surface Elemental Composition

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	Collection	Exhasut	Exhaust Mass	Est. Final DPF	Total Mass Flow	Sample Mass
	Duration	Soot	Flow	Soot Mass	Through DPF	Extracted
Description	(min)	(g/h)	(kg/h)	(g)	(kg)	(g)
EN590 55% EGR	9.3	216.6	40.46	33.57	6.27	1.3
EN590 10% EGR	84	17.0	119.82	23.79	167.75	3.3
B100 55% EGR	37	85.8	42.42	52.93	26.16	1.1
B100 12% EGR	197	3.3	111.73	10.74	366.84	2.5

Table 8.3: 16.5:1 Low and High EGR Experiment DPF Soot Collection Summary

Table 8.3 reveals that the total mass of soot sample extracted from the DPF was higher for both the low EGR experiments. This however was opposite to the estimated soot mass for both low and high EGR which is based on the measured exhaust soot concentration and exhaust mass flow. It is believed that this discrepancy is attributable to the reliability and robustness of the AVL 415 smoke meter (Section 3.2.2.5) exhaust soot concentration measurements for the high EGR conditions.

To explain; Table 8.1 details how both the CO and HC emissions were extremely high for these two experiments and therefore the composition of the sampled exhaust was significantly changed with a possibility that the optical filter paper based technique of the AVL 415 is less robust with such extreme exhaust gas compositions leading to inaccurate measurements of the carbonaceous soot fraction. Indeed, the AVL 415 reported smoke numbers were at the extreme end of the device's range (maximum of 10) (Table 8.1) and the device's calibrated conversion to mg/m³ could be questioned in such extremes. The extent of the FSN variation reported in Table 8.1 is attestable to this.

8.4 Soot Surface Elemental Composition

Table 8.4 summarises the soot surface carbon, oxygen, nitrogen, sulphur and chlorine as well as the ratios of surface oxygen/carbon and sulphur/carbon for the two fuels investigated. All soot samples were collected with and then subsequently extracted from the DPF Section 3.5.2.

 Table 8.4: 16.5:1 Low and High EGR DPF Soot Surface Elemental Composition (XPS)

	wt%C	wt% O	wt%N	wt%S	wt% Cl	0	/C	S	/C
Description						ratio	precision	ratio	precision
16.5:1 EN590, 55% EGR	94.6	5.4	0.0	0.0	0.0	0.0571	0.0113	0.000	0.0000
16.5:1 EN590, 10% EGR	93.1	6.9	0.0	0.0	0.0	0.0741	0.0117	0.000	0.0000
16.5:1 B100, 55% EGR	93.6	6.4	0.0	0.0	0.0	0.0684	0.0115	0.000	0.0000
16.5:1 B100, 12% EGR	89.3	10.2	0.5	0.3	0.0	0.1142	0.0126	0.003	0.0057

Soot Surface Elemental Composition

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Table 8.4 details how the soots collected for both the EN590 and B100 low EGR test conditions matched more closely with the rated power DPF sampled soot surface elemental composition (Section 7.3) than was observed for the high EGR soots, as would be expected.

Unusual concentrations of nitrogen and sulphur were observed for the low EGR B100 experiment soot sample. The nitrogen observation was particularly unusual as nitrogen was not detected in the surface chemistry for any other sample investigated in this work. The source of this observation was therefore not clear and multiple re-tests with the engine would be required to validate if the nitrogen was present in the sampled soot surface (unlikely) or whether this was subsequent contamination of the sample (more likely). Unfortunately, due to sample mass limitations, repeat XPS tests using another part of the soot sample could not be performed.

A similar observation of sulphur on the surface of the B100 soot was detailed previously in Section 6.3 and Section 7.3 for the rated engine condition experiments where the soot was also sampled at the DPF having travelled down the exhaust. The concentration of sulphur observed for the low EGR B100 soot sample was however somewhat higher at 0.3% weight compared to 0.05%.

As discussed in Section 6.3, the presence of surface sulphur for the B100 fuel proved difficult to explain due to the low (<10 ppm) sulphur content of the B100 fuel, Appendix 1 (Table A1.1), and the lack of any sulphur on the surface of the EN590 soot in any of the samples investigated in this work. In Section 6.3 and Section 7.3 it was proposed that the sulphur was deposited as an existing contaminate from the exhaust system with the measured high HCs emissions (Table 4.10 Part C) indicating the potential for a high SOF which potentially could have encouraged the entrapment of existing exhaust deposits onto the soot.

It is possible a similar mechanism may have been behind the B100 soot surface sulphur observations at low EGR and strong support for this comes from the thermogravimetrical results presented later in Section 8.9 (Table 8.11) which detail how a higher SOF was indeed present for the B100 low EGR soot sample in comparison to the other EGR soot samples. It is also possible that the same mechanism may have occurred for EN590 soot but the resulting sulphur concentration was below the XPS detection threshold. This hypothesis however contrasts with Table 8.1 where the HC emissions of the B100 and EN590 fuels are reported to have been quite similar at low EGR. Since the soot sulphur result

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> in Table 8.4 and the soot SOF result in Table 8.11 agree and are derived from the same soot sample, then this postulation from Section 6.3 and Section 7.3 remains the most likely.

Table 8.11 also reports that the SOF was also higher but to a lesser extent for the high EGR B100 soot relative to both the low and high EGR EN590 soot. In contrast, Table 8.4 indicates that there was no surface sulphur detected for this sample. However, since the proceeding analysis in Section 8.5 shows that the carbonaceous fraction of soot was likely significantly higher for the high EGR B100 soot, this greater carbon content can be assumed to have suppressed any low level surface sulphur concentration. This is indicated by the significant increase in surface carbon for the high EGR B100 soot relative to the low EGR soot, Table 8.4.

Figure 8.1 details the surface oxygen and O/C ratio for the soot from the EGR experiments and shows that there was both lower oxygen concentration and O/C ratio for the high EGR experiments for both fuels. The reduction for both parameters with the change from low to high EGR was most significant for the B100 soot by virtue of the very high surface oxygen and surface O/C ratio observed for B100 soots for the low EGR condition. This high O/C ratio for B100 soot at low EGR was reflective of the observation for the DPF sampled soot from the 16.5:1 experiments at rated engine condition as was discussed previously in Section 6.3 and Section 7.3.



Figure 8.1: 16.5:1 Low and High EGR DPF Soot Surface Elements for EN590 and B100 Fuels (XPS)

Soot Surface Elemental Composition

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> Therefore, this high O/C was indicative of a high rate of B100 soot oxidation between the engine cylinder and the DPF collection location for the low EGR soot. Since the O/C ratio for the EN590 soot was much lower, these two sets of measurements add further supporting evidence to the much greater rate of B100 soot oxidation proposed to explain the high O/C ratio observed for B100 soot in the exhaust for the rated power experiments discussed in Section 6.3 and Section 7.3.

The observation of the much lower surface O/C ratio for the soot from the high EGR experiments is very interesting as this is indicative of the oxidative reaction process that the soot underwent in the exhaust being limited or even shut down completely.¹⁴ Such an observation is very important as it would be of interest in exhaust aftertreatment systems design and thus it requires explanation.

To explain this observation it is necessary to refer to the engine performance and emissions data for the experiments which is presented in Table 8.1. Three parameters from Table 8.1 are important for explaining the restricted soot oxidation in the exhaust and these are the AFR and the measured O_2 and NO_x concentrations in the exhaust. The AFR data showed that for the high EGR experiments the AFR was about stoichiometry (~14.5) and consequently the measured exhaust O_2 was very low, between 1.9 to 3.1%. It is thus believed that the very low O_2 ratio in combination with the very low exhaust NO_x concentration were the primary causes of the very low surface O/C ratio at high EGR as there was essentially little free oxygen available to oxidise the soot both in-cylinder and in the exhaust system.

To illustrate the significance of this change in O/C ratio, Figure 8.2 presents the change and percentage change for the two fuel soots. The reduction in O/C ratio for the EN590 soot was 21.7% and for the B100 soot the reduction was 37.3% and the error bars show that in both cases these changes were in excess of the measurement error.

¹⁴ The high EGR O/C ratios were the lowest observed for any soot samples in this work and similar for both fuel soots.

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8.5 Soot Bulk Elemental Composition

Table 8.5 presents the percentage weight of inorganics for the bulk composition of the sampled exhaust soot for both high and low EGR; this data has been converted into the percentage contribution of each element to the total sample inorganics and this set of results is presented in Table 8.6.

Table 8.5: 16.5:1 Low and High EGR DPF Soot Bulk Elemental Composition (% weight) (ICP-MS)

						Bulk Inorg	anic Conta	aminants (wt%)				
Description	%Ca	%Cu	%Fe	%Mg	%Mn	%Na	%Р	%S	%Si	%Zn	%AI	%Cd	Total wt%
16.5:1 EN590, 55% EGR	0.10	0.00	0.04	0.00	0.00	0.00	0.03	0.00	0.05	0.05	0.00	0.00	0.27
16.5:1 EN590, 10% EGR	0.60	0.00	0.17	0.00	0.00	0.00	0.35	0.00	0.07	0.34	0.00	0.00	1.53
16.5:1 B100, 55% EGR	0.37	0.00	0.14	0.00	0.00	0.00	0.19	0.00	0.15	0.20	0.00	0.00	1.05
16.5:1 B100, 12% EGR	1.18	0.00	0.40	0.00	0.00	0.00	0.67	0.00	0.21	0.67	0.00	0.00	3.13

Table 8.6: 16.5:1 Low and High EGR DPF Soot Bulk Elemental Composition (% weight/total % weight) (ICP-MS)

				E	Bulk Inorga	nic Conta	minants (v	vt%/Total	wt% Inorg	anics)			
Description	%Ca	%Cu	%Fe	%Mg	%Mn	%Na	%Р	%S	%Si	%Zn	%Al	%Cd	Total %
16.5:1 EN590, 55% EGR	37.04	0.00	14.81	0.00	0.00	0.00	11.11	0.00	18.52	18.52	0.00	0.00	100.0
16.5:1 EN590, 10% EGR	39.22	0.00	11.11	0.00	0.00	0.00	22.88	0.00	4.58	22.22	0.00	0.00	100.0
16.5:1 B100, 55% EGR	35.24	0.00	13.33	0.00	0.00	0.00	18.10	0.00	14.29	19.05	0.00	0.00	100.0
16.5:1 B100, 12% EGR	37.70	0.00	12.78	0.00	0.00	0.00	21.41	0.00	6.71	21.41	0.00	0.00	100.0

The change in EGR is observed to have had a significant effect on the soot elemental composition, Table 8.5; this is most clearly illustrated by the significant reduction in total bulk inorganics for both fuel soots with the increase in EGR. This result is illustrated in Figure 8.3.



Figure 8.3: 16.5:1 Low and High EGR DPF Soot Bulk Elemental Analysis for EN590 and B100 Fuels (total wt %) (ICP-MS)

Figure 8.3 illustrates that in respect to the change in total percentage weight of inorganics, it was observed that the concentration of inorganics was highest for the B100 soot for both low and high EGR and it therefore follows that this was a consequence of the much lower carbonaceous soot fraction at both low and high EGR relative to the EN590 experiments, Table 8.1. This effect is thought to have been amplified by the higher rate of B100 soot oxidation in the exhaust, as outlined earlier in Section 8.4, which is postulated to have further reduced the B100 soot relative carbonaceous fraction prior to the DPF.

Figure 8.4 presents the soot sample percentage weight data from Table 8.5 for all experiments and makes clear that for all elements, the B100 soot had higher concentration of each and that the principal elements were those reported in previous chapters i.e. (Ca, Fe, P, Zn).

An important observation from Figure 8.4 is the presence of the element silicon which was not discussed in previous chapters. Silicon however, was also observed in the rated engine power soot collection experiments but was one of the identified foreign contaminates subtracted from the rated engine power soot collection results as detailed in Appendix 8 (Section A8.2.2). Ergo, silicon was not discussed in these earlier chapters. Appendix 8 (Section A8.2.2) explains that the source of this silicon was identified to be principally a Loctite 5367 silicon sealant used to seal up the low compression cylinder head gasket, Section 3.3.4. Since silicon contamination was only present for the 16.5:1 compression ratio engine experiments, it was therefore observed in all the EGR experiments. This coupled to the fact that it was also the least significant inorganic contaminate in the

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majority of the EGR soot samples, resulted in silicon not being subtracted from the EGR soot sample data.





The change in the percentage weight of each bulk inorganic element with the change from low to high EGR is presented in Figure 8.5.



Figure 8.5: 16.5:1 Low to High EGR DPF Soot Bulk Elemental Analysis for EN590 and B100 Fuels (wt % change) (ICP-MS)

Comparison of Figure 8.4 and Figure 8.5 reveals that the reduction in concentration of soot inorganics with the reduction in EGR was very similar across all elements for the soot from each fuel. It is also clear that there were reductions for all elements without exception (including silicon) and taken

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together these observations gave confidence in the consistency of the results. The individual reductions in each element also mirrored the pattern of the original concentration of each element in the soot Figure 8.4; this indicates that the reduction in total inorganics was caused principally by an increase in the carbonaceous concentration in the soot samples with the increased EGR rate, rather than any other process.

Due to the greater reduction in the B100 soot inorganics with the change from low to high EGR, it is useful to consider individual elements as a percentage of the total inorganics in the sample as is detailed in Table 8.6 and this data is presented in Figure 8.6.



Figure 8.6: 16.5:1 Low and High EGR DPF Soot Bulk Elemental Analysis for EN590 and B100 Fuels (wt %/total wt %) (ICP-MS)

The results in Figure 8.6 confirm that the highest contributing inorganic contaminate was calcium, with the concentrations of the two next most significant elements, phosphorous and zinc, contributing roughly equally. This pattern of key contaminating elements is therefore consistent with that observed for the rated engine power experiments reported earlier in Chapter 5, Chapter 6 and Chapter 7. The relative contribution of iron is however much lower than that observed (35-50%) for the soot collected in the DPF at 16.5:1 for the rated engine experiments Figure 7.7.

The lower contamination of iron and zinc likely results from the combination of increased exhaust soot concentration and lower exhaust mass flow rate (i.e. potentially reduced abrasion of the surfaces of the exhaust). A shorter length of

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exhaust from the exhaust manifold to the DPF for the EGR tests was also utilised due to the lower exhaust temperatures (Figure 3.30 vs. Figure 3.31) and this also likely contributed to the reduced iron and zinc contamination. By comparison, the EGR change was observed to only change the contribution of iron in a narrow range (<5%) as reported in Figure 8.6 relative to the (15-35%) higher iron content reported in Figure 7.7. This observation is useful information which could assist in the design of engine exhaust soot collection techniques and experiments beyond this work.

Figure 8.7 presents the change in percentage of each element of the total percentage of inorganics in the soot and shows that with the increase in EGR there was observed a reduction in (Ca, P, Zn), all of which were components of the lubricant, Appendix 2 (Table A2.1). If these reductions were associated with the lubricant, then it is postulated that the lubricant consumption rate could have been reduced at high EGR; thus having the effect of proportionally reducing the (Ca, P, Zn) elements in the environment where the soot formed and evolved.

Since the engine load was somewhat reduced for the high EGR experiments, Table 8.1; then it is possible there was indeed reduced lubricant consumption. This is because in literature, lubricant consumption has been reported to increase with speed and load [325]. Therefore, attributing the reduction in (Ca, P, Zn) element concentration illustrated in Figure 8.7 to a reduction in lubricant consumption rate brought about via the EGR rate change, is a viable explanation.



Figure 8.7: 16.5:1 Low to High EGR DPF Soot Bulk Elemental Analysis for EN590 and B100 Fuels (change wt %/total wt %) (ICP-MS)

Opposite to the (Ca, P, Zn) reductions, Figure 8.7 shows that the iron and silicon concentrations increased. It is postulated that the increase in iron was attributable to an increase in iron contamination from the engine which was most likely because of the higher recycling rate of exhaust gas which meant the gas was resident longer in the engine thus increasing the concentration of metals such as iron in the soot. The silicon change also appeared to reflect the same trend as iron due to the same higher recycling of the exhaust which meant more silicon contamination.

At this point it is worth reflecting that the soot for the EGR experiments was collected using the DPF (Section 3.5.2) due to the impracticality of collecting sufficient soot mass using the ceramic thimble methodology (Section 3.5.1) at the low EGR condition with the B100 fuel, as described in Section 3.1.5.4. Thus, in respect to the EGR experiment, the bulk soot analysis at the DPF means it is not possible to separate the influence of the exhaust system metallurgy e.g. iron from the effects induced by the EGR rate change. However, there are several key findings that can still be drawn from a more searching analytical analysis the EGR bulk inorganic data.

Since in the EGR experiments the AVL 415 smoke meter sample probe was located closer to the DPF (Figure 3.30) than was the case in the rated engine power experiments (Figure 3.31); the FSF based bulk inorganic data scaling method utilised earlier in Section 6.4 could be employed once more to provide a qualitative indication of the relative effects of the fuel and the EGR change on the total mass of inorganics, with the fuel rate reduction and the increase in carbonaceous concentration isolated. This method involves scaling the bulk inorganic % wt data by the FSF for the EGR experiments which is recorded in Table 8.2.

First, the total percentage weight of inorganics of the DPF soot samples detailed previously in Figure 8.3 are better grouped into low and high EGR categories rather than fuel so that the distinctions of low and high EGR are clearer. Therefore, the data in Figure 8.3 is re-presented as Figure 8.8.

The FSF for the EGR experiments is reported in Table 8.2 and is illustrated in Figure 8.9. The FSF presented in Figure 8.9 illustrates that for both fuels, significantly more carbonaceous soot formed relative to the amount of fuel injected at high EGR.
8.5



Figure 8.8: 16.5:1 Low and High EGR DPF Soot Bulk Elemental Analysis for EN590 and B100 Fuels Total (% wt) (ICP-MS)

Figure 8.9 also reveals that at both high and low EGR, the EN590 fuel had a greater relative sooting tendency than the B100 fuel with the differences in fuel consumption rate accounted for (note that the fuel consumption rate for the B100 fuel was greater due to higher fuel density, Appendix 1 (Table A1.1)).



Figure 8.9: 16.5:1 Low and High EGR Fuel-Soot-Factor (FSF)

Figure 8.9 illustrates what was discussed earlier in Section 8.2; for the EN590 soot the FSF increased by a factor of 29 but for the B100 soot it increased by a factor of 58.2 due to the very low FSF at low EGR for the B100 fuel. Thus, it appears that the B100 fuel was nearly twice as sensitive to the change in EGR in

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terms of the carbonaceous soot fraction produced during combustion and measured at the AVL 415 sample probe.

However, this single point measurement of carbonaceous soot concentration on which the FSF calculation is reliant, cannot account for the effects of any changes in the relative rate of oxidation of the B100 and EN590 soots in the exhaust. For the EGR experiments this was an important consideration as at high EGR the free oxygen in the exhaust was reduced from an average of 6.7% down to 2.5% (Table 8.1) and such a change was observed to influence the oxidation experienced by the soots in the exhaust based on the change in surface O/C ratio discussed earlier in Section 8.4.

From Table 8.4 the DPF soot surface O/C ratio at low EGR for the B100 soot was observed to be 0.1142 compared to that of the EN590 soot 0.0741, i.e. a factor of 1.54 greater. At high EGR the two ratios were 0.0684 and 0.0571, i.e. a factor of 1.2 and thus the increased rate of oxidation for the B100 soot was therefore believed to have been reduced somewhat at high EGR.

Therefore as the AVL 415 sample probe was located in the exhaust roughly 1 meter upstream of the DPF, there would have been some loss of the carbonaceous fraction between the probe sample point and the DPF and this would mean that the carbonaceous fraction at the DPF would be slightly lower than what the AVL 415 based FSF suggested and also therefore lower than at the exhaust manifold. Unfortunately it was not possible to quantify the effect of this and equate into the (FSF x % weight inorganic) result which is discussed next.

It is postulated that this increase in sooting tendency of the B100 fuel and reduced oxidation potential are related to structural changes in the B100 soot caused by the change in EGR which were distinct from those of the EN590 soot. These structural differences, it is believed, are recorded in the soot density measurements discussed later in Section 8.6.2. It is thought that the changes in the conditions under which the soot formed and evolved in the cylinder resulted in these structural differences and these then impacted on the sooting tendency of the B100 fuel.

The scaling of the total percentage weight of soot inorganics to adjust for fuel rate is important for the EGR experiments due to the engine losing boost pressure at high EGR and causing the ECU cut the fuel injection quantity to compensate. For example, from Table 8.1 it can be observed that the increase

Soot Bulk Elemental Composition

from 10% to 55% EGR for the EN590 experiments resulted in a reduction of fuel consumption of 56%. Therefore, using the FSF to factor out the change in fuel rate and also exhaust soot concentration, results in a far more significant amendment of the relative contribution of inorganics to the soot sample than when the same methodology was applied previously in Section 6.4.

The total percentage weight of inorganics of the DPF soot samples detailed in Figure 8.8 has been multiplied by the FSF of the respective EGR experiment from Figure 8.9. The result from this provides a qualitative representation of the relative differences in concentration of soot bulk inorganics resulting from the EGR rate change alone for the two fuels and this result is presented in Figure 8.10. In other words, the result in Figure 8.10 is more illustrative of the actual effect of EGR change on the concentration of inorganic contaminates in the soot than the result indicated by Figure 8.8.





Referring back to the original total weight of inorganics data of Figure 8.8, it is clear that the total contribution of inorganics to the soot sample was reduced at high EGR and was due most likely to the much higher fraction of carbonaceous soot in the sample and also for the same reason the B100 organics fraction was higher than that of the EN590 soots at both EGR conditions as the measured exhaust soot concentration (carbonaceous fraction) was lower, AVL415 mg/m³ Table 8.1.

Soot Bulk Elemental Composition

Compared to Figure 8.8, Figure 8.10 reveals that qualitatively there was actually a relative increase in the total inorganic content for both fuels with the transition from low to high EGR when other confounding factors are accounted for. It is postulated that the relative inorganic concentration could be greater at high EGR due to the effects of the greater proportion of recirculated exhaust gas present in the cylinder during soot formation. For example, it is assumed that there was an increased concentration of inorganic material and carbonaceous soot in the cylinder at the start of combustion relative to a lower EGR condition. The carbonaceous soot part introduced during induction could have partially oxidised and then been replaced by newly formed carbonaceous soot but the inorganic material elements (i.e. the metals) would have survived combustion and thus increased in concentration in the cylinder in proportion to the EGR increase.

Further analysis of the data presented in Figure 8.10 for the EN590 soot samples reveals that the ratio of FSF scaled total percentage weight of inorganics between high/low EGR conditions for the two data sets was 5.13 which was close to the EGR 55/10 % ratio and therefore suggestive that the underlying increase in soot inorganic content was proportional to the change in EGR rate for the EN590 soot.

However, for the B100 soot, the same ratio was found to be 19.5 and therefore considerably greater. This was possibly related to the effects of the increased oxidation of the B100 soot in the exhaust and the apparent increase in sensitivity of the B100 fuel to the EGR changes as described previously based on the FSF presented in Figure 8.9 and the change in surface oxygen concentration presented in Figure 8.2. It is also possible that there was an increase in the lubricant consumption rate at high EGR with the B100 fuel. Previously in Section 5.4 this was observed to contribute to the increase in the contamination of bulk inorganics in the soot.

Although there are several plausible explanations for the much greater apparent factor increase in B100 soot bulk inorganics contamination indicated by Figure 8.10; it is advised that the earlier concerns raised regarding the inability to account for loss of soot carbonaceous fraction in the exhaust between the AVL 415 probe measurement location and the DPF, do reduce the robustness of the FSF approach for the EGR soot data. There is confidence that the general trend presented in Figure 8.10 is valid for both fuel soots but the individual factor change is less robust.

8.6 Soot A

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Soot Morphology

8.6 Soot Morphology

Presented in Table 8.7 are the complete morphological results for the soot collected at 16.5:1 at the DPF for both low and high EGR conditions for the EN590 and B100 fuels.

Table 8.7: 16.5:1 Low and High EGR DPF Soot Morphological Characteristics¹⁵

	BET Method		BET Method BJH Adsorption		N2 Pycnometry		Primary Particle Diameter	
Description	Suface area (S _{BET}) (m ² /g)	Error	Average pore diameter (Å)	Density (ρ) (g/cm ³)	Error	Dpp = $6/(\rho S_{BET})$ (nm)		
EN590 55% EGR	82.073	0.3947	NA	1.8607	0.0085	39.289		
EN590 10% EGR	465.9806	2.3506	NA	2.1498	0.009	5.989		
B100 55% EGR	105.2695	0.537	NA	2.2101	0.0081	25.789		
B100 12% EGR	567.4451	3.158	NA	1.9999	0.0065	5.287		

8.6.1 Surface Area

The soot surface area results from the EGR experiments showed a very significant influence from the change in EGR from low to high and this is illustrated in Figure 8.11 for the data from Table 8.7.





With the increase from low to high EGR the soot surface area for both fuel soots reduced significantly, by 81.4% for the B100 soot and 82.4% for EN590. These reductions were suggestive of much larger primary particle diameters for the high EGR soot which likely resulted from the very high relative exhaust soot concentration for the high EGR experiments, Table 8.1. This higher carbonaceous content would likely have been deposited as successive layers of graphene planes around the soot core, thus growing the size of the primary

¹⁵ The BJH porosity results for the EGR soot samples are not reported as these results were not available for these four soot samples.

8.6

particles. This then combined with a very low rate of oxidation in the exhaust due to the high EGR and low exhaust O_2 as the soots travelled down to the DPF. Therefore the soot trapped in the DPF at high EGR had a much larger diameter and smaller surface area compared to the low EGR soots.

For the low EGR condition, the surface area was observed for both fuel soots to be higher than the equivalent observed surface area for the soots sampled from the DPF in the 16.5:1 rated power experiments, (235 to 353 m²/g) Section 7.5.1. As stated previously, the surface area of soot in general was postulated to be a function of the physical diameter of the individual soots, the surface porosity and the aggregate form. Since the porosity of the EGR soots was unknown for these samples, it was not possible to identify the contribution of the changes in these individual factors to the observed changes in soot surface area with EGR.

However, since the soot collected at rated engine conditions was also from a low (<10%) EGR condition, it is possible that the high surface areas of the soot from the low EGR experiments were related to the lower engine speed and load of the EGR experiments (i.e. 1400 rpm, 170-180 Nm vs. 4000 rpm, +200 Nm). In respect to engine speed this is opposite however to the observations of Stanmore et al. [139]. Therefore, due to different engine design such a generalisation is possibly not robust.

Furthermore, since soot surface area is frequently reported in literature to be sensitive to the temperature of the gas medium to which the soot is exposed [130, 131, 132, 133, 135], it is sensible to also consider the exhaust manifold temperatures for the rated power (Table 4.10 Part B) and EGR experiments (Table 8.1) but these are revealed to be close; 604/593.2°C for EN590 and 531/548.6°C for B100 respectively. Therefore, temperature does not appear to have been a factor in the greater surface area of the EGR experiments.

Finally, another consideration is the oxygen concentration in the exhaust and hence the potential oxidation rate for the soots but again the O_2 concentration for the rated power experiments (Table 4.10 Part C) was greater than the equivalent EGR experiments (Table 8.1); 7.73/5.91% for EN590 and 8.11/7.42% for B100 respectively. The high surface area of the low EGR experiment soots therefore does not have a clear association with any of the principal mechanisms known and may thus be something specific to the soot morphology originating from the low EGR experiments.

8.6

At both low and high EGR the surface area of the B100 soot was observed to be greater than the equivalent EN590 soot, Figure 8.11, which is opposite to the observations for the rated power soot collection experimental results, Figure 7.15. It is possible to infer from this that there was potentially greater SOF adsorbed onto the soot in the case of the B100 soot sampled at the DPF for the rated power experiments and indeed a comparison between the TGA results in Section 5.8 and Section 8.9 later in this chapter reveals that there was a higher SOF for the rated power tests, that is, the % weight of sample mass loss between room temperature and 400°C was 5% for the rated power experiment and 3.6% for the low EGR experiment. It is therefore believed that this higher SOF fraction for the B100 soot collected at rated power acted to both increase the primary particle size and fill the pores of the soot thus resulting in the lower surface areas for these soots compared to the low EGR soots reported in this section and also explaining the reversed relationship in respect to the EN590 soot.

It is also postulated that the greater surface area of the B100 soot compared to soot from the EN590 fuel for both low and high EGR could be related to a higher rate of oxidation for the B100 soot in the exhaust. This is because the O/C ratio for the B100 soot was greater at both low and high EGR, Figure 8.1. With greater oxidation it is postulated that the regular graphene planes that form the shell of soot are more amorphous/irregular in nature and therefore possessing greater porosity and hence surface area.

Another possibility is that the greater concentration of inorganic matter in the B100 soot bulk, Figure 8.3, also acts to introduce greater non-uniformity or surface irregularities into the soot structure [118]. Therefore several plausible explanations exist to describe the B100 soot surface area distinctions.

8.6.2 Density

The changes in soot density with EGR were observed to be opposed for the two fuel soots as illustrated in Figure 8.12, with the density of the B100 soot increasing 10.5% with EGR and that of the EN590 soot reducing 13.5%.

Comparing the low EGR density results with those from the rated power soot collection experiments reported in the analysis of the exhaust evolution in the exhaust Figure 7.17. Firstly the EN590 soot density is higher than observed for the equivalent rated power soot sample and secondly the B100 soot density is lower than the rated power equivalent. Thus, the low EGR soot density results were almost reversed to the rated condition findings. Soot density thus appears

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to be quite sensitive to the engine operating conditions but the relationship is not clear.





In Section 5.5.3 two models for the B100 soot are proposed to explain the observed B100 soot density and these are discussed again in Section 7.5.3. These models attempt to explain why it was observed that the B100 soot density reduced between the exhaust manifold and DPF for the 16.5:1 rated power experiments, Figure 7.17. From the reasoning in Section 7.5.3 it was concluded that B100 soot Model 2 offers a better description for the B100 soot observations for B100 soot exhaust evolution.

Model 2 describes the primary particles of the B100 soot at the exhaust as having a far more regular graphene plane internal arrangement with fewer isolated internal voids than was the case for the mineral fuel derived soot. This was then combined with a low surface porosity which also resulted from the highly regular arrangement of the graphene planes in the soot outer shell. This would in principle give rise to soots with small surface area, low pore volume and higher density as observed but if this is how the B100 soots were structured physically, then it is important to note that it is opposite to the description derived from TEM micrographs by Song et al. [16].

Model 2 proposes that isolated internal voids (Section 7.5.3) must have then been forming in the highly organised B100 soot core as the soot transited the exhaust and oxidised in the high temperatures of the exhaust. These trapped voids would result in the N2 pycnometry method over-estimating the skeletal volume, Section 3.6.4.3, thereby giving a lower density measurement as was

observed in the rated power DPF soot samples. Therefore, the B100 soot structure must have evolved such that the soot became more akin to the hollowed out soot core with intact outer shell in the form of that described by Song et al. [16].

This model when applied to the B100 soot observations for low and high EGR also appears to provide answers for the somewhat higher B100 soot density observed at high EGR. From the analysis of the behaviour of the soot O/C ratio in Figure 8.1 earlier, it is concluded that for the high EGR experiments the very low exhaust O₂ concentration (and likely also NO_x), Table 8.1, resulted in significant suppression of the soot oxidation process in the exhaust. For soot model 2 this would mean that the soot in the high EGR experiments should have a very high density due to it possessing a highly ordered soot core with minimal internal voids - which is indeed what was observed, Figure 8.12.

Importantly, this linking of the B100 soot oxidation and density does not describe the EN590 soot density change as the reduction in density coincided with a reduction in surface O/C ratio and hence the assumed oxidation for the EN590 soot was much lower at high EGR but the density of this soot was much lower too. These findings suggest that the physical structure of the EN590 and B100 soots were different and thus they responded differently morphologically to the change in conditions during formation and oxidation but a fully matured description of these processes is not possible with the available results. Therefore, to more fully understand the actual physical structural different rates of EGR, additional soot morphological examination methods such as TEM are necessary.

Though this is the case, to see the proposed model 2 for the B100 soot carry all the way through the observations of the work herein is a very encouraging sign that the model has strong validity. Importantly, these very high EGR experiments provided an excellent opportunity to evaluate B100 vs. EN590 soot behaviour at similar exhaust temperatures to those of the rated engine power experiments but with far lower exhaust oxygen concentrations. It is this comparison which really solidifies the clear distinctions in mineral and biodiesel soot physiochemical and morphological properties and behaviours that is a key general contribution of the work herein.

8.6

8.6.3 Primary Particle Diameter

The estimated soot primary particle diameter results from Table 8.7 are presented in Figure 8.13 and these results describe how the size of primary particles was largest for the high EGR experiments due principally to the much lower surface areas for these soots as detailed earlier in Section 8.6.1.





The range of soot primary particle size for the EGR experiments was from 5.2 to 39.3 nm. In Section 2.4.2.4 it was identified that the quoted range in literature for primary soot diameters is 15-30 nm, therefore the estimates using the method outlined in Section 3.6.4.4 spanned both below and above the range identified from literature. The low EGR diameters were both the smallest two diameters observed in the work herein as a consequence of the surface area being the highest of all soots.

The earlier discussions in Section 5.5.4 and also Section 7.5.4 concerning the methodology for estimating soot primary particle diameter (Section 3.6.4.4) had both concluded that the application of Equation 3.9 to diesel exhaust soot is subject to somewhat low robustness due to the clear findings throughout the work herein that diesel exhaust soot possess very clear porosity behaviour which Equation 3.9 ignores.

Although porosity information was not available for the EGR experiments, it can be assumed from both the significant surface area and O/C ratio changes that porosity must also have changed with EGR. Therefore, it is advised that Equation 3.9, which is also reported elsewhere for soot (e.g. Lapuerta et al. [136],

Soot Surface Acid Functionality

Table 2.7), is not sufficiently reliable or accurate for application to diesel engine soot. Therefore the results of Figure 8.13, whilst likely indicative of the primary particle diameter trends with EGR, are likely inaccurate with regard to the precise primary particle diameter. It is highly recommended that direct measurement methods such as TEM be employed in engine soot research to measure soot primary particle diameter.

In summary, it is useful to combine the three soot morphological parameters from Table 8.7 into a single figure to illustrate the overall behaviour of the two fuel soots to the change in EGR and this is presented in Figure 8.14; note that the size of the circles represent the relative surface area of the soots. Figure 8.14 is a concise description of the differences in the soot morphological changes of the two fuel soots to EGR. The three clear observations are the opposed changes in density, the significant reduction in surface area and increase in primary particle size under high EGR rate conditions. Figure 8.14 therefore is very effective example of the clear distinctions in mineral and biodiesel soot morphological properties and behaviours observed in the work herein.



Figure 8.14: 16.5:1 Low and High EGR DPF Soot Summary Morphology for EN590 and B100 Fuels

8.7 Soot Surface Acid Functionality

The soot surface acidic functionality results for the low and high EGR experiments are presented in Table 8.8 and are defined for both the total and carboxylic acid concentrations.

<u>8</u> 8.7 Soot Surface Acid Functionality

 Table 8.8: 16.5:1 Low and High EGR DPF Soot Surface Acid Functionality (Boehm titration)

	Boehm Titration								
	Total surface	Total surface stdev Surface carboxylic stdev							
Description	acids (mmol/g)	(mmol/g)	acids (mmol/g)	(mmol/g)					
EN590 55% EGR	0.001	0.000	0.001	0.000					
EN590 10% EGR	0.407	0.002	0.145	0.001					
B100 55% EGR	0.001	0.000	0.001	0.000					
B100 12% EGR	0.724	0.048	0.359	0.008					

The soot surface acidity data detailed in Table 8.8 is summarised in Figure 8.15 and details one of the most important observations of this work which was the absence of surface acidity for the soot sampled in the high EGR experiments for both EN590 and B100 fuels. Such a result implied that the surface chemistry of the soot produced in high EGR conditions was quite unique as these were the only soots observed to possess no surface acid functionality.





For the low EGR conditions, the surface acidity was found to be quite similar to that observed for the 16.5:1 rated power experiments where the soot was collected from the DPF, Section 7.6. For example, the soot surface acidity results from the EGR experiments also showed an apparent correlation between the carboxylic acid concentration and the surface O/C ratio. i.e. the carboxylic acid content of the EN590 low EGR samples was 35.6% of the total acidity and for the equivalent B100 samples it was 49.5%. These two ratios and the surface O/C ratios for these soots were a little higher than the equivalent ratios for the 16.5:1

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rated power soot collected from the DPF. Furthermore, the total acid concentration of the B100 low EGR sample was 1.8 times that of the EN590 low EGR sample and compared favourably to the 1.5 times higher surface O/C ratio.

The EGR surface acidity results also provide additional supporting evidence for a possible correlation between the carboxylic acid concentration and total acidity; with soots with higher surface acidity typically observed to have a higher proportion of the total acidy composed of carboxylic acid.

These very important observations concerning the effect of EGR on soot surface acidity and the identification of a possible correlation with the surface O/C ratio contributed significantly in the development of fundamental relationships to characterise soot surface acidity which are presented in the proceeding chapter. Consequently, it can be reiterated that the large exhaust O₂ change of the EGR experiments proved highly valuable for broadening the scope of understanding of exhaust soot physiochemical and morphological characteristics and behaviour for the mineral and biodiesel fuels investigated.

8.8 Soot Polycyclic Aromatic Hydrocarbon Profile

A total of sixteen PAH were investigated in the soot samples for the low and high EGR experiments and the results are presented across Table 8.9 and Table 8.10.

PAH (μg PAH/g)	Naphthalene	1- methylnapht halene	2- methylnaphth alene	Acenaphthylene or biphenylene	Acenaph thene	Phenanthrene	Anthracene	Fluoranthene
EN590 55% EGR	0.000	0.000	0.000	0.000	0.000	2.320	0.720	1.650
EN590 10% EGR	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
B100 55% EGR	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
B100 12% EGR	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

Table 8.9: 16.5:1 Low and High EGR DPF Soot Polycyclic Aromatic HydrocarbonProfile (Naphthalene to Fluoranthene) (GC-MS)

Table 8.10: 16.5:1 Low and High EGR DPF Soot Polycyclic Aromatic HydrocarbonProfile (Pyrene to Benzo-perylene) (GC-MS)

PAH (µg PAH/g)	Pyrene	Benz(a)anth racene	Chrysene	Benzo(b)fluorant	Benzo(k) fluoranth	Indeno(1,2,3- cd)pyrene	Dibenz(a,h)a nthracene	Benzo(g,l,h) pervlene	total
Description					ene			P = .)	
EN590 55% EGR	2.340	0.920	3.530	0.000	0.000	0.000	0.000	0.000	11.480
EN590 10% EGR	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
B100 55% EGR	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
B100 12% EGR	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

The results from the PAH analysis performed on the EGR soots proved to be somewhat different in comparison to the earlier reported results for the soot

Soot Polycyclic Aromatic Hydrocarbon Profile

8 8.8

> sampled at rated engine conditions (Section 5.7, Section 6.6 and Section 7.7). The main distinction was the lack of any PAH being detected in the soot samples apart from the high EGR EN590 soot and that the total concentration of PAH in this soot was substantially higher than any of the other soot samples analysed in the work herein.

> The results from the rated power experiments reported earlier (Section 5.7) indicated that at 19.5:1 at the exhaust manifold that the total PAH concentration for the B100 soot was very low (0.021 ppm) compared to the nearly 250 times higher EN590 total PAH (5.212 ppm). Thus, comparing these results to the EGR PAH soot results of Table 8.9 and Table 8.10 implies that the level of PAH in the B100 soot was too low to be detected at the reduced speed and load operating conditions where the EGR experiments were conducted. It was therefore not possible to conclude if the B100 fuel soot was sensitive to EGR or the different engine speed-load operating condition.

The failure to observe PAH for the EN590 low EGR condition was an indication that the PAH for this sample were also below the detection threshold assuming there were no anomalies with the gas chromatograph testing which was done by a third party (Section 3.6.6).¹⁶ Therefore this low EGR EN590 soot PAH was the most unusual result observed for all the EGR experiments especially as it was at low EGR where the operating conditions were closer to the almost zero EGR of the rated power soot collection tests where EN590 soot PAHs were found to be relatively abundant.

The PAH profile for the EN590 soot from the high EGR experiment is detailed in Figure 8.16 and shows that the measured PAH were distributed only among the mid-molar mass PAH and thus the pattern was similar to that observed for the rated power DPF soot also collected at 16.5:1, Section 7.7. However, the distribution for the soot from the EN590 high EGR experiment was centred at a higher molar mass. The commonality between the PAH profile presented in Figure 8.16 to that presented in Figure 7.22 for the rated engine power 16.5:1 compression ratio DPF samples is important. When compared to the quite different PAH profile observed at the exhaust manifold, Figure 7.21 demonstrates that there was a clear change in PAH profile that most likely was in response to the catalysing reactions of the oxidation catalyst.

¹⁶ It proved infeasible to perform a repeat soot analysis due to the low soot mass yields.



Figure 8.16: 16.5:1 High EGR DPF Soot PAH Profile for EN590 (GC-MS)

Figure 8.16 illustrates that Phenanthrene (atomic mass 178) was present, as was reported in all preceding PAH results discussion. Therefore this result extends this observation to also include low and high EGR combustion regimes. This reinforces the statement in Section 5.7 that Phenanthrene is believed to be what is called a 'stabilomer specie' (Section 2.4.4), that is a PAH which has been shown to be very stable at temperatures typical of hydrocarbon flames [25, 180]. The review by Dobbins [181] specifically identifies alkylated phenanthrenes as a dominant PAH for hydrocarbon flames. This work herein therefore indicates that Phenanthrene is a stabilomer specie for both mineral diesel and biodiesel fuel combustion and which also appears regardless of change in engine compression ratio, soot evolution in the exhaust through a diesel oxidation catalyst and also EGR rate.

Figure 8.17 by virtue of the comparison of three different experimental configurations for the same fuel, demonstrates that the PAH profile was highly dynamic and difficult to characterise and relate to any specific factor which has been investigated in the work herein.

Ultimately, the analysis of the total PAH concentrations for the EGR experiments left unresolved questions as to the processes behind the observations, specifically for the EN590 soot, therefore the understanding of the coupling between EGR and soot PAH is suggested as an area for potential future study.

8 8.9

Soot Thermogravimetrical Analysis



Figure 8.17: EN590 Exhaust Manifold, DPF and high EGR PAH Atomic Mass Profile (GC-MS)

8.9 Soot Thermogravimetrical Analysis

Summarised in Table 8.11 are the thermogravimetrical results for the 16.5:1 low and high EGR DPF sampled soot.

 Table 8.11: 16.5:1 Low and High EGR DPF Soot Thermogravimetrical Analysis (TGA)

	RT to 300 °C	300 to 400 °C	400 to 700 °C	700 to 1000 °C	Residue at 1000 °C
Description	Oil Residue & Lighter Ends	Polymers & 'Sludge'	Mostly Traditional 'Soot'	Additional Carbonaceous Content	Non-combustible 'Ash'
EN590 55% EGR	1.2	0.3	96.1	0.2	2.2
EN590 10% EGR	1.2	0.5	82.3	11.8	4.2
B100 55% EGR	1.7	0.4	96.7	0.3	0.9
B100 12% EGR	2.7	1.2	87	0.2	8.9

The thermogravimetrical results detailed in Table 8.11 are summarised in Figure 8.18 and describe the percentage weight loss from the soots in the indicated temperature ranges. Up to 300°C for both low and high EGR, the percentage contribution of residue for the EN590 soot was unchanged at 1.2% but for the B100 soot this was higher for both low and high EGR and a maximum in the latter case.

This was indicative of the increase in EGR not influencing the amount of absorbed HCs or SOF on the surface of the EN590 soot and also that the amount absorbed was somewhat greater for the B100 soot. These results also showed that the SOF of the B100 soot increased with the increase in EGR and this related to the proposed mechanism discussed in Section 8.4 which described Soot Thermogravimetrical Analysis

how the increased SOF may have encouraged the take-up of sulphur contaminate from the exhaust onto the B100 soot surface.



Figure 8.18: 16.5:1 Low and High EGR DPF Soot TGA for EN590 and B100 Fuels (TGA)

The presence of increased volatiles for the B100 soot relative to the EN590 soot was also observed in the temperature range 300 to 400°C, particularly for the high EGR condition, Figure 8.18. Interestingly, in this temperature range there was also observed a higher percentage of weight loss for the EN590 soot at low EGR although the increase was relatively small.

Referral to the gaseous emissions measurements for the EGR experiments, Table 8.1, shows that the percentage weight lost from the soot up to 400°C failed to agree with the EN590 and B100 HC emissions for low EGR where the HC emissions were substantially higher for the EN590 fuel low EGR experiment. This was an indication that the volatile temperature for HC components in the exhaust may have been higher for the B100 fuel and thus it would have been more likely these condensed onto the soot. This is suggested by Lapuerta et al. [326] for biodiesel fuels where it is also noted that this can also influence the HC emissions measurements and therefore the EGR results could have been influenced by this effect.

The soot sample weight loss in the temperature range 400 to 700°C was largely due to the combustion of the carbonaceous part of the soot and interestingly it was observed that both the EN590 and B100 soot for the high EGR experiments lost almost the same percentage weight of sample in this temperature range, Figure 8.18. At low EGR the percentage weight loss in this temperature range was lower for both fuel soots. These differences between the

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Soot Thermogravimetrical Analysis

two EGR conditions reflected the total bulk inorganic analysis of Section 8.5, the surface O/C ratio observations of Section 8.4 and also the much higher exhaust soot concentration at high EGR detailed in Table 8.1. i.e. there was a much higher concentration of carbonaceous soot at high EGR due to the high rate of EGR and very low AFR and this therefore resulted in soot forming with a much higher percentage of carbonaceous components and lower inorganics. The lower exhaust O_2 (and likely NO_x) then suppressed the oxidation of the soot as discussed earlier in Section 8.4 such that a greater proportion of the carbonaceous part remained when the soot reached the DPF thereby resulting in the TGA observations.

The TGA results for the residue remaining at the end of the TGA analysis showed that the 'ash' or residual metals remaining agreed well with the total bulk inorganic analysis (Section 8.5) for the low EGR condition with approximately double the ash observed between the B100 and EN590 soot which compared to a ratio of 2.1 between the total weight of inorganics for these same samples. However, in the case of high EGR, the relative EN590 and B100 soot residual ash fractions were the inverse of the respective total bulk inorganics with quite different low/high EGR ratios for ash and total bulk contaminates. The cause for this discrepancy could not be identified from the analysis of the available data and it is thought that it may have been the result of the much lower level of contaminates in the high EGR samples introducing more measurement uncertainty. It is also possible that the the bulk elemental analysis only partially considered the totality of contaminating elements present in the soot sample.

One point of distinction in the EGR TGA analysis results was the high 11.8% weight loss for the EN590 low EGR soot in the temperature range 700 to 1000°C. A weight loss of this magnitude was not observed for any of the other samples analysed in this work in this temperature range and contrasted the more typical 0.2% weight loss observed for this soot at high EGR and also the lack of any sensitivity of the B100 soot with change of EGR to this parameter. It was not precisely clear what mechanism was responsible for this isolated result.

Summarised in Figure 8.19 is the TGA percentage weight loss profile for the four EGR experiments and this illustrates very clearly that both the high EGR experiments resulted in soot with very similar TGA characteristics principally because of the dominance of the carbonaceous soot fraction in the sample. The low EGR soot were distinct due to the anomalous high fraction of sample weight loss for the EN590 soot between 400-700°C.





8.10 Concluding Remarks

In summary, the changes in the soot physiochemical characteristics which were observed for the change in EGR proved to be comparable to those observed for the compression ratio change but more clearly identifiable enabling the mechanisms and processes behind the observations to be elucidated with greater certainty. Importantly, the very high EGR rate investigated proved an excellent opportunity to evaluate B100 vs. EN590 soot behaviour at similar exhaust temperatures to those of the rated engine power experiments but with far lower exhaust oxygen concentrations. It is this comparison which really solidifies the clear distinctions in mineral and biodiesel soot physiochemical and morphological properties and behaviours that is a key general contribution of the work herein.

The FSF for the EGR experiments showed that by this measure the EN590 fuel had a soot producing tendency equivalent to 5 times the B100 fuel at low EGR, however this reduced to just below a factor of 3 for the high EGR condition, implying that the B100 fuel under high rates of EGR is relatively more prone to producing carbonaceous soot than at low EGR. When FSF was used to scale the soot bulk inorganic results it was observed that the increase in relative (fuel and exhaust soot concentration effects accounted for) contribution of bulk inorganics with EGR rate was somewhat greater for the B100 soot, reinforcing the a general

Concluding Remarks

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finding that the B100 soot has a more sensitive response to EGR change compared to the mineral diesel fuel.

For the high EGR experiments there was both lower soot surface oxygen concentration and O/C ratio for both fuels with the most significant reductions observed for the B100 soot. This greater sensitivity in the O/C ratio of the B100 soot was attributed to the generally greater rate of B100 soot oxidation also defined previously in Chapter 6 and Chapter 7. The high EGR soot surface O/C ratios for both fuels were the lowest of any observed in the work herein and it is postulated that this was due to very low exhaust O₂ concentration due to the AFR being about stoichiometry (~14.5) i.e. there was very little free oxygen available to chemisorb to the soot surface. From the thermogravimetrical analysis a higher SOF concentration for the B100 soots was found at both low and high EGR, mirroring the observations for B100 soot produced at rated engine conditions. This low O/C ratio at high EGR correlated with soot surface acidity being observed to be negligible for both fuel soots and this important observation therefore indicated a possible minimum O/C ratio required to establish soot surface acid functionality and this finding is explored in greater detail in Chapter 9.

The concentration of total soot bulk inorganics at the DPF for the EGR experiments was lower than observed for the rated power tests and is attributable to the higher concentration of carbonaceous soot in the exhaust for the EGR experiments. Evaluation of the raw soot bulk inorganics revealed that following the increase in EGR there was a general reduction in the concentration of inorganics in the soot. This was supported by the TGA results which saw a reduction in ash content and increase in the carbonaceous soot fraction. Application of the FSF however showed that although the concentration of inorganics reduced, relatively more inorganics were entrained when fuel rate and exhaust soot concentration changes were accounted for. This was attributed to the increased concentration of exhaust products in the cylinder during combustion with the carbonaceous part of the recycled soot subject to oxidation but the ash part persisting so as to increase the relative concentration in the soot.

There was a very significant almost identical decrease in the BET soot surface area with the increase in EGR which is believed to be an indication of an appreciably larger particle diameter for both fuel soots at high EGR due to the much larger carbonaceous soot fraction and a low porosity due to the much lower surface oxidation indicated by the low O/C ratios. Interestingly, the increase in

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> EGR greatly affected the skeletal density of the soots. The change was opposite in both cases with the EN590 soot density decreasing 13.5% and the B100 soot increasing 10.5%. This reflected the observations for soot evolution in the exhaust from Chapter 7 and further increased the validity of the 2nd of the proposed B100 soot models from Chapter 5 by virtue of the ability of this model to also account for the B100 soot EGR rate morphological response.

PAH were only detected for the high EGR EN590 soot sample; in contrast the concentration of total PAH in this sample was the highest observed in the work herein. The measured PAH were distributed only among the mid-molar mass PAH and thus the pattern was similar to that observed for the 16.5:1 rated power DPF soot, however the distribution was centred at a higher molar mass. Comparison to the quite different PAH profile observed at the exhaust manifold demonstrated that there was a clear change in PAH profile that is most likely explained by the catalysing reactions of the oxidation catalyst. Phenanthrene (atomic mass 178) was observed, therefore reinforcing the statements in forgoing results chapters that Phenanthrene is a 'stabilomer specie'.

Chapter 9

9 Soot Surface Acidity Relationships

The results discussion of the proceeding Chapters 5-8 established that there existed an outline fundamental relationship between the soot surface O/C ratio and soot surface acidity which was sensitive to the presence of soot surface sulphur. The aim of the present chapter is to explore these relationships in greater detail by collating the various soot physiochemical results across all experiments and then analysing collectively to find the underlying links between different physiochemical properties, ultimately leading to a more fundamental understanding of soot surface acidity.

9.1 The Relationship between Carboxylic Acid and Total Acid Concentration

From collating and analysing the surface acidity data presented across previous Chapters 5-8, the first observation is that the contribution of the carboxylic acids to total surface acids forms a clear relationship which appears to encompass the three fuels, both compression ratios, soot location in the exhaust and also the EGR low and high experimental conditions. This finding is presented in Figure 9.1 and illustrates an outline second order relationship between the concentration of surface carboxylic acid and soot total surface acidity. (Note that in Figure 9.1, and indeed all the relevant figures in this chapter, error bars have been added to assist the result interpretation).

Although the data presented in Figure 9.1 is thinly populated and considers a broad set of experimental conditions, the R² confidence level of the quadratic fit is reasonable, indicating that this finding could be broadly applicable in respect to diesel engine soot. Figure 9.1 also highlights how the presence of surface sulphur in the 19.5:1 PC9 exhaust manifold soot sample significantly influenced the soot surface acidity; this result being distinct from the others in the study by virtue of a far higher carboxylic acid concentration which therefore contributed to a higher total surface acidity.

Soot Surface Acidity Relationships

9 9.1

The Relationship between Carboxylic Acid and Total Acid Concentration



Figure 9.1: Relationship of Soot Total Surface Acidity to Carboxylic Acid Part (Boehm titration)

The result from Figure 9.1 suggests that the total surface acidity of soot may be constrained principally by the carboxylic fraction when sulphur is accounted for and thus the next appropriate step is to consider the percentage of carboxylic acids as a function of total acids to understand the nature of this alternate relationship. This analysis is presented in Figure 9.2 and reveals an outline linear correlation between the fraction of total acidity which is carboxylic. The degree of scatter in the available data yields an R² value of 0.55, so this relationship is less robust than that identified in Figure 9.1 but the linear characteristic is evident.



Figure 9.2: Relationship of the Percentage of Total Acids which are Carboxylic to Total Surface Acidity (Boehm titration)

With this linear correlation it is possible to underline the very close interplay between these two measures of soot surface acidity but it is only applicable as

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O/C Relationship to Carboxylic Acid Concentration

predictive tool if at least one of the measures of surface acidity is known. i.e. if the total surface acidity of diesel soot is known, then the carboxylic acid concentration can be estimated both as a fraction of the total acidity and as a concentration and vice versa.

A far more useful capability is to relate the surface acidity to other soot surface properties in order to predict soot surface acidity when nothing pertaining to surface acidity is known. The usefulness of such a capability is clear from the literature review in Chapter 2, which identified a general paucity of diesel engine exhaust soot characterisation data in open literature with soot surface acidity being one of the least discussed soot attributes. Therefore in the next section, relationships between soot surface elemental composition and surface acidity and also the morphological properties of soot are investigated to help improve understanding of soot surface acidity.

9.2 O/C Relationship to Carboxylic Acid Concentration

In Chapters 5-8 it was observed that the soot surface O/C ratio appeared to correlate generally with surface acidity. This observation is supported by a correlation between soot surface acidity and surface oxygen concentration reported by Studebaker [163] in which soots with higher surface oxygen content were observed to have greater surface acidity. However, from the results presented in Chapters 5-8, it is possible to be more specific and link the surface area and surface O/C ratio of the soot to the concentration of surface carboxylic acid, which in turn from the proceeding analysis of Section 9.1; confers the potential to estimate the soot total surface acidity.

First, a relationship has been drawn from a comparison of soot O/C ratio to soot surface area; the result of this comparison is presented in Figure 9.3 for all the different soot samples collected in this work.

Figure 9.3 reveals that for all but one of the soot samples analysed, there was an outline linear relationship between the soot surface area and the surface O/C ratio. Therefore, Figure 9.3 implies that soot surface O/C ratio is not just a direct function of say the equivalence ratio during combustion but is also governed partly by the oxidation processes which the soot experienced following formation. This is because soot oxidation processes have been shown previously in literature by Ahlstrom et al. [130], Ishiguru et al. [131] and others [132, 133, 135], and also in this work principally in Chapter 7; to directly affect physical properties of soot - especially surface area and therefore in turn the soot surface O/C ratio.

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O/C Relationship to Carboxylic Acid Concentration

The linear relationship depicted in Figure 9.3 is an intuitive result as a greater surface area should in principle increase the population of exposed edges of the graphite platelets which are the known sites of the functional groups responsible for soot oxidation and acidity [120, 156].





Figure 9.3 emphasises the significant difference in the oxidation pathway of the B100 soot produced at rated engine power at 16.5:1 as the soot evolved in the exhaust compared to all other soots analysed, Chapter 7. In contrast to this, Figure 9.3 also importantly shows that the B100 soot at both low and high EGR during the EGR experiments (Chapter 8) did not experience the same 'accelerated' oxidation pathway as the B100 soot sampled at rated power engine conditions and instead conformed to the 'normal' O/C ratio-surface area pattern.

This contrast in the B100 soot results was assumed initially to be related to the difference in exhaust manifold temperature of these tests. However upon closer inspection; for the rated power experiments at 16.5:1, the B100 fuel exhaust temperature was 530°C (Table 4.10 Part B) and for the EGR tests it ranged from 415 to 550°C for 12-55% EGR (Table 8.1). Therefore in both sets of experiments, the B100 fuel exhaust temperatures were essentially equivalent. Additionally, since Ahlstrom et al. [130] and Ishiguro et al. [131] detail that the temperature of around 550°C is the temperature when carbonaceous soot spontaneously undergoes exothermic combustion; then both sets of experiments were either only just at or below this temperature. What Figure 9.3 suggests is that the concentration of the functional groups responsible for oxidation [116, 118, 156] were either more concentrated on the surface of the B100 soot or

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O/C Relationship to Carboxylic Acid Concentration

alternatively the functional groups inside of the amorphous soot core [120] were exposed and detected by the XPS examination and it was these exposed internal sites which were amplifying the soots apparent surface oxygen concentration. This latter postulation links back to the proposed B100 soot models in Chapters 5-8 and therefore the findings from Figure 9.3 provide a further point of support for the unique nature of the B100 soot physiochemical properties for which postulations have been previously proposed.

Following further analysis, a second O/C relationship has been identified which establishes a link between the {surface area - O/C ratio relationship} detailed in Figure 9.3 and the carboxylic acid concentration on the surface of the soot. This correlation is presented in Figure 9.4 for data collated from the soot results presented and discussed in Chapter 5-8. This relationship describes soot surface carboxylic acid concentration as a function of surface O/C ratio and is far more complex than the forgoing correlations but also more fundamental.



Figure 9.4: Relationship of Soot Surface Carboxylic Acid to Soot Surface O/C Ratio (Boehm titration, XPS)

Several very interesting and important observations can be determined from Figure 9.4. Firstly, the central area of the figure presents the soots which did not follow the 'accelerated' oxidation pathway of the B100 soot and also had low surface sulphur concentrations at or below 0.3 % weight. These soots lying in the O/C ratio range of 0.075 to 0.12 appeared to have strongly linear carboxylic acid concentration in relation to O/C ratio. This is defined as fundamental observation as it encompassed soots from different compression ratios, sample locations and from both the rated power/EGR experiments and is therefore a somewhat unique

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9.3

finding. Secondly, below an O/C ratio of approximately 0.075 there are only two soots observed, the two high EGR soots, and both of these have negligible surface acidity.

It is worth noting that for the 16.5:1 exhaust manifold soot samples, the surface acid functionality was not determined due to limited sample mass which meant that the EN590 result in particular which had an O/C of 0.0627 is not available to refine the 'knee point' identified by Figure 9.4. Such a result would have been very advantageous as it may have been possible to identify whether the 'knee point' is a specific consequence of the very high EGR rates of these experiments or whether in this O/C ratio region the carboxylic surface acidity and thus soot total acidy becomes suspended due to the surface chemistry in this region no longer supporting surface acid sites.

Consequently, the surface carboxylic acid and O/C ratio relationship in the limited region of 0.06 to 0.075 depicted in Figure 9.4 is a very interesting area for future research focus to help develop a clearer understanding for why the carboxylic acid concentration falls so abruptly in these results. This is likely described by an underlying fundamental soot surface physiochemical process that could be modelled with the availability of a broader spectrum of data in the form of the results that populate Figure 9.4.

9.3 Soot Surface Acidity with Surface Sulphur

A further interesting observation derived from Figure 9.4 is that all soots in the central group, and also the heavily oxidised B100 soot (highlighted on the far right), had surface sulphur concentrations at or below 0.3 % weight. The 19.5:1 PC9 soot at the exhaust manifold had a surface sulphur concentration x5.2 this concentration and the relationship of carboxylic acid to the O/C ratio is entirely different for this soot suggesting that the sulphur is introducing considerable additional carboxylic functionality. An important contrast to this is the observation that the soot from the same fuel but at 16.5:1 compression and extracted from the DPF. This soot had a carboxylic acid vs. O/C ratio that placed it perfectly on the linear trend of the central group depicted in Figure 9.4.

This outlying result for the 19.5:1 PC9 soot highlighted in Figure 9.4 and the related discussion in preceding chapters, demonstrate conclusively that the presence of surface sulphur was associated with the significant changes in PC9 soot surface acidity and more specifically the carboxylic acid concentration.

Soot Surface Acidity with Surface Sulphur

As an example, the processes such as the oxidation of the PC9 soot in the exhaust (Chapter 7) which acted to increase surface sulphur should also have increased surface acidity in proportion to the increase in concentration of surface sulphur. Consequently, it is believed that the reduction in compression ratio which reduced the PC9 soot surface sulphur concentration by 97% should also have reduced the surface acidity of the PC9 soot (as measured at the exhaust manifold) and when this soot was then transported down the exhaust, the oxidation processes in the oxidation catalyst liberated the sulphur from the soot core and this then increased the concentration on the surface markedly, which in turn increased the surface acidity through sulphur oxygenates. This process, according to the result of Figure 9.4, must have occurred in addition to the basic processes related to surface area and O/C ratio identified earlier in Section 9.2.

From collating these observations, it is postulated that the influence of surface sulphur on soot surface carboxylic acidity may have a threshold level (e.g. 0.3 % weight) below which the sulphur is no longer influential and the soot carboxylic surface acidity relates directly to the surface O/C ratio. Future research into this postulated threshold level would be very useful to understand more precisely how lower soot surface sulphur concentrations influence surface acidity since the influence of sulphur is so specific and significant [138].

Although not something which was specifically investigated in this work, it is worth mentioning related findings in earlier Lubrizol work by Covitch et al. and Ripple et al. [138, 165] (work which contributed to the development of the research pathway for this work). In these works it was concluded there is a direct correlation between fuel sulphur level and sulphur concentration in the soot. Covitch et al. ascribed a factor of 1.7 for the increase in percentage weight sulphur in soot relative to the associated change in concentration of sulphur in the fuel. Further, it was also found that reducing sulphur content in the fuel appeared to increase the level of soot contamination of the lubricant suggesting that there was an increase in the deposition of soot into the lubricant. Covitch et al associated this with the reduction in soot surface sulphur which changed the acidity and made the soot potentially more oleophilic thereby more easily being absorbed through thermophoretic deposition into the lubricant film on the cylinder wall. Consequently, the sensitivity of soot surface acidity to surface sulphur concentration identified by the PC9 soot outliner result in Figure 9.4 is of very great importance to research field of diesel engine lubricants.

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In the present work, the lubricant was sampled at 5 hour intervals (Section 3.2.1.6) to investigate soot loading and rheometry for Lubrizol as a separate study to the soot physiochemical investigation. It was found however that the soot loading for all samples was too low to reveal if there were any sulphur related effects on the soot which influenced the lubricant rheology.¹⁷

In addition to the findings above of Covitch et al. and Ripple et al. [138, 165], Kittelson et al. [24] state that the surface acid/sulphate fraction of soot is roughly proportional to the fuel sulphur content. Therefore, it can be postulated that the PC9 soot outliner in Figure 9.4 has a higher carboxylic surface acidity in proportion to the higher surface sulphur concentration of this single sample relative to all the other examined soot samples. This conclusion, in addition to the earlier postulated threshold of ~0.3 % weight sulphur concentration (below which there is no sulphur related increase in soot surface acidity), provides both validation and extension of the relationship described by Kittelson at al [24].

9.4 Soot Surface Acidity with High EGR

A final and very important observation from the analysis of the surface acidity data presented in Figure 9.4 is that under the conditions of very high EGR (~55%), the soot surface O/C ratio remained very low even at the DPF and in particular for the more oxidation reactive B100 soot. Thus, it appears that in the case of high EGR, the process of soot surface oxidation is impeded and that it can be effectively 'frozen' or slowed such that it process at a very low rate relative to the linear central section of Figure 9.4.

Understanding fully what are the attribute(s) of these two high EGR experiments that fundamentally result in the negligible soot surface acidity is not achievable with simply two available experimental results. Since the same observation was made for both the EN590 mineral diesel fuel and B100 fuel soots, it is highly likely that the negligible surface acidity developed principally from the significant reduction in available oxygen (both O₂ and NO_x) for oxidisation both in-cylinder and the exhaust due to the very high rate of EGR. This is borne out in the other available soot characterisations which failed to reveal any specific soot related property, either physical or chemical, which would have impeded oxidation in the manor observed.

¹⁷ Standard industry tests such as the Mack T11 which look for soot-lubricant rheological effects require the engine to run upwards of 80 hours, some tests also employ artificially increased soot formation [184].

Empirical Equations for Estimating the Surface Acidity of Soots

Therefore this observation for the two high EGR soot samples is considered a potentially fundamental finding concerning the effect of very high EGR rates (and therefore very low combustion equivalence ratio and exhaust oxygen concentrations) on soot surface development both in-cylinder and in the exhaust with implications for both aftertreatment system and lubricant system fields of research. The main uncertainty in the finding is the limited number of data points. It is therefore advised that research into this behaviour would be a very worthwhile parallel activity to the need proposed earlier in Section 9.2 to better understand the effect of soot surface O/C ratio on soot carboxylic acid concentration in the region of the 'knee point' identified in the linear relationship depicted in Figure 9.4.

9.5 Empirical Equations for Estimating the Surface Acidity of Soots

The forgoing correlations theoretically provide the capability to estimate the carboxylic and surface acidity for samples where direct measurement was not possible. Two cases where this is applicable are the 19.5:1 exhaust manifold sample for the B100 soot and the three exhaust manifold samples at 16.5:1.

The two empirical relationships utilised to estimate soot surface acidity can be defined as follows in Equation 9.1 and Equation 9.2:

carboxylic acid (CA)
$$\left(\frac{mmol}{g}\right) = 5.274 \left(\frac{o}{c} ratio\right) - 0.244$$
 Equation 9.1

Equation 9.1 is only applicable in the O/C range (0.075 to 0.12) since it is derived from the linear relationship in the central region depicted in Figure 9.4 and it has an R^2 value of 0.9975. The second empirical relationship derives from the finding presented in Figure 9.1 which relates the total surface acidity to the surface concentration of Carboxylic Acid (CA) and it has an R^2 value of 0.9556:

total acids
$$\left(\frac{mmol}{g}\right) = -2.42CA^2 + 3.3382CA$$
 Equation 9.2

Thus, by combining Equation 9.1 and Equation 9.2 it is possible to use only the measured soot surface O/C ratio to estimate the carboxylic acid concentration and from this the total soot surface acidity with the stipulation that the concentration of soot surface sulphur is below 0.3% weight as detailed in Section 9.3.

9.5

Empirical Equations for Estimating the Surface Acidity of Soots

The results from the application of Equations 9.1 and 9.2 to soot data reported in Chapters 5-8 are detailed in Table 9.1. The results of Table 9.1 can be compared to the surface acidity results presented in Chapter 6, Table 6.5 (reproduced here as Table 9.2 for convenience).

	Total Acidity	Carboxylic Acidity	Carbon	Oxygen	Sulphur	O/C
Reference	(mmol/g)	(mmol/g)	(% weight)	(% weight)	(% weight)	
16.5:1 CT, EN590	0.269	0.086	94.1	5.9		0.0627
16.5:1 CT, PC9	0.659	0.239	91.6	8.4	0.05	0.0917
16.5:1 CT, B100	0.544	0.189	92.4	7.6		0.0823
19.5:1 CT, B100	0.598	0.211	92	8		0.0865
	(Equation) on 9.2)	(Ed	quation 9.	1)	ノ

 Table 9.1: Estimated Surface Acidity for Unavailable Soot Surface Data

The estimation for the 19.5:1 B100 sample suggested a carboxylic acid concentration just slightly higher than that of the 19.5:1 CT EN590 sample by virtue of the slightly higher O/C ratio. The total surface acidity estimation is however lower and potentially an indication of the limitation of this part of the surface acidity estimation i.e. an R^2 value of 0.9556 vs. 0.9975 for the carboxylic estimation equation. The estimation however appeared reasonable in relation to the 19.5:1 data in general.

Table 9.2: 19.5:1 a	and 16.5:1 E	Exhaust M	lanifold and I	DPF Soot	Surface Acid
Functionality					

	Total surface	stdev	Surface carboxylic	stdev				
Description	acids (mmol/g)	(mmol/g)	acids (mmol/g)	(mmol/g)				
19.5:1 CT, EN590	0.621	0.083	0.181	0.008				
19.5:1 CT, PC9	1.163	0.010	0.749	0.001				
19.5:1 CT, B100	NA	NA	NA	NA				
16.5:1 DPF, EN590	0.601	0.045	0.169	0.004				
16.5:1 DPF, PC9	0.575	0.004	0.207	0.004				
16.5:1 DPF, B100	0.850	0.005	0.311	0.016				

When computing estimates for the 16.5:1 exhaust manifold soot surface acidity, it is first necessary to check that for all samples the level of surface sulphur is below the 0.3 % weight threshold identified previously so the empirical relationships can be utilised with confidence. The estimation for the EN590 carboxylic and total acidity is comparatively low but reflects the low O/C ratio which occupies the region where the high EGR test results suggest a 'knee point'

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Empirical Equations for Estimating the Surface Acidity of Soots

on the carboxylic to O/C ratio correlation, Figure 9.4. Thus, the reliability of this estimation is less than for the calculation examples.

For the 16.5:1 exhaust manifold PC9 soot, the surface acidity is estimated to be slightly more than half that observed in the 19.5:1 exhaust manifold sample which is in line with the much lower surface concentration of sulphur. The lower O/C ratio for the PC9 soot at the DPF indicates that on the basis of Figure 9.4 the surface acidity should be slightly less than that at the exhaust manifold and this also agrees with the estimated surface acidity finding.

Finally, for the B100 soot a slightly lower estimated acidity is predicted at the lower compression condition at the exhaust manifold compared to at the DPF, again because of the lower O/C ratio. The surface acidity change with compression ratio for this fuel is much lower than for either the EN590 or PC9 fuel soots as a result of the O/C changing much less with compression ratio, with estimated acidity at each compression ratio being quite similar.

Although in the preceding estimation of soot surface acidity the measured O/C ratio has been used, Figure 9.3 indicates that it is also feasible to first use the measured soot surface area to initially estimate the soot surface O/C ratio and then utilise this to calculate the soot surface acidity. The empirical relation that can be applied to estimate soot surface O/C ratio from surface area is presented in Equation 9.3:

$$\left(\frac{o}{c} \ ratio\right) = 0.00006 \left(surface \ area \ \left(\frac{m^2}{g}\right)\right) - 0.618$$
 Equation 9.3

However, for Equation 9.3 the R^2 is low at 0.4247 as a result of this simple empirical model not capturing all of the additional factors that also govern O/C ratio such as; the conditions in which the soot formed, the age of the soot, the composition of the exhaust gas, the exhaust soot sampling location etc. It is therefore advised that use of the empirical soot relations in this chapter should be restrained to Equations 9.1 and 9.2 and Equation 9.3 is only used when direct measurement is not available.

In conclusion, the projected surface acidity results using the developed empirical correlations appear to work sensibly and may find application in other work to estimate soot surface acidity when it is not feasible to measure surface acidity directly.

Concluding Remarks

9 9.6

9.6 Concluding Remarks

Through a process of aggregating the soot results and findings from the earlier Chapters 5-8, it has been possible to build three empirical models to estimate soot surface acidity characteristics from alternative soot physiochemical properties which include surface O/C ratio and soot surface area. The simplicity of these empirical models points to there being fundamental properties of the soot formation and oxidation processes that govern diesel engine soot surface acidity, irrespective of factors investigated in this work that include mineral/biodiesel fuel and geometric compression ratio.

The findings in this chapter also point the direction of future research to focus on the soot surface O/C ratio and the identified proportional relationship to soot surface acidity in the range 0.075-0.12 O/C ratio. A possible threshold of 0.3 % weight of surface sulphur is also identified in this work, beyond which the surface sulphur concentration proportionally starts to increase soot surface acidity regardless of the O/C ratio. Finally, at high EGR (~55%), it has been shown that the very low combustion equivalence ratio and free oxygen and NO_x in the exhaust products act to supress the soot surface oxidation processes leading to an O/C ratio below 0.06, and soots in this category consistently showed negligible surface acidy with the absence of surface sulphur.

10 Conclusions and Contributions

The work reported herein provides a reference for the impact of diesel engine geometric compression ratio change and low/high EGR (10/55%) on a breadth of exhaust soot physiochemical properties and engine performance/emissions for a group of three mineral diesel and biodiesel fuels on an otherwise unmodified VW 1.9TDI engine. Consideration is also given to the changes in the soot physiochemical properties as soot matures in the exhaust system between the exhaust manifold and a DPF located after a diesel oxidation catalyst.

10.1 Engine Performance and Emissions

Prior to the experimental soot collection experiments, a parametric study was undertaken to understand the engine performance and emissions with the three fuels (EN590, PC9, B100) and the two compression ratios (19.5:1, 16.5:1) selected for the soot physiochemical investigation. This determined that the highest exhaust soot concentration occurred at 4000 rpm/maximum torque (engine rated power) with >40°C IMAT. This operating point was used for the soot physiochemical result discussion in Chapters 5-7.

The comparison of PC9 and B100 fuels to the baseline EN590 found that generally the two mineral fuels (EN590, PC9) resulted in similar engine performance and emissions whilst there was much greater differentiation observed between the B100 and EN590 fuels. The majority of the significant engine performance parameter distinctions for the B100 fuel (e.g. BMEP, BSFC, exhaust temperature etc.) are ascribed to the B100 fuel's combination of higher fuel density and lower energy density. Such were these changes that the AFR was between 5-12% lower compared to EN590 and yet there was an 80-90% reduction in exhaust soot concentration.

The reduction in compression ratio caused a general increase in AFR of a few percent that stemmed from an increase in MAF and is attributed to the increase in cylinder volume. It was also observed to reduce the estimated average in-cylinder temperature by 2.3% and the peak cylinder pressure by 17.5%; thus the compression ratio influences on exhaust soot discussed in Chapter 6 are likely dominated by cycle pressure reductions.

Soot Physiochemical Properties

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10.2

10.2 Soot Physiochemical Properties

All the factors originally highlighted in the aims and objectives were observed to influence soot physiochemical properties with fuel generally being the factor of most significance followed by EGR and lastly the reduction in compression ratio. The measured physiochemical properties of the soots in this work agreed well with those outlined in the literature review reported in Chapter 2.

The PC9 and EN590 mineral diesel soots sampled at the exhaust manifold at the same compression ratio were initially observed to have points of commonality which distinguished these soots from the B100 soot, Chapter 5. The presence of bulk and surface sulphur proved to be the main distinguishing feature of the PC9 soot. Surface sulphur was found to correlate with an increase in the surface O/C ratio and this in turn correlated with a higher carboxylic and total surface acidity suggesting a strong link between soot surface oxidation and surface acidity which is modulated through adsorption of sulphur from the fuel.

However, the compression ratio reduction triggered a 97% reduction in PC9 soot surface sulphur concentration at the exhaust manifold which in turn saw the surface total acidity reduce by 50%. This reduction in PC9 soot surface sulphur did not appear to amplify the reduction in surface oxygen when compared to the EN590 soot and thus the sulphur-oxygen proportionality relation is concluded to have additional complexity, specifically at low surface sulphur concentrations of <0.3 % weight.

Further complexities in the PC9 soot surface sulphur behaviour were observed as the soot evolved in the exhaust. It is believed that during the oxidation catalyst reactions, the PC9 soot sulphur migrated (possibly through pores in the soot) to the surface of the soot, oxidised with surface oxygen and free oxygen in the exhaust and was then volatilised. This process caused a reduction in bulk sulphur and reduction in surface oxygen. The volatilised sulphur compounds then condensed onto the surface of the soot as the exhaust gas temperature reduced between the oxidation catalyst and the DPF where the soot was collected resulting in dynamic changes in surface acidity.

Therefore the environment where the PC9 soot surface sulphur compounds formed and adsorbed onto the surface of the soot could be quite different, thereby influencing the impact of sulphur on soot. For example, soot at the exhaust manifold which is derived from high temperature in-cylinder reactions is postulated to have had a different influence of the soot surface functional groups

Soot Physiochemical Properties

compared to sulphates released and then adsorbed when the soot passed through the oxidation catalyst. Further work is required to understand the complexities of these outline findings regarding soot surface sulphur.

After accounting for differences in fuel rate, lubricant consumption rate and exhaust soot concentration, it was observed that the bulk inorganic content of the three fuel soots were similar for the rated engine power experiments. This confirmed the hypothesis that the concentration of soot bulk inorganics is largely tied to these three factors. Principal inorganic contaminates were observed to be (Ca,Fe,Na,S,Zn) in order of concentration indicating fuel, lubricant and engine metallurgy as sources.

B100 soot was found to have distinct morphological characteristics and to rationalise the observations this thesis has developed a proposal for a B100 soot model which is introduced in Chapter 5. This regards B100 soot primary particles as having a far more regular graphene plane internal arrangement with fewer isolated internal voids compared to the mineral diesel soot when the B100 soot first forms and is expelled from the cylinder. This uniform structure with minimal trapped voids also possesses a higher proportion of inorganics due to a lower carbonaceous fraction and collectively these characteristics endow the B100 soot with a higher density. This regular graphene plane arrangement extends to the B100 soot outer shell giving the soot a low porosity and surface area.

From examination in Chapter 7 of the soot transformation in the exhaust, this young soot model was extended to account for ageing processes by proposing that initially trapped inter-particle voids [141] form in the young B100 soot as it is exposed to heat and oxygen in the exhaust. It is thought that this initial process causes the N2 pycnometry method to over-estimate the skeletal volume (Section 3.6.4.3) thereby giving a lower density measurement as was observed when the soot was sampled after it had passed through an oxidation catalyst. Therefore, the B100 soot structure is postulated to have evolved or aged in the exhaust such that the soot became more akin to the hollowed out soot core with intact outer shell described by Song et al. [16].

The validity of this B100 soot model was strengthened by the finding from the high EGR experiment (Chapter 8) that the B100 soot had a relatively high density when sampled after the oxidation catalyst. This is because the soot surface O/C ratio for the same sample was very low indicating that at high EGR there had been significantly reduced oxidation occurring; a finding confirmed by the

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Conclusions and Contributions

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relatively low proportion of inorganics and negligible surface acidity and explained by the low concentration of gaseous O_2 and likely also NO_x in the exhaust. Therefore the proposed model predicts that this young initial state of the B100 soot persisted beyond the oxidation catalyst such that the soot when collected in the DPF had a high density and low surface area characteristic of 'young' soot - such was observed at the exhaust manifold for the B100 soot produced at rated engine power.

The reduction in compression ratio caused a reduction in the soot surface O/C ratio, regardless of fuel and appeared to be the inverse of the change in the AFR, Chapter 6. This change in O/C ratio was also opposite to the exhaust O_2 concentration change but did align with a reduction in NO_x . It is postulated that the reduction in compression ratio, which acted to reduce the peak and average in-cylinder temperature, in turn reduced both the formation of NO_x and also therefore the reaction rate between the NO_x and the soot – thereby inhibiting the formation of surface functional groups.

The soot surface O/C ratio reduction in response to compression ratio reduction was more significant for both mineral fuel soots and this is thought to be a consequence of the significant morphological distinction of the B100 soot. It is postulated that one explanation based on the proposed soot model, is that the greater proportion of inorganics in the B100 soot increases the potential for more local irregularity in the graphene planes of its structure [118]. These local sites of discontinuity are reported elsewhere to be distributed over both the inner and outer surfaces of the soot [120] and can potentially increase soot reaction rate [16, 143] because they are sites for the surface functional groups which chemisorb O_2 .

Importantly, the reduction in O/C ratio combined with the reduction in surface sulphur for the PC9 fuel, demonstrated that engine geometric compression ratio can influence soot surface reactivity indirectly via in-cylinder temperature based soot formation and oxidation processes. This is an important observation that should be considered in the engine design process that defines engine compression ratio. This observation is also of potential interest to the disciplines of lubricant and aftertreatment research.

The reduction in compression ratio was also suspected of causing an increase in lubricant consumption for all rated engine power soot collection experiments and this was most likely because of increased blowby. This increase

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in lubricant consumption is believed to be a contributing factor to the clear step increase in the fraction of bulk inorganic contaminate in all soots. However, it is also postulated that the reduction in compression ratio also affected the sootlubricant interaction mechanism by increasing the relative entrainment into the soot of the lubricant derived inorganic contaminates (Ca,P,Zn) in comparison to the metals from the engine metallurgy (Fe,Mg). Further research is required to understand the details of this behaviour.

It is clear that soot transformation in the exhaust is highly dependent on the original structural form and surface state of the soot as it exits the cylinder i.e. the physiochemical soot properties 'baked in' during combustion, Chapter 7. This is especially true of the B100 soot which appeared to undergo a much higher rate of oxidation compared to the mineral fuel soots with the surface O/C ratio increased by a factor of 1.8 relative to the EN590 soot as the B100 soot evolved in the exhaust during the rated engine power experiments. This was supported by the changes observed in the bulk inorganics concentration which indicated the carbonaceous fraction loss was 3-4 times that of the mineral soots.

There was a small change in the concentration of total PAH in the EN590 soot samples between the exhaust manifold at 19.5:1 and the DPF at 16.5:1; however in the case of the PC9 soot there was a significant increase of 4732% in the total concentration of PAH. It is thought likely that the reduction in compression ratio which caused a significant reduction of PC9 soot surface sulphur concentration also resulted in an increase in the PC9 soot surface PAH adsorption with further increases then occurring as the soot evolved in the exhaust with condensation/adsorption of material released in the oxidation catalyst reactions.

The PAH molar mass profiles for the two mineral fuel soots also changed markedly with both the compression ratio reduction and exhaust evolution with the result being a much narrower distribution of PAH. It is concluded that the soot evolution was more significant in the change in PAH distribution than compression ratio due to the behaviour of the EN590 soot which did not incorporate sulphur effects. Furthermore, Phenanthrene (molar mass 178 g/mol) was found to be persistent in the PAH profile of all fuel soots even after the oxidation catalyst reactions, therefore this is identified as a PAH 'stabilomer specie'.

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The changes in the soot physiochemical characteristics which were observed for the change in EGR (Chapter 8) proved to be comparable to those observed for the compression ratio change but more clearly identifiable enabling the mechanisms and processes behind the observations to be elucidated with greater certainty.

The FSF for the EGR experiments showed that by this measure the EN590 fuel had a soot producing tendency equivalent to 5 times the B100 fuel at low EGR, however this reduced to just below a factor of 3 for the high EGR condition implying that the B100 fuel under high rates of EGR is relatively more prone to producing carbonaceous soot than at low EGR. When FSF was used to scale the soot bulk inorganic results it was observed that the increase in relative (fuel and exhaust soot concentration effects accounted for) contribution of bulk inorganics with EGR rate was somewhat greater for the B100 soot, reinforcing the general finding that the B100 soot has a more sensitive response to EGR change compared to the mineral diesel fuel.

The concentration of total soot bulk inorganics at the DPF for the EGR experiments was lower than observed for the rated power tests and is attributable to the higher concentration of carbonaceous soot in the exhaust for the EGR experiments. Evaluation of the raw soot bulk inorganics revealed that following the increase in EGR there was a general reduction in the concentration of inorganics in the soot. This was supported by the TGA results which saw a reduction in ash content and increase in the carbonaceous soot fraction. Application of the FSF however showed that although the concentration of inorganics reduced, relatively more inorganics were entrained when fuel rate and exhaust soot concentration changes were accounted for. This is attributed to the increased concentration of exhaust products in the cylinder during combustion with the carbonaceous part of the recycled soot subject to oxidation but the ash part persisting so as to increase the relative concentration of inorganics in the soot.

Through a process of aggregating the soot results and findings from the Chapters 5-8 it was possible to develop three empirical models to estimate soot surface acidity characteristics from alternative soot physiochemical properties which include surface O/C ratio and the soot surface area, Chapter 9. The simplicity of these empirical models points to there being fundamental properties of soot formation and oxidation processes that govern diesel engine soot surface

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acidity irrespective of factors investigated in this work that include mineral/biodiesel fuel and geometric compression ratio.

The principal surface acidity model enables estimation of soot surface carboxylic acid concentration from the surface O/C ratio limited to the O/C ratio range of 0.075-0.12 O/C and for soots with surface sulphur concentration of < 0.3 % - beyond this, surface sulphur concentration proportionally starts to increase soot surface acidity regardless of the O/C ratio. Most interestingly, only EN590 and B100 high EGR (~55%) soot were observed to have an O/C ratio of <0.06; for both of these soots, negligible surface acidity was detected with the absence of surface sulphur. It is postulated therefore that there may be a threshold below an O/C ratio of 0.06 at which point soot surface acidity 'switches off'. This finding could be an important contribution to both lubricant and aftertreatment research disciplines.

10.3 Soot Sampling Methods

The ceramic thimble collection system developed in this work was found to have a fundamental sampling characteristic which was roughly exponential in regard to the concentration of exhaust soot and the rate at which soot accreted in the ceramic thimble, Section 3.5.1.2. Therefore the application of this sampling method to engines with low concentrations of exhaust soot is challenging. This soot sampling methodology proved successful at the exhaust manifold where there was high exhaust gas pressure but was not suited to sampling post turbocharger. A reduction of >80% in the exhaust soot concentration with the transition from mineral diesel to biodiesel fuel exposed the key limitation of the ceramic thimble method which was the difficulty in collecting in excess of 2g of soot. This was the minimum required to enable all the soot physiochemical analysis techniques used in the work herein to be performed on each soot sample.

It recommended that the ceramic thimble sampling methodology reported herein should only be considered when certain requirements/conditions exist: 1) the required soot sample size is limited to 1-2 g, 2) it is necessary to sample from points in the engine exhaust manifold, 3) a high pressure ratio across the ceramic thimble can be maintained and controlled as the ceramic thimble plugs.

A DPF was used for sampling soot post turbocharger but this methodology was also found to have some limitations which included: 1) the need to tightly control the temperature of the DPF to avoid condensation and oxidisation of the

Exhaust Smoke Measurement

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soot, 2) difficulty in extracting reliable soot samples, 3) contamination from the exhaust system metallurgy, 4) risk of longer-term build-up of ash deposits in the DPF with repeat use, 5) the need to consider the evolution of the soot in the exhaust system.

Consequently, the ceramic thimble method is a very useful and highly adaptable technique and is to be preferred for ensuring reliable soot samples from a turbocharged diesel engine exhaust manifold when low soot sample mass <2g can be tolerated. For post-turbocharger soot sampling or for cases where >2g soot is required; a sampling method such as a DPF is a more feasible route but soot evolution in the exhaust needs to be separately accounted for and is dependent upon the exhaust system configuration (i.e. whether an intermediate oxidation catalyst is present).

10.4 Exhaust Smoke Measurement

The soot physiochemical observations in the work herein provided evidence for a generally higher rate of B100 soot carbonaceous mass loss in the exhaust relative to conventional mineral diesel fuels. This highlights a concern with the standard approach to measuring exhaust soot concentration with a device such as the AVL 415 smoke meter and a single measurement location in the exhaust. This is because the higher rate of B100 soot carbonaceous mass loss was found to be likely influenced by such things as the levels of exhaust O₂, exhaust temperature and soot residence time in the exhaust. Thus, depending on the location of the single point measurement, the observed differences in exhaust soot concentration at like engine operating conditions between mineral and biodiesel fuels could appear to change due to changes in the higher rate of B100 soot carbonaceous mass loss and factors that influence it. It is postulated that this is a factor in the diverse results reported in literature regarding the magnitude of the beneficial reduction in exhaust soot concentration with biodiesel based fuels.

10.5 Injector Coking with Biodiesel Fuels

Injector coking was observed to be 2-4 times more significant for the B100 fuel compared to the two mineral diesel fuels studied. Further, the B100 fuel sensitivity to coking increased with the reduction in compression ratio which was not the case for both mineral diesel fuels. It is concluded that this was related to the factor 2 higher viscosity of the B100 fuel which impaired the fuel atomisation

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leading most likely to greater fuel impingement as evidenced by the greater HC emissions observed. This poor quality combustion was probably exaggerated by the lower cylinder charger pressures and temperatures at the lower compression ratio. Supporting evidence from literature is found in Argawal et al. [87] and others [330, 336-339] which state that the higher viscosity of biodiesel fuel is the causative factor responsible for increased injector coking.

10.6 Contributions

This thesis has the following contributions to knowledge:

- A positive linear correlation has been identified between soot surface carboxylic acid concentration and soot surface O/C ratio between an O/C ratio of (~ 0.07 to 0.12); this applies to mineral and biodiesel soot with surface sulphur concentrations (< 0.3%) weight with the following exceptions:
 - a. Surface sulphur concentrations (>0.3%) weight lead to substantially higher carboxylic surface acidity than is described by the O/C ratio correlation of contribution 1.
 - b. At high rates of EGR (~55%) both mineral and biodiesel soot was observed to have no surface acidity and this correlated with a soot surface O/C ratio (<0.07), this produces a 'knee' in the linear correlation of contribution 1.
- The reduction in compression ratio reduced the medium sulphur (497 ppm) mineral fuel soot surface sulphur concentration by 97%. This surface sulphur reduction influenced the surface acidity as outlined in contribution (1a).
- At high rates of EGR (~55%) the *low exhaust O₂ concentration (1.93-3.09%) and low NO_x concentration (23-24ppm) suppressed the oxidation based soot surface O/C ratio increase* in the exhaust system and is thought to be the causative effect of contribution (1b).
- 4. The B100 soot exhaust evolution through oxidation was distinct from that of the mineral fuel soot in that it *typically increased in surface O/C ratio by a factor of 1.2 to 1.8 relative to the mineral fuel soots* and had associated large *changes in surface area, porosity and density.*
- When PAH were detected, the PAH molar mass profile analysis showed a preference for the PAH molar mass 178 g/mol (Phenanthrene, Anthracence) for all mineral and biodiesel fuels, speed/load, compression ratio, exhaust sample location and EGR condition.

11 Future Work

As the work reported herein considered a broad spectrum of diesel exhaust soot physiochemical properties there were many potential areas of future research interest identified and these have been distilled into just four primary research topics which are summarised below.

11.1 Refinement of the Soot Surface O/C Ratio and Carboxylic Acid Correlation

A potentially very useful relationship was observed which described the diesel exhaust soot carboxylic acid concentration in respect to soot surface O/C ratio. This relationship was linear down to an O/C ratio of around 0.07 for soots with low surface sulphur and which did not experience the high rate of oxidation of the B100 soot. At the ratio of around 0.07 a 'knee' was observed and the two high EGR experiments with O/C ratios below this threshold were observed to have essentially no acidity.

Thus, the clarification of whether this is specifically an EGR related phenomenon or a more fundamental link between surface O/C ratio and carboxylic acid is needed. An additional observation from this data was that there may also be a threshold level of soot surface sulphur between 0.3 and 1.545 % weight which leads to greatly increased carboxylic surface acid functionality. The confirmation/rejection of this threshold would also be of interest although the relevancy of such research will reduce as fuels globally are converging towards 10 ppm sulphur or less. Such ULSD fuels in this study were observed to have no significant sulphur based influences on the soot.

11.2 Soot Density and Soot Exhaust Evolution

The results reported herein raised many interesting questions concerning soot skeletal density and how it relates to soot structure and reactivity. For example, the soot density for the two mineral fuel soots was observed to remain very stable even as the soots travelled down the exhaust to the DPF and underwent oxidation and addition of iron and zinc contamination from the exhaust system. In contrast, the B100 soot density was observed to reduce during the

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Compression Ratio and Soot Surface Sulphur

same processes in the exhaust system, likely due to a physically different oxidation transformation such as the internal oxidation mode described by Song et al. [17]. Therefore, improving the understanding soot density, specifically what influences it, would be a valuable area of future research as it appears to be coupled to the much higher reactivity of biodiesel soot.

11.3 Compression Ratio and Soot Surface Sulphur

The reduction in compression ratio from 19.5:1 to 16.5:1 was observed to influence the deposition of sulphur in the soot of the PC9 medium sulphur mineral fuel at the exhaust manifold. The reduction in surface sulphur concentration was very significant (-97%) and from the surface O/C ratio to surface acidity correlation discovered in the present work and also the previous work of Covitch et al. and Ripple et al. [210, 165]; this change in surface sulphur can potentially affect soots oleophilic tendency and hence absorption into the engine lubricant. A useful future area of research would therefore be to investigate what specifically occurs in the cylinder during the soot formation process to change the surface deposition of sulphur onto soot i.e. is this related to the cylinder charge density and temperature during combustion and is there a fundamental understanding of soot formation which may be drawn from this.

11.4 Soot Sulphur Deposition Change in the Exhaust

The interesting transformation of the PC9 soot in the exhaust suggested significant reaction processes occurred in the diesel oxidation catalyst which influenced the soot composition, surface chemistry and morphology. The key findings of the loss of 94% of the bulk sulphur, the 500% increase in surface sulphur, a reduction in surface oxygen and almost unchanged density were a very intriguing combination of observations. These could be explored in more detail by sampling exhaust soot both before and after a diesel oxidation catalyst at different exhaust temperatures to better understand what physical processes are driving these observed changes in the soot characteristics. Such knowledge would benefit aftertreatment system development.

- European Automobile Manufacturers Association (ACEA) <u>http://www.acea.be/images/uploads/files/ACEA_POCKET_GUIDE_2012_UP</u> <u>DATED.pdf</u> (Page 61), 2013-05-26
- Daily Mail Article, UK: 'Great diesel myth: They DON'T save you money and petrol models are more economical for most makes of car', <u>http://www.dailymail.co.uk/news/article-2175111/Great-diesel-myth-They-</u> <u>DONT-save-money-petrol-models-economical-makes-</u> <u>car.html#ixzz2ATyTA5rp</u>, 2013-05-26
- 3. US Energy Information Administration (EIA) <u>http://www.eia.gov/tools/faqs/faq.cfm?id=9&t=5, 2013-05-26</u>
- 4. <u>http://www.biodiesel.org/production/production-statistics</u>, 2013-05-26
- Kyeong Ook Lee and Jinyu Zhu, Effects of Exhaust System Components on Particulate Morphology in a Light-duty Diesel Engine, SAE Technical Paper 2005-01-0184, 2005
- H. Burtscher, Physical characterization of particulate emissions from diesel engines: a review, Aerosol Science 36 (2005) 896 – 932
- World Health Organization (WHO) classifies diesel exhaust as a carcinogen, 2012-06-12, <u>http://www.iarc.fr/en/media-centre/pr/2012/pdfs/pr213_E.pdf</u>, 2013-05-26
- EU Emissions Legislation, <u>http://dieselnet.com/standards/eu/ld.php</u>, 2013-05-26
- 9. EU Renewable Energy Directive 2003/30/EC: <u>http://eur-</u> lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2003:123:0042:0042:EN:P DF, 2013-05-26
- 10. Environmental Protection Agency, Renewable Fuel Standard: http://www.epa.gov/otaq/fuels/renewablefuels/index.htm, 2013-05-26
- 11. Renewable Energy Directive: <u>https://www.gov.uk/government/policies/reducing-greenhouse-gases-and-other-emissions-from-transport/supporting-pages/supporting-the-use-of-biofuels</u>, 2013-05-26
- 12. Brent D. Yacobucci, Biofuels Incentives: A Summary of Federal Programs, Congressional Research Service, 2012

- 13. Reuters Article: 'US Biodiesel on life support but smiling': http://uk.reuters.com/article/2011/02/04/us-usa-bi0dieselidUSTRE7130H920110204, 2013-05-26
- 14. GMA News Article: 'EU to limit use of crop-based biofuels draft law': <u>http://www.gmanetwork.com/news/story/273424/economy/agricultureandmini</u> ng/eu-to-limit-use-of-crop-based-biofuels-ndash-draft-law, 2013-05-26
- 15. Renewable Fuels Agency, The Gallagher Review of the indirect effects of biofuels production, July 2008
- Juhun Song, Mahabubul Alam, André L. Boehman, Unjeong Kim, Examination of the oxidation behavior of biodiesel soot, Combustion and Flame 146 (2006) 589–604
- Juhun Song, Mahabubul Alam, and Andre L. Boehman, Impact of Alternative Fuels on Soot Properties and DPF Regeneration, Combust. Sci. and Tech., 179: 1991–2037, 2007
- Randy L. Vander Wal, Aaron J. Tomasek, Soot oxidation: dependence upon initial nanostructure, Combustion and Flame 134 (2003) 1–9
- Jinyu Zhu and Kyeong Lee, Effects of Exhaust Gas Recirculation on Particulate Morphology for a Light-Duty Diesel Engine, SAE Technical Paper 2005-01-0195, 2005
- 20. Sarangi, A., McTaggart-Cowan, G., and Garner, C., The Effects of Intake Pressure on High EGR Low Temperature Diesel Engine Combustion, SAE Technical Paper 2010-01-2145, 2010
- Lyle M. Pickett * and Dennis L. Siebers, Soot in diesel fuel jets: effects of ambient temperature, ambient density, and injection pressure, Combustion and Flame 138 (2004) 114–135
- Dale R. Tree, Kenth I. Svensson Soot processes in compression ignition engines, Progress in Energy and Combustion Science 33 (2007) 272–309
- 23. K. Lombaert, L. Le Moyne, J. Tardieu De Maleissye & J. Amouroux, Experimental Study Of PAH In Engine Soot By Isotopic Tracing, Combustion Science and Technology, Volume 178, Issue 4, 2006
- 24. David B. Kittelson, Megan Arnold and Winthrop F. Watts, Jr., Review Of Diesel Particulate Matter Sampling Methods, EPA Final Report, 1999: <u>http://www.me.umn.edu/centers/cdr/reports/EPAreport3.pdf, 2013-05-26</u>
- Richard A. Dobbins, Hydrocarbon Nanoparticles Formed in Flames and Diesel Engines, Aerosol Science and Technology, Volume 41, Issue 5, 2007
- 26. Ullman TL. Investigation of the effects of fuel composition on heavy-duty diesel engine emissions. SAE Paper 892072, 1989.

- 27. Lee R, Pedley J, Hobbs C. Fuel quality impact on heavy duty diesel emissions—a literature review. SAE Paper 982649, 1998.
- Paul T. Williams, Montadher K. Abbass and Gordon E. Andrews, Keith D. Bartle, The influence of PAH contamination of Lubricating Oil on Diesel Particulate PAH Emissions, SAE Technical Paper 890825
- Barry A. A. L. van Setten, Michiel Makkee, and Jacob A. Moulijn, Science And Technology Of Catalytic Diesel Particulate Filters, Catalysis Reviews, 43(4), 489–564, 2001
- 30. Cooper, B.J.; Thoss, J.E. Role of NO in Diesel Particulate Emission Control. SAE Paper 890404, 1989.
- Lide, D.R., Ed. Handbook of Chemistry and Physics; 73rd Ed.; CRC Press: Boca Raton, FL, 1993.
- Annele K. K. Virtanen, Jyrki M. Ristimäki, Kati M. Vaaraslahti, and Jorma Keskinen, Effect of Engine Load on Diesel Soot Particles, Environ. Sci. Technol., 2004, 38 (9), pp 2551–2556
- 33. Kirby J. Baumgard and John H. Johnson, The Effect of Fuel and Engine Design on Diesel Exhaust Particle Size Distributions, SAE Technical Paper 960131
- 34. S. Schraml, S. Will and A. Leipertz, Simultaneous Measurement of Soot Mass Concentration and Primary Particle Size in the Exhaust of a DI Diesel Engine by Time-Resolved Laser-Induced Incandescence (TIRE-LII), SAE Technical Paper 1999-01-0146, 1999
- 35. Thomas W. Hesterberg, Christopher M. Long, Sonja N. Sax, Charles A. Lapin, Roger O. McClellan, William B. Bunn & Peter A. Valberg, Particulate Matter in New Technology Diesel Exhaust (NTDE) is Quantitatively and Qualitatively Very Different from that Found in Traditional Diesel Exhaust (TDE), J. Air & Waste Manage. Assoc. 61:894–913, 2011
- Hesterberg, T.W.; Lapin, C.A.; Bunn, W.B. A Comparison of Emissions from Vehicles Fueled with Diesel or Compressed Natural Gas; Environ. Sci. Technol. 2008, 42, 6437-6445.
- Tami C. Bond, David G. Streets, Kristen F. Yarber, Sibyl M. Nelson, Jung-Hun Woo, and Zbigniew Klimont, A technology-based global inventory of black and organic carbon emissions from combustion, Journal Of Geophysical Research, VOL. 109, D14203, doi:10.1029/2003JD003697, 2004

38.	. Horvath, H., Comparison of measurements of aerosol optical absorption by
	filter collection and a transmissometric method, Atmos. Environ., Part A, 27,
	319–325, 1993

- Petzold, A., C. Kopp, and R. Niessner, The dependence of the specific attenuation cross-section on black carbon mass fraction and par- ticle size, Atmos. Environ., 31, 661–672, 1997
- Bond, T. C., T. L. Anderson, and D. Campbell, Calibration and intercomparison of filter-based measurements of visible light absorption by aerosols, Aerosol. Sci. Technol., 30, 582–600, 1999
- Ogren, J. A., P. J. Groblicki, and R. J. Charlson, Measurement of the removal rate of elemental carbon from the atmosphere, Sci. Total Environ., 36, 329– 338, 1984
- Parungo, F., C. Nagamoto, M.-Y. Zhou, A. D. A. Hansen, and J. Harris, Aeolian transport of aerosol black carbon from China to the ocean, Atmos. Environ., 27, 3251–3260, 1994
- 43. Muller, J., Atmospheric residence time of carbonaceous particles and particulate PAH-compounds, Sci. Total Environ., 36, 339–346, 1984
- 44. Chameides, W.L., and M. Bergin, Soot takes center stage. Science, 297, 2214-2215, 2002
- 45. J.-F. Lamarque et al., Historical (1850–2000) gridded anthropogenic and biomass burning emissions of reactive gases and aerosols: methodology and application, Atmos. Chem. Phys., 10, 7017–7039, 2010
- 46. A.R. Chughtai, G.R. Williams, M.M.O. Atteya, N.J. Miller, D.M. Smith, Carbonaceous particle hydration, Atmospheric Environment 33, 1999
- 47. Sundeep Salvi, Anders Blomberg, Bertil Rudell, Frank Kelly, Thomas Sandström, Stephen T. Holgate, And Anthony Frew, Acute Inflammatory Responses in the Airways and Peripheral Blood After Short-Term Exposure to Diesel Exhaust in Healthy Human Volunteers, Am J Respir Crit Care Med Vol 159. pp 702–709, 1999
- Vistal, J. J. Health effects of diesel exhaust particulate emissions. Bull. N.Y. Acad. Med. 56:914–934, 1980
- 49. Quality of Urban Air Review Group. Sources and emissions of primary particulate matter. In Airborne Particulate Matter in the United Kingdom. Third Report of the Quality of Urban Air Review Group. Department of Environment, London. 37–55, 1996
- 50. Seaton, A.; MacNee, W.; Donaldson, K.; Godden, D. Particulate Air Pollution and Acute Health Effects. Lancet 1995, 345, 176–178.

- 51. Donaldson, K.; Beswick, P.H.; Gilmour, P.S. Free Radical Activity Associated with the Surface of Particles: A Unifying Factor in Determining Biological Activity? Toxicol. Lett. 1996, 88, 293–298.
- 52. Ferin, J.; Oberdo rster, G.; Penney, D.P. Pulmonary Retention of Ultrafine and Fine Particles in Rats. Am. J. Respir. Cell. Mol. Biol. 1992, 6, 535–542
- A. Tsolakis, Effects on Particle Size Distribution from the Diesel Engine
 Operating on RME-Biodiesel with EGR, Energy & Fuels 2006, 20, 1418-1424
- 54. Andrew J. Ghio, Candice B. Smith, and Michael C. Madden, Diesel exhaust particles and airway inflammation, Curr Opin Pulm Med 2012, 18:144 150
- 55. Gilman P. Health assessment document for diesel engine exhaust.Washington DC: U.S. Environmental Protection Agency; 2002
- 56. Corfa E, Maury F, Segers P, et al. Short-range evaluation of air pollution near bus and railway stations. Sci Total Environ 2004; 334 – 335:223 – 230
- 57. Cyrys J, Pitz M, Bischof W, et al. Relationship between indoor and outdoor levels of fine particle mass, particle number concentrations and black smoke under different ventilation conditions. J Expo Anal Environ Epidemiol 2004; 14:275 – 283
- Harrison, R. M., P. Brimblecombe, and R. G. Dervent.. Health effects of nonbiological particles. In Airborne Particulate Matter in the United Kingdom: Third Report of the Quality of Urban Air Review Group. Department of Environment, London. 115–118, 1996
- Lave, Lester B.; Eugene P. Seskin, An Analysis of the Association Between
 U.S. Mortality and Air Pollution. J. Amer. Statistical Association 68: 342, 1973
- 60. Jenny Rissler, Erik Swietlicki, Agneta Bengtsson, Christoffer Boman, Joakim Pagels, Thomas Sandstrom, Anders Blomberg ,Jakob Londah, Experimental determination of deposition of diesel exhaust particles in the human respiratory tract, Journal of Aerosol Science 48 (2012) 18–33
- Chalupa, D.C., Morrow, P.E., Oberdo rster, G., Utell, M.J., & Frampton, M.W., Ultrafine particle deposition in subjects with asthma., Environ health perspective, 112, 879–882, 2004
- 62. Londahl, J., Massling, A., Pagels, J., Swietlicki, E., Vaclavik, E., & Loft, S., Size-resolved respiratory-tract deposition of fine and ultra fine hydrophobic and hygroscopic aerosol particles during rest and exercise. Inhalation Toxicology, 19, 109–116, 2007
- Randy L. Vander Wal, Vicky M. Brygb, Michael D. Haysc , Fingerprinting soot (towards source identification): Physical structure and chemical composition, Aerosol Science 41, 108 – 117, 2010

- 64. JoAnn Slama Lighty, John M. Veranth & Adel F. Sarofim, Combustion Aerosols: Factors Governing Their Size and Composition and Implications to Human Health, Journal of the Air & Waste Management Association, 50:9, 1565-1618
- 65. Sarofim et al., Report on Carcinogens, Twelfth Edition, National Toxicology Program, Department of Health and Human Services, 2011
- 66. Ostro, B., The association of air pollution and mortality: examining the case for inference. Arch. Environ. Health 48:336–342., 1993
- Dockery, D. W., A. Pope, III, X. Xu, J. D. Spengler, J. H. Ware, M. E. Fay, B. G. Ferris, Jr., and F. E. Speizer. An association between air pollution and mortality in six U.S. cities. N. Engl. J. Med. 329:1753–1759, 1993
- Schwartz, J..Air pollution and daily mortality in Birmingham, Alabama. Am. J. Epidemiol. 137:1136–1147, 1993
- Schwartz, J., and D. W. Dockery. Particulate air pollution and daily mortality in Steubenville, Ohio. Am. J. Epidemiol. 135:12–19., 1992
- Dockery, D. W., and C. A. Pope, III. Acute respiratory effects of particulate air pollution. Annual Rev. Public Health 15:107–132, 1994
- 71. Report on Carcinogens, Twelfth Edition (2011), National Toxicology Program, Department of Health and Human Services
- Somers, C. M., McCarry, B. E., Malek, F., & Quinn, J. S. Reduction of particulate air pollution lowers the risk of heritable mutations in mice. Science, 304, 1008–1010, 2004
- 73. Guardian UK Article: 'Air pollution 'may cause 35,000 premature deaths a year in Britain', <u>http://www.guardian.co.uk/environment/2010/feb/23/air-pollution-deaths-sooty-particles</u>, 2013-05-26
- 74. Official Report 2352 of the Umweltbundesamt Berlin (Federal Environmental Agency of Germany)
- Mokdad, Ali H.; et al. Actual Causes of Death in the United States, 2000. J. Amer. Med. Assoc. 291 (10): 1238–45, 2004
- 76. Singh P, DeMarini DM, Dick CA, et al. Sample characterization of automobile and forklift diesel exhaust particles and comparative pulmonary toxicity in mice. Environ Health Perspect; 112:820 – 825., 2004
- 77. Su D.S., Serafino A., Müller J.O., Jentoft R.E., Schlögl R., Fiorito S., Cytotoxicity and inflammatory potential of soot particles of low-emission diesel engines, Environ Sci Technol. Mar 1;42(5):1761-5, 2008
- 78. Maria Sehlstedt, Annelie F. Behndig, Christoffer Boman, Anders Blomberg, Thomas Sandström, and Jamshid Pourazar, Airway inflammatory response to

diesel exhaust generated at urban cycle running conditions, Inhalation Toxicology, Vol. 22, No. 14 : Pages 1144-1150, 2010

- Bagley, S.T.; Baumgard, K.J.; Gratz, L.D.; Johnson, J.H.; Leddy, D.G.
 Characterization of Fuel and Aftertreatment Device Effects on Diesel
 Emissions, Technical Report; Health Effects Institute: Cambridge, MA, 1996
- Ferin, J., R. Gelein, S. C. Soderholm, and J. Finkelstein., Role of alveolar macrophage in lung injury: studies with ultrafine particles. Environ. Health Perspect. 97:193–199, 1992
- Peters, A., H. E. Wickmann, T. Tuch, and J. Heyder., Respiratory effects are associated with the number of ultrafine particles. Am. J. Respir. Crit. Care Med. 155:1376–1383, 1997
- Albelda, S. M., C. W. Smith, and P. A. Ward. 1994. Adhesion molecules and inflammatory injury. F.A.S.E.B. J. 8:504–512
- B. Kittelson, Engines And Nanoparticles: A Review, J. Aerosol Sci. Vol. 29, No. 5/6, pp. 575—588, 1998
- 84. Donaldson, K.; Li, X. Y.; MacNee, Ultrafine (nanometre) particle mediated lung injury, W. J. Aerosol Sci., 29, 553-560, 1998
- Oberdörster G, Sharp Z, Atudorei V, Elder A, Gelein R, Kreyling W, Cox C., Translocation of inhaled ultrafine particles to the brain., Inhal Toxicol. Jun;16(6-7):437-45, 2004
- Brown, K.F., Chadderton, J., Daly, D.T., Langer, D.A., and Duncan, D.
 Opportunity for diesel emission reductions using advanced catalysts and water blend fuel, SAE Technical Paper 2000-01-0182, SP 1647, 2000
- 87. Avinash Kumar Agarwal, Tarun Gupta & Abhishek Kothari, Toxic Potential Evaluation of Particulate Matter Emitted from a Constant Speed Compression Ignition Engine: A Comparison between Straight Vegetable Oil and Mineral Diesel, Aerosol Science and Technology, Volume 44, Issue 9, 2010
- Valavanidis, A., Salika, A., and Theodosopoulou, A., Generation of Hydroxyl Radicals by Urban Suspended Particulate Air Matter. The Role of Iron Ions. Atmos. Environ. 34:2379–2386, 2000
- Californian Environmental Protection Agency; Health Risk Assessment for Diesel Exhaust, Report May 1998
- Canagaratna, M. R., Jayne, J. T., Jimenez, J. L. et al., Chemical and microphysical characterization of ambient aerosols with the aerodyne aerosol mass spectrometer. Mass Spectrometry Reviews, 26, 185–222, 2007
- 91. Forschungsvereinigung Verbrennungskraftmaschinen, "Partikelkenngrößen", Final Report of Project 595, Frank- furt (Main), 1997

- 92. Lammel, G., Novakov, T., Water nucleation properties of carbon black and diesel soot particles, Atmospheric Envir- onment 29, 813–823, 1995
- Smith, D.M., Chughtai, A.R., Reaction kinetics of ozone at low concentration with n-hexane soot. Journal of Geophysical Research Atmospheric 101(D14), 19,607—19,620, 1996
- Menon, S., J. Hansen, and L. Nazarenko, Climate effects of black carbon aerosols in China and India, Science, 297, 2250–2253, 2002
- 95. Sokolik, I. N., and O. B. Toon, Direct radiative forcing by anthropogenic airborne mineral aerosols, Nature, 381, 681–683, 1996
- Jacobson, M. Z. Isolating nitrated and aromatic aerosols and nitrated aromatic gases as sources of ultraviolet light absorption, J. Geo- phys. Res., 104(D3), 3527–3542, 1999
- Rosen, H., A. D. A. Hansen, L. Gundel, and T. Novakov, Identification of the optically absorbing component in urban aerosols, Appl. Opt., 17(24), 3859– 3861, 1978
- 98. S. C. Anenberg, K. Talgo, S. Arunachalam, P. Dolwick, C. Jang, and J. J. West, Impacts of global, regional, and sectoral black carbon emission reductions on surface air quality and human mortality, Atmos. Chem. Phys. Discuss., 11, 10653–10691, 2011
- Horvath, H.: Atmospheric light absorption A review, Atmos. Environ., 27A, 293–317, 1993
- 100. Mark Z. Jacobson, Testimony for the Hearing on Black Carbon and Global Warming House Committee on Oversight and Government Reform United States House of Representatives, The Honorable Henry A. Waxman, Chair, October 18, 2007
- Koch, D. and Del Genio, A. D.: Black carbon semi-direct effects on cloud cover: review and synthesis, Atmos. Chem. Phys., 10, 7685–7696, doi:10.5194/acp-10-7685-2010, 2010
- S. Twomey, Pollution and the planetary albedo, Atmospheric Environment, Volume 8, Issue 12, December 1974, Pages 1251–1256
- Hansen, J. and Nazarenko, L.: Soot climate forcing via snow and ice albedos, P. Natl. Acad. Sci., 101, 423–428, 2004
- I. Colbeck, L. Appleby, E.J. Hardman, Roy M. Harrison, The optical properties and morphology of cloud-processed carbonaceous smoke, Journal of Aerosol Science, Volume 21, Issue 4, 1990, Pages 527–538
- 105. Jana Moldanova, Erik Fridell, Olga Popovicheva, Benjamin Demirdjian, Victoria Tishkova, Alessandro Faccinetto, Cristian Focsa, Characterisation of

particulate matter and gaseous emissions from a large ship diesel engine, Atmospheric Environment 43 (2009) 2632–2641

- U. Kirchner, V. Scheer, and R. Vogt, FTIR Spectroscopic Investigation of the Mechanism and Kinetics of the Heterogeneous Reactions of NO₂ and HNO3 with Soot, J. Phys. Chem. A, 104, 8908-8915, 2000
- 107. P. Kumar, A. Robins, H. Ap Simon, Nanoparticle emissions from biofuelled vehicles – their characteristics and impact on the number-based regulation of atmospheric particles, Atmos. Sci. Lett. 11, 327–331, 2010
- 108. L. Lou, L. Luo, W. Wang, X. Xu, J. Hou, B. Xun, Y. Chen, Impact of black carbon originated from fly ash and soot on the toxicity of pentachlorophenol in sediment, J. Hazard. Mater. 190, 474–479, 2011
- 109. John H. Priester, et al., Soybean susceptibility to manufactured nanomaterials with evidence for food quality and soil fertility interruption, http://www.pnas.org/content/109/37/E2451, 2013-05-26
- 110. Kyeong Ook Lee, Roger Cole and Raj Sekar, Mun Young Choi, Jinyu Zhu, Jinsuk Kang and Choongsik Bae, Detailed Characterization of Morphology and Dimensions of Diesel Particulates via Thermophoretic Sampling, SAE Technical Paper 2001-01-3572, 2001
- Juhun Song, Mahabubul Alam, André L. Boehman, Unjeong Kim, Examination of the oxidation behavior of biodiesel soot, Combustion and Flame 146, 589–604, 2006
- 112. Nora Lamharess, Claire-Noelle Millet, Laurie Starck, Eric Jeudy, Jacques Lavy, Patrick Da Costa, Catalysed diesel particulate filter: Study of the reactivity of soot arising from biodiesel combustion, Catalysis Today 176, 219–224, 2011
- 113. Khalid Al-Qurashi 1, Angela D. Lueking, André L. Boehman, The deconvolution of the thermal, dilution, and chemical effects of exhaust gas recirculation (EGR) on the reactivity of engine and flame soot, Combustion and Flame 158, 1696–1704, 2011
- 114. R. Vander Wal, A.J. Tomasek, Soot nanostructure: dependence upon synthesis conditions, Combust. Flame 136 (2004) 129–140
- 115. Ewa A. Bardasz et al., Understanding Soot Mediated Oil Thickening Through Designed Experimentation Part 4: Mack T-8 Test, SAE Technical Paper 971693, 1997.
- H. Muckenhuber and H. Grothe, The reaction between soot and NO₂ investigation on functional groups using TPD-MS, Topics in Catalysis Vols. 30/31, Nos. 1–4, July 2004

- 117. Ewa A. Bardasz et al., Understanding Soot Mediated Oil Thickening Through Designed Experimentation - Part 1: Mack EM6-287, GM 6.2L, SAE Technical Paper 952527, 1995
- 118. H.P. Boehm, Surface oxides on carbon and their analysis: a critical assessment, Carbon 40 (2002) 145–149
- Ewa A. Bardasz et al., Understanding Soot Mediated Oil Thickening Through Designed Experimentation - Part 2: GM 6.5L, SAE Technical Paper 961915, 1996.
- Kuznetsova A, Mawhinney DB, Naumenko V, Yates Jr JT, Liu J, Smalley RE., Enhancement of adsorption inside of single walled nanotubes: opening the entry ports. Chem Phys Lett; 321:292–6, 2000
- 121. Leon y Leon C.A, Radovic L.R. In, Thrower PA, editor, Chemistry and physics of carbon, vol. 24, New York: Marcel Dekker, 1994, pp. 213–310.
- 122. Lewis I.C., Singer L.S. In: Walker PL, Thrower PA, editors, Chemistry and physics of carbon, vol. 17, New York: Marcel Dekker, 1981, pp. 1–88
- 123. B.R. Stanmore, J.F. Brilhac, P. Gilot, The oxidation of soot: a review of experiments, mechanisms and models, Carbon 39 (2001) 2247–2268
- Thanhh. Nguyen, William P. Ball, Absorption and Adsorption of Hydrophobic Organic Contaminants to Diesel and Hexane Soot, Environ. Sci. Technol. 2006, 40, 2958-2964
- 125. Liu, Z.G.; Berg, D.R.; Swor, T.A.; Schauer, J.J. Comparative Analysis on the Effects of Diesel Particulate Filter and Selective Catalytic Reduction Systems on a Wide Spectrum of Chemical Species Emissions; Environ. Sci. Technol, 42, 6080-6085, 2008
- 126. Khalek, I.A.; Bougher, T.L.; Merritt, P.M.; Zielinska, B. Regulated and Unregulated Emissions from Highway Heavy-Duty Diesel Engines Complying with U.S. Environmental Protection Agency 2007 Emissions Standards; J. Air Waste Manage. Assoc. 2011, 61, 427-442; doi: 10.3155/ 1047-3289.61.4.427
- 127. Merkel, G.A.; Cutler, W.A.; Warren, C.J. Thermal Durability of Wall-Flow Ceramic Diesel Particulate Filters. SAE Technical Paper 2001-01-0190, 2001
- 128. National Toxicology Program, Department of Health and Human Services Report on Carcinogens, Twelfth Edition (2011)
- Darmstadt H, Roy C, Donnelly PJ. Comparative inve tigation of defects on carbon black surfaces by nitrogen adsorption and SIMS. In: Third international conference on carbon black (Mulhouse), 2000, pp. 77–9
- Ahlstrom AF, Odenbrand CUI. Combustion characteristics of soot deposits from diesel engines. Carbon 1989;27:475–83

- Tomoji Ishiguro, Noritomo Suzuki, Yoshiyasu Fujitani, Hidetake Morimoto, Microstructural Changes of Diesel Soot During Oxidation, Combustion and Flame 85: 1-6 (1991)
- 132. Smith WR, Polley MH. The oxidation of graphitized carbon black. J Phys Chem 1956:689–91
- Bonnefoy F, Gilot P, Stanmore BR, Prado G. A comparative study of carbon black and diesel soot reactivity in the temperature range 500–600 °C– – effect of additives. Carbon 1994;7: 1333–40
- 134. S. Collura, N. Chaoui, B. Azambre, G. Finqueneisel, O. Heintz, A. Krzton, A. Koch, J.V. Weber, Influence of the soluble organic fraction on the thermal behaviour, texture and surface chemistry of diesel exhaust soot, Carbon 43 (2005) 605–613
- K. Otto, M. H. Sieg, M. Zinbo, and L. Bartosiewicz, The Oxidation of Soot Deposits from Diesel Engines, SAE Paper 800336, 1980
- 136. Magín Lapuerta and Fermín Oliva, Simón Martínez-Martínez, Modeling of the Soot Accumulation in DPF Under Typical Vehicle Operating Conditions, SAE Int. J. Fuels Lubr. Volume 3 | Issue 2
- T.W. Zerda, X. Yuan, S.M. Moore, C.A. Leon y Leon, Surface area, pore size distribution and microstructure of combustion engine deposits, Carbon 37 (1999) 1999–2009
- Michael J. Covitch, Oil Thickening in the Mack T-7 Engine Test. of Fuel Composition on Soot Chemistry, SAE Technical Paper 880259
- Brian Stanmore, Jean-François Brilhac and Patrick Gilot, P. Gilot, The Ignition and Combustion of Cerium Doped Diesel Soot, SAE Technical Paper 1999-01-0115, 1999
- 140. Guoxian Yu, Shanxiang Lu, Hui Chen, Zhongnan Zhu, Diesel fuel desulfurization with hydrogen peroxide promoted by formic acid and catalyzed by activated carbon, Carbon 43 (2005) 2285–2294
- 141. Katsumi Kaneko, Determination of pore size and pore size distribution 1.Adsorbents and catalysts, Journal of Membrane Science 96 (1994) 59-89
- 142. Pei Lu, Caiting Li, Guangming Zeng, Xuwen Xie, Zhihong Cai, Yangxin Zhou, Yapei Zhao, Qi Zhan, Zheng Zeng, Research on soot of black smoke from ceramic furnace flue gas: Characterization of soot, Journal of Hazardous Materials 199– 200, 272– 281, 2012
- 143. Randy L. Vander Wal, Aleksey Yezerets, Neal W. Currier, Do Heui Kim, Chong Min Wang, HRTEM Study of diesel soot collected from diesel particulate filters, Carbon 45, 70–77, 2007

- Donnet J-B. Fifty years of research and progress on carbon black. In: Second international conference on carbon black (Mulhouse), 1993, pp. 1–10
- Stoeckli F, Guillot A, Slasli A, Hugi-Cleary D. Microporosity in carbon blacks. In: Third international conference on carbon black (Mulhouse), 2000, pp. 67–75
- Neoh KG, Howard JB, Sarofim AF. Effects of oxidation on the physical structure of soot. Proc Combust Inst 1984;20:951–7
- 147. Angelo W. Kandas, I. Gokhan Senel, Yiannis Levendis, Adel F. Sarofim, Soot surface area evolution during air oxidation as evaluated by small angle X-ray scattering and CO₂ adsorption, Carbon 43 (2005) 241–251
- Barrett, E.P., L.G. Joyner and P.H. Halenda, The determination of pore volume and area distributions in porous substances. I. Computations from nitrogen isotherms. J. Am. Chem. Soc., 73: 373-380, 1951.
- D. Dollimore, G. R. Heal, An improved method for the calculation of pore size distribution from adsorption data, Journal of Applied Chemistry Volume 14, Issue 3, pages 109–114, March 1964
- 150. Nicolas Coudray, Alain Dieterlen, L. Vidal, Estelle Roth, G. Trouve, Sophie Bistac, Image processing nanoparticle size measurement for determination of density values to correct the ELPI measures, Precision Engineering 32 (2008) 88–99
- 151. S. Bau, O. Witschger, F. Gensdarmes, O. Rastoix, D. Thomas A TEMbased method as an alternative to the BET method for measuring off-line the specific surface area of nanoaerosols, Powder Technology 200 (2010) 190– 201
- 152. Kihong Park, David B. Kittelson, Michael R. Zachariah and Peter H. McMurry, Measurement of inherent material density of nanoparticle agglomerates, Journal of Nanoparticle Research 6: 267–272, 2004
- 153. Choi MY, Hamins A, Mulholland GW, Kashiwagi T. Simultaneous optical measurement of soot volume fraction and temperature in premixed flames. Combust Flame 1994;99:174–86.
- 154. M. Matti Maricq, Ning Xu, The effective density and fractal dimension of soot particles from premixed flames and motor vehicle exhaust, Journal of Aerosol Science, Volume 35, Issue 10, October 2004, Pages 1251–1274
- 155. Anne Smekens, Ricardo Henrique Moreton Godoi, Patrick Berghmans And Rene V´An Grieken, Characterisation of Soot Emitted by Domestic Heating, Aircraft and Cars Using Diesel or Biodiesel, Journal of Atmospheric Chemistry (2005) 52: 45–62

- H. P. Boehm, Some Aspects Of The Surface Chemistry Of Carbon Blacks And Other Carbons, Carbon, Vol. 32, No. 5, pp. 759-769, 1994
- 157. Boehm HP. In: Eley D, Pines H, Weisz PB, editors. Advances in catalysis. New York: Academic Press, 1966:179.
- Puri BR. In: Walker PL, editor. Chemistry and physics of carbon. New York: Dekker, 1970:191
- 159. Mattson JS, Mark HB. Activated carbon: surface chemistry and adsorption from solution. New York: Dekker, 1971:1
- 160. Boehm HP, Voll M. Carbon 1970;8:227
- 161. Papirer E, Li S, Donnet JB. Carbon 1987;25:243
- 162. Papirer E, Dentzer J, Li S, Donnet JB. Carbon 1991;29:69
- M. L. Studebaker. Oxygen-Containing Groups on the Surface of Carbon Black, Rubber Chem. Technol. 30. 1400 (1957)
- Kotzick, R.; Niessner, R. Changes in condensation properties of ultrafine carbon particles subjected to oxidation by ozone, J. Aerosol Sci. 1997, 28, S165
- 165. David E. Ripple and Jane F. Guzauskas, Fuel Sulfur Effects on Diesel Engine Lubrication, SAE Technical Paper 902175, 1990
- 166. O. B. Popovitcheva, N. M. Persiantseva, M. E. Trukhin, G. B. Rulev, N. K. Shonija, Yu. Ya. Buriko, A. M. Starik, B. Demirdjian, D. Ferryc and J. Suzanne, Experimental characterization of aircraft combustor soot: Microstructure, surface area, porosity and water adsorption, Phys. Chem. Chem. Phys., 2000, 2, 4421-4426
- Y Matsumura, Some Physico-Chemical Properties Of Soot From Fuel Oil Burners And Automobile Engines, Atmospheric Environment Pergamon Press 1973. Vol. 7, pp. 219-224.
- 168. P. Kotin, H. L. Falk, and M. Thomas, Aromatic Hydrocarbons. II. Presence in the Particulate Phase of Gasoline-Engine Exhaust and the Carcinogenicity of Exhaust Extracts. Archives of Industrial Hygine and Occupational Medicine 9 (1954):164–177.
- 169. P. Kotin, H. L. Falk, and M. Thomas, Aromatic Hydrocarbons. III. Presence in the Particulate Phase of Diesel-Engine Exhaust and the Carcinogenicity of Exhaust Extracts. Archives of Industrial Health 11 (1955):113–120
- 170. Durant, J. L., Busby, W. F., Jr., Lafleur, A. L., Penman, B.W., and Crespi,C. L. (1996). Human Cell Mutagenicity of Oxygenated, Nitrated and Unsubsti-

tuted Polycyclic Aromatic Hydrocarbons Associated with Urban Aerosols, Mutation Res. 371:123–157.

- H.J. Gotze, J. Schneider, and H.-G. Herzog, Determination of polycyclic aromatic hydrocarbons in Diesel soot by high-performance liquid chromatography, J Anal Chem (1991) 340:27—30
- 172. Gudipati, Murthy S.; Yang, Rui, In-Situ Probing Of Radiation-Induced Processing Of Organics In Astrophysical Ice Analogs—Novel Laser Desorption Laser Ionization Time-Of-Flight Mass Spectroscopic Studies. The Astrophysical Journal Letters 756 (1). doi:10.1088/2041-8205/756/1/L24, September 1, 2012
- Williams P.T. Andrews G.E. and Bartle K.D. Diesel particulate emissions: the role of unburnt fuel in the organic fraction composition. SAE Paper 870554 (1987)
- Williams P.T. Bartle K.D. and Andrews G.E. The relation between polyaromatic compounds in diesel fuels and particulates. Fuel Vol. 65, 1150-1158 (1986)
- 175. M. M. Rhead and R. D. Pemberton, Sources of Naphthalene in Diesel Exhaust Emissions, Energy Fuels, 1996, 10 (3), pp 837–843
- 176. Williams P.T., Andrews G.E. and Bartle K.D. The role of lubricating oil in diesel particulate and particulate PAC emissions. SAE Paper 872084 (1987)
- 177. Abbass M.K., Williams P.T., Andrews G.E. and Bartle K.D. The aging of lubricating oil, the influence of unburnt fuel and particulate SOF contamination. SAE Paper 872085 (1987)
- 178. Henderson T.R., Sun J.D, Li A.P. Hanson R.L. Bechtold W.E. Harvey T.M. Shabanowitz J. and Hunt D.F. GC/MS and MS/MS studies of diesel exhaust mutagenicity and emissions from chemically defined fuels. Environ. Sci. Tech. Vol 18 p428-434 (1984).
- 179. Williams, P. T.; Abbass, M. K.; Andrews, G. E. Combust Flame 1989, 75, 1-24.
- Stein, S. E., and Fahr, A. (1985). High Temperature Stability of Hydrocarbons, J. Phys. Chem. 89:3714–3725
- Dobbins, R. A., Fletcher, R. A., Benner, B. A., and Hoeft, S. (2006).
 Polycyclic Aromatic Hydrocarbons in Flames. In Diesel Fuels, and in Diesel Emissions, Combust. Flame 144:773–781
- M. Matti Maricq, Chemical characterization of particulate emissions from diesel engines: A review, Aerosol Science 38 (2007) 1079 – 1118

- 183. Dianne L. Poster, Maria J. Lopez de Alda, Michele M. Schantz, Lane C. Sander, Stephen A. Wise, Mark G. Vangel, Development And Analysis Of Three Diesel Particulate-Related Standard Reference Materials For The Determination Of Chemical, Physical, And Biological characteristics, Polycyclic Aromatic Compounds, 23:141–191, 2003
- Mortier R.M., Orszulik S.T. Chemistry and Technology of Lubricants, 2nd Edition. *Blackie Academic & Professional*. 1997 ISBN 0-7514-0246-X
- 185. <u>http://www.cpchem.com/bl/specchem/en-us/tdslibrary/diesel_PC-9.pdf</u>, 2013-05-26
- 186. <u>http://www.infineum.com/sitecollectiondocuments/notebooks/pc10/august</u> 2007/pc10.pdf , 2013-05-26
- V.W. Group. Self-Study Program Course Number 841303. Auburn Hills, MI 48326, USA:, 2003., V.W. Group.
- 188. VW 1.9I Engine Workshop Manual. VW Group, 2001., V.W. Group. VW1.9I TDI Engine Manual. VW, 2001
- K. Shaine Tyson. Biodiesel handling and use guide. Technical report, National Renewable Energy Laboratory, 2001
- 190. <u>ftp://ftp.ni.com/pub/branches/uk/academic/edward_winward_tdi_engine_ri</u> <u>g_control.pdf</u>, 2013-05-26
- 191. Ross-Tech, <u>http://www.ross-tech.com, 2013-05-26</u>
- 192. Plint Michael Alexander: Apparatus for measuring fuel consumption of a liquid-fuel burning engine. Plint & Partners Jul, 25 1979: EP0003170
- Hsu B.D., Practical Diesel-Engine Combustion Analysis. SAE International. 2002 ISBN 0-7680-0914-6
- 194. AVL 415 Variable Sampling Smoke Meter Manual (Software version 2.1 and above Hardware rev. 16 and above, January 1998, Section 5.3.3
- 195. C. Arcoumanis and A. Nagwaney, W. Hentschel and S. Ropke, Effect of EGR on Spray Development, Combustion and Emissions in a 1.9L Direct-Injection Diesel Engine. SAE Technical Paper 952356. 1995
- 196. C. Arcoumanis, C. Bae, A. Nagwaney, and J. H. Whitelaw, Effect of EGR on Combustion Development in a 1.9L DI Diesel Optical Engine. SAE Technical Paper 950850. 1995
- 197. Gerhard Ohmstede and Matthias Stein. Oil-air-mixture-behaviour inside the cooling-channel of a VW-TDI-piston with 2-phase-piv (2-p-piv). In 19th Annual Meeting of the Institute for Liquid Atomization and Spray Systems (Europe) Nottingham, 6-8 September 2004. ILASS, 2004

- 198. David Blank and Andrew Pouring. Frozen equilibrium and EGR effects on radical-initiated h2 combustion kinetics in low-compression d.i. engines using pistons with micro-chambers. 2003. doi: 10.4271/2003-01-1788
- David Blank, Andrew Pouring, and Jiang Lu. Methanol combustion in low compression ratio DI engines enabled by sonex piston design. 2001. doi: 10.4271/2001-01-1197
- 200. Jiang Lu and Andrew Pouring. Development of a new concept piston for alcohol fuel use in a cl engine. 1996. doi: 10.4271/961078.
- 201. Jiang Lu, Ashwani Gupta, Andrew Pouring, and Eugene Keating. A preliminary study of chemically enhanced autoignition in an internal combustion engine. 1994. doi: 10.4271/940758.
- Andrew Pouring. Sonex research, <u>http://www.sonexresearch.com/</u>, 2013-05-26
- 203. Leto di Priolo and Andrew Pouring. Patent no. 6,178,942 b1 piston configuration for reducing smoke and particulate emissions from direct injected engines, 2001.
- 204. Andrew Pouring and Leto di Priolo. Patent no. 5,862,788 combustion chamber for direct injected reciprocating internal combustion engine, 1999.
- 205. Andrew Pouring and McCowan. Patent no. 5,855,192 charge conditioning system for enabling cold starting and running of spark-ignited diesel fueled piston engines, 1999.
- 206. Andrew Pouring and Leto di Priolo. Patent no. 5,322,042 combustion chamber for internal combustion engine and process of combustion using fuel radical species, 1994.
- 207. Andrew Pouring. Patent no. 4,898,135 piston and process for achiev- ing controlled combustion of hydrocarbon fuels in internal combustion en- gines by generation and management of fuel radical species, 1990.
- 208. BJ Rogers, G Li, and CH Such. The reduction of soot emissions by the use of a piston with micro-chambers on a medium duty diesel engine. 2002. doi: 10.4271/2002-01-1682.
- 209. VW Technical Document (page 33), rom: http://www.volkspage.net/ technik/ ssp/ ssp/ ssp200d2.pdf
- 210. M. J. Covitch, B. K. Humphrey, and D. E. Ripple, Oil Thickening in the Mack T-7 Engine Test® Fuel Effects and the Influence of Lubricant Additives on Soot Aggregation. SAE Technical Paper 852126, 1985

- Ewa A. Bardasz et al., Understanding Soot Mediated Oil Thickening Through Designed Experimentation - Part 5: Knowledge Enhancement in the GM 6.5L, SAE Technical Paper 972952, 1997.
- Ralph E. Kornbrekke et al., Understanding Soot Mediated Oil Thickening Part 6: Base Oil Effects, SAE Technical Paper 982665, 1998.
- Ewa A. Bardasz et al., Effects of Lubricant Derived Chemistries on Performance of the Catalyzed Diesel Particulate Filters, SAE Technical Paper 2005-01-2168, 2005
- Stationary Source Emissions Manual Determination of Mass Concentration of Particulate Matter Stationary Source Emissions. International Organisation for Standardization, ISO 9096:2002 edition.
- Stationary source emissions. Determination of low range mass concentration of dust. Manual gravimetric method, BS EN13284-1:2002 edition.
- Determination of particulate emissions from stationary sources (in stack filtration method). Environmental Protection Agency, EPA 40 cfr 60, method 17 edition.
- 217. Method for measurement of particulate emission including grit and dust (simplified method), BS3405 edition.
- M Sharma, A Agarwal, and K Bharathi. Characterization of exhaust particulates from diesel engine. Atmospheric Environment, 39(17):3023– 3028, 2005. ISSN 13522310. doi: 10.1016/j.atmosenv.2004.12.047
- Akira Obuchi, Hyogoro Aoyama, Akihiko Ohi, and Hideo Ohuchi. Appplication of thin-layer chromatography with flame ionization detection to the characterization of organic extracts from diesel exhaust particulates. Journal of Chromatography A, 288:187–194, 1984. ISSN 00219673. doi: 10.1016/S0021-9673(01)93693-3.
- 220. Ya-Fen Wang, Kuo-Lin Huang, Chun-Teh Li, Hsiao-Hsuan Mi, Jih-Haur Luo, and Perng-Jy Tsai. Emissions of fuel metals content from a diesel vehicle engine. Atmospheric Environment, Volume 37, Issue 33, October 2003, Pages 4637–4643
- 221. K. Lombaert, S. Morel, L. Le Moyne, P. Adam, J. Tardieu de Maleissye, and J. Amouroux, Nondestructive Analysis of Metallic Elements in Diesel Soot Collected on Filter: Benefits of Laser Induced Breakdown Spectroscopy, Plasma Chemistry and Plasma Processing, Vol. 24, No. 1, March 2004
- James H. Vincent. Aerosol Sampling. Number 978-0-470-02725-7. Wiley, 2007

- 223. David Kittelson, Winthrop Watts, and Megan Arnold. Review of diesel particulate matter sampling methods, supplimentary report no. 1. 1998
- David Kittelson and Winthrop Watts. Diesel aerosol sampling methodology - crc e-43. 2002.
- 225. Winthrop Watts. Diesel particulate matter sampling methods: Statistical comparison. 2000.
- Imad Khalek. 2007 diesel particulate measurement research. SwRI 03.10415.
- 227. SE Mischler, AD Bugarski, and JD Noll. Instrumentation for diesel particulate matter emissions research.
- 228. Linda Dorie, Susan Bagley, Peter Woon, David Leddy, John Johnson, Paul Wiczynski, and Jiangang Lu. Collection and characterization of particulate and gaseous-phase hydrocarbons in diesel exhaust modified by ceramic particulate traps. 1987. doi: 10.4271/870254.
- 229. Westech instruments, http://www.westechinstruments.com, 2013-05-26
- 230. Randy L. Vander Wal, Vicki Bryg Michael D. Hays , X-Ray Photoelectron Spectroscopy XPS Applied to Soot - What It Can Do for You, Deer Conference 2006
- 231. USGS Technical Note, 'What is ICP-MS?... and more importantly, what can it do?'; <u>http://minerals.cr.usgs.gov/icpms/intro.html</u>, 2013-05-26
- M. I. Szynkowska, A. Pawlaczyk, J. Rogowski, K. Bawolak, T. Paryjczak, Characterization of Chosen Products of Combustion Processes, Polish J. of Environ. Stud. Vol. 17, No. 3 (2008), 411-419
- 233. A.D.H. Claguea, J.B. Donnetb, T.K. Wangb, J.C.M. Peng, A comparison of diesel engine soot with carbon black, Carbon 37 (1999) 1553–1565
- 234. Andrea Ulrich, Adrian Wichser, Analysis of additive metals in fuel and emission aerosols of diesel vehicles with and without particle traps, Journal Chem (2003) 377 : 71–81 DOI 10.1007/s00216-003-2054-3
- 235. Wiki Article: Inductively coupled plasma mass spectrometry: <u>http://en.wikipedia.org/wiki/Inductively coupled plasma mass spectrometry,</u> <u>2013-05-26</u>
- 236. G. Thiele, M. Poston, R. Brown, A Case Study in Sizing Nanoparticles, Micromeritics Analytical Services Technical Note, <u>http://www.micromeritics.com/repository/files/a_case_study_in_sizing_nano_particles.pdf</u>, 2013-05-26

- 237. Roger Mueller, Rainer Jossen, Hendrik K. Kammler, and Sotiris E. Pratsinis, Growth of Zirconia Particles Made by Flame Spray Pyrolysis, AIChE Journal, December 2004, Vol. 50, No. 12
- 238. An Introduction To Calculation Methods For Surface Area And Pore Size From Gas Sorption Data, Quantachrome Instruments Technical Note, <u>http://www.atomikateknik.com/pdf/Porous_Materials_Primer_gas_sorption_ca</u> <u>lculation_methods.pdf, 2013-05-26</u>
- M. Y. Choi, G. W. Mulholland, A. Hamins And T. Kashiwagi, Comparisons of the Soot Volume Fraction Using Gravimetric and Light Extinction Techniques, Combustion and Flame 102: 161-169 (1995)
- Volume and Density Determinations for Particle Technologists, Technical Note, Micromeritics Instrument Corp. 2001, http://www.particletesting.com/docs/density_determinations.pdf, 2013-05-26
- 241. R.B.Bird, W.E. Stewart, E.N. Lightfoot, Transport Phenomena, Wiley New York, 1960, P190, Eq6.4-6 (Spherical particles assumption)
- 242. Dr. H.-P. Boehm, Dr. E. Diehl, W. Heck, R. Sappok, Angew. Surface Oxides of Carbon, Chem inlernat. Edit. Vol. 3 (1964) No. 10
- 243. Sarah L. Goertzen, Kim D. Theriault, Alicia M. Oickle, Anthony C.
 Tarasuk, Heather A. Andreas, Standardization of the Boehm titration. Part I.
 CO₂ expulsion and endpoint determination, Carbon 48 (2010) 1252–1261
- Alicia M. Oickle, Sarah L. Goertzen, Katelyn R. Hopper, Yasmin O.
 Abdalla, Heather A. Andreas, Standardization of the Boehm titration: Part II.
 Method of agitation, effect of filtering and dilute titrant, Carbon 48 (2010)
 3313–3322
- Hung-Lung Chiang, C.P. Huang, P.C. Chiang, The surface characteristics of activated carbon as affected by ozone and alkaline treatment, Chemosphere 47 (2002) 257–265
- 246. US EPA, Method 610—Polynuclear Aromatic Hydrocarbons, Appendix A To Part 136 Methods For Organic Chemical Analysis Of Municipal And Industrial Wastewater
- J. Swarin and A. M. Mims, Applications of Integral and Derivative Thermogravimetry to the Analysis of Rubber Formulations, Rubber. Chem. Tech., 47 (5), 1974.
- Peter W. Albers , Harald Klein, Egbert S. Lox , Klaus Seibold , INS-, SIMS- and XPS-investigations of diesel engine exhaust particles, Phys. Chem. Chem. Phys., 2000,2, 1051-1058

- 249. Steffen Antusch, Martin Dienwiebel, Eberhard Nold Peter Albers, Ulrich Spicher, Matthias Scherg, On the tribochemical action of engine soot, Wear, Volume 269, Issues 1–2, 20 May 2010, Pages 1–12
- S.G. Chang, T. Novakov, Formation of pollution particulate nitrogen compounds by NO-soot and NH3-soot gas-particle surface reactions, Atmospheric Environment (1967), Volume 9, Issue 5, May 1975, Pages 495– 504
- 251. Salvatore Collura, Nouari Chaoui, Alain Koch, Jean Victor Weber, On the composition of the soluble organic fraction and its influence during the combustion of exhaust diesel soot, Letters to the Editor / Carbon 40 (2002) 2263 –2284
- U. Kirchner, R. Vogta, C. Natzeck, J. Goschnick, Single particle MS, SNMS, SIMS, XPS, and FTIR, spectroscopic analysis of soot particles during the AIDA campaign Aerosol Science 34 (2003) 1323–1346
- 253. Jian Liu , Zhen Zhao, Chunming Xu, Aijun Duan and Guiyuan Jiang, Comparative Study on Physicochemical Properties and Combustion Behaviours of Diesel Particulates and Model Soot
- Muller et al., Diesel Engine Exhaust Emission: Oxidative Behavior and Microstructure of Black Smoke Soot Particulate, Environ. Sci. Technol. 2006, 40, 1231-1236
- 255. Muller et al., Bulk and surface structural investigations of diesel engine soot and carbon black, Physical Chemistry Chemical Physics
- 256. Mihir Patel, Cristy Leonor Azanza Ricardo, Paolo Scardi, Pranesh B.Aswath, Morphology, structure and chemistry of extracted diesel soot—Part I: Transmission electron microscopy, Raman spectroscopy, X-ray photoelectron spectroscopy and synchrotron X-ray diffraction study, , Tribology International 52 (2012) 29–39
- 257. R. Rausa, C. Carati and M. Vanelli, G. Ponti, Synthesis of Diesel-Like Soots. Influence of the Operative Parameters on the Chemico-Physical and Morphological Characteristics, International Fall Fuels and Lubricants Meeting and Exposition San Francisco, California October 19-22, 1998
- 258. M.P. Ruiz, R. Guzmán de Villoriab, A. Milleraa, M.U. Alzuetaa, R. Bilbao Influence of the temperature on the properties of the soot formed from C2H2 pyrolysis, Chemical Engineering Journal, Volume 127, Issues 1–3, 1 March 2007, Pages 1–9
- 259. G. C. Smith, A. B. Hopwood, K. J. Titchener, Microcharacterization of heavy-duty diesel engine piston deposits, Surface and Interface Analysis

Special Issue: Festschrift in celebration of the 60th birthday of Dr Martin P. Seah, Volume 33, Issue 3, pages 259–268, March 2002

- Randy L. Vander Wal, Vicky M. Bryg, and Michael D. Hays, XPS Analysis of Combustion Aerosols for Chemical Composition, Surface Chemistry, and Carbon Chemical State, Anal. Chem., 2011, 83 (6), pp 1924–1930
- H. Saathoff, O. Moehler, U. Schurath, S. Kamm, B. Dippel, D. Mihelcic, The AIDA soot aerosol characterisation campaign 1999, Aerosol Science 34 (2003) 1277–1296
- Agus Setiabudi, Michiel Makkee, Jacob A. Moulijn, The role of NO₂ and O₂ in the accelerated combustion of soot in diesel exhaust gases, Applied Catalysis B: Environmental 50 (2004) 185–194
- 263. Jussi Lyyranen, Jorma Jokiniemi, Esko Kauppinen, The effect of Mgbased additive on aerosol characteristics in medium-speed diesel engines operating with residual fuel oils, Aerosol Science 33 (2002) 967–981
- 264. Okada et al., Measurement of Trace Metal Composition in Diesel Engine Particulate and its Potential for Determining Oil Consumption, 2003
- 265. R. Vlasankova, V. Otruba, J. Bendl, M. Fisera, V. Kanicky, Preconcentration of platinum group metals on modified silicagel and their determination by inductively coupled plasma atomic emission spectrometry and inductively coupled plasma mass spectrometry in airborne particulates, Talanta 48 (1999) 839–846
- 266. Jitendra N. Gangwara, Tarun Guptab, Avinash K. Agarwal, Composition and comparative toxicity of particulate matter emitted from a diesel and biodiesel fuelled CRDI engine, Atmospheric Environment 46, 2012
- 267. Minoru Arai, Impact of Changes in Fuel Properties and Lubrication Oil on Particulate Emissions and SOF, International Congress & Exposition Detroit, Michigan February 24-28,1992
- El Ghzaoui, M. Lindheimer, A. Lindheimer, S. Lagerge, S. Partyka, Surface characterization of diesel engine soot inferred from physico-chemical methods, Colloids and Surfaces A: Physicochem. Eng. Aspects 233 (2004) 79–86
- Daniel G. Aubin and Jonathan P. Abbatt, Adsorption of Gas-Phase Nitric Acid to n-Hexane Soot: Thermodynamics and Mechanism, J. Phys. Chem. A, 2003, 107 (50), pp 11030–11037
- 270. Baoliang Chen, Wenhai Huang, Effects of compositional heterogeneity and nanoporosity of raw and treated biomass-generated soot on adsorption

and absorption of organic contaminants, Environmental Pollution, Volume 159, Issue 2, February 2011, Pages 550–556

- Milena B Fernandes, Jan O Skjemstad, Bruce B Johnson, John D Wells, Peter Brooks, Characterization of carbonaceous combustion residues. I. Morphological, elemental and spectroscopic features
- Stephen J. Harris and Anita M. Weiner, Chemical Kinetics Of Soot Particle Growth, Annual Review of Physical Chemistry, Vol. 36: 31-52ts 233 (2004) 79–86
- Nicholas P Levitt, Renyi Zhang, Huaxin Xue and Jianmin Chen,.
 Heterogeneous Chemistry of Organic Acids on Soot Surfaces, J. Phys.
 Chem. A 2007, 111, 4804-4814
- 274. Nicholas P Levitt, Heterogeneous organic acid uptake on soot surfaces, PhD Thesis
- 275. O. B. Popovicheva and N. M. Persiantseva, B. V. Kuznetsov, T. A. Rakhmanova, and N. K. Shonija, J. Suzanne and D. Ferry, Microstructure and Water Adsorbability of Aircraft Combustor Soots and Kerosene Flame Soots: Toward an Aircraft-Generated Soot Laboratory Surrogate, J. Phys. Chem. A 2003, 107, 10046-10054
- 276. F Pott, Dieselmotorabgas-Tierexperimentelle Ergebnissezur Risikoabschätzung, Krebserzeugende Stoffe in der Umwelt
- Karl J. Rockne, Gary L. Taghon, David S. Kosson, Pore structure of soot deposits from several combustion sources, Chemosphere 41 (2000) 1125-1135
- S.A.M. Silvaa, J. Pereza, R.M. Torresia, C.A. Luengob, E.A. Ticianellia, Surface and electrochemical investigations of a fullerene soot, Electrochimica Acta 44 (1999) 3565±3574
- Karsten Wegner, Wendelin J Stark, Sotiris E Pratsinis, Flame-nozzle synthesis of nanoparticles with closely controlled size, morphology and crystallinity, Materials Letters. Volume 55, Issue 5, August 2002, Pages 318– 321
- Tue Johannessen, Sotiris E. Pratsinis, Hans Livbjerg, Computational Fluid-particle dynamics for the Flame synthesis of alumina particles, Chemical Engineering Science 55 (2000) 177-191
- 281. Johan C. Groen, Louk A.A. Peffer a, Javier Perez-Ramırez, Pore size determination in modified micro and mesoporous materials. Pitfalls and limitations in gas adsorption data analysis, Microporous and Mesoporous Materials 60 (2003) 1–17

- Peter H. McMurry, Xin Wang, Kihong Park, and Kensei Ehara, The Relationship between Mass and Mobility for Atmospheric Particles: A New Technique for Measuring Particle Density, Aerosol Science and Technology 36: 227–238 (2002)
- 284. Gottfried Hänel and Jürg Thudium, Mean bulk densities of samples of dry atmospheric aerosol particles: A summary of measured data, Pure And Applied Geophysics, Volume 115, Number 4 (1977), 799-803
- 285. Stephen J. Harris, M.Matti Maricq, Signature size distributions for diesel and gasoline engine exhaust particulate matter, Journal of Aerosol Science, Volume 32, Issue 6, June 2001, Pages 749–764
- M.V. Lopez-Ramona, F. Stoecklib, C. Moreno-Castillaa, F. Carrasco-Marin, On the characterization of acidic and basic surface sites on carbons by various techniques, Carbon 37 (1999) 1215–1221
- 287. Yern Seung Kim, Seung Jae Yang, Hyeong Jun Lim, Taehoon Kim, Kunsil Lee, Chong Rae Park, Effects of carbon dioxide and acidic carbon compounds on the analysis of Boehm titration curves, CARBON 50 (2012) 1510–1516
- 288. Yern Seung Kim, Seung Jae Yang, Hyeong Jun Lim, Taehoon Kim, Chong Rae Park, A simple method for determining the neutralization point in Boehm titration regardless of the CO₂ effect, CARBON 50 (2012) 3315–3323
- Harald Muckenhuber, Hinrich Grothe, The heterogeneous reaction between soot and NO₂ at elevated temperature, Carbon, Volume 44, Issue 3, March 2006, Pages 546–559
- B. Manoj, S. Sreelaksmi, Anu. N. Mohan, A.G. Kunjomana, Characterization of Diesel Soot from the Combustion in Engine by X-ray and Spectroscopic techniques
- 291. O. B. Popovitcheva, N. M. Persiantseva, M. E. Trukhin, G. B. Rulev, N. K. Shonija, Yu. Ya. Buriko, A. M. Starik, B. Demirdjian, D. Ferryc and J. Suzanne, Microstructure and Water Adsorbability of Aircraft Combustor Soots and Kerosene Flame, J. Phys. Chem. A 2003, 107, 10046-10054
- 292. Barbella, R., Bertoli, C., Ciajolo, A., D'Anna, A., In-Cylinder Sampling of High Molecular weight Hydrocarbons From a D.I. Light Duty Diesel Engine, SAE Technical Paper 890437, 1989

- 293. Barbella, R., Bertoli, C., Ciajolo, A., D'Anna, A., In-Cylinder Sampling of High Molecular weight Hydrocarbons From a D.I. Light Duty Diesel Engine, SAE Technical Paper 890437, 1989
- R. Barbella, A. Ciajolo, A. D'Anna, Effect of fuel aromaticity on diesel emissions, Combustion and Flame, Volume 77, Issues 3–4, September 1989, Pages 267–277
- 295. Ciajolo , B. Apicella ,R. Barbella ,A. Tregrossi ,F. Beretta , and C. Allouis, Depletion of Fuel Aromatic Components and Formation of Aromatic Species in a Spray Flame as Characterized by Fluorescence Spectroscopy, Energy Fuels, 2001, 15 (4), pp 987–995
- 296. Yuan-Chung Lin, b, Wen-Jhy Leea, Hsiao-Chung Houa, PAH emissions and energy efficiency of palm-biodiesel blends fueled on diesel generator, Atmospheric Environment, Volume 40, Issue 21, July 2006, Pages 3930– 3940
- 297. K. Lombaert, L. Le Moyne, J. Tardieu De Maleissye, J. Amouroux, Experimental validation of PAH growth during combustion process by added isotopic PAH in fuel, Proceeding of the European Combustion Meeting 2003
- 298. Thomas R. Henderson, James D. Sun, Albert P. LI, Ray L. Hanson, Willlam E. Bechtold, 1. Michael Harvey, Jeffry Shabanowitz, and Donald F. Hunt, GC/MS and MS/MS Studies of Diesel Exhaust Mutagenicity and Emissions from Chemically Defined Fuels, Environ. Sci. Technol. 1084, 18, 428-434
- O. B. Popovicheva, E. D. Kireeva, N. K. Shonija, and T. D. Khokhlova, Water Interaction with Laboratory-Simulated Fossil Fuel Combustion Particles, J. Phys. Chem. A 2009, 113, 10503–10511
- 300. Hsi-Hsien Yang, Wen-Jhy Lee, Hsiao-Hsuan Mi, and Chih-Ho Won, PAH Emissions Influenced By Mn-Based Additive And Turbocharging From A Heavy-Duty Diesel Engine, Environment International, Vol. 24, No. 4, pp. 389-403, 1998
- 301. Sandro Brandenbergera, Martin Mohra, Koni Grobb, Hans Peter Neukom, Contribution of unburned lubricating oil and diesel fuel to particulate emission from passenger cars, Atmospheric Environment, Volume 39, Issue 37, December 2005, Pages 6985–6994
- 302. R. Lemaire, A. Faccinetto, E. Therssen, M. Ziskind, C. Focsa, P. Desgroux, Experimental comparison of soot formation in turbulent flames of Diesel and surrogate Diesel fuels, Proceedings of the Combustion Institute 32 (2009) 737–744

- 303. C. Allouisa, B. Apicellaa, R. Barbellab, F. Berettab, A. Tregrossib & A. Ciajolob, Soot and PAH Formation in Rapeseed Oil Spray Combustion, Clean Air, Volume 3, Issue 1, 2002
- 304. Zuliang Jin' and Stephen M. Rappaport, Microbore Liquid Chromatography with Electrochemical Detection for Determination of Nitro-Substituted Polynuclear Aromatic Hydrocarbons in Diesel Soot Analytical Chemistry, Vol. 55, No. 11, September 1983 1779
- 305. Khalid Al-Qurashi, André L. Boehman, Impact of exhaust gas recirculation (EGR) on the oxidative reactivity of diesel engine soot, Combustion and Flame 155 (2008) 675–695
- 306. Andre´ L. Boehman, Juhun Song, and Mahabubul Alam, Impact of Biodiesel Blending on Diesel Soot and the Regeneration of Particulate Filters, Energy & Fuels 2005, 19, 1857-1864
- 307. A. Brauna, N. Shah, F.E. Huggins, K.E. Kelly, A. Sarofim, C. Jacobsen, S. Wirick, H. Francis, J. Ilavsky, G.E. Thomas, G.P. Huffman, X-ray scattering and spectroscopy studies on diesel soot from oxygenated fuel under various engine load conditions, Carbon, Volume 43, Issue 12, October 2005, Pages 2588–2599
- Ki-Hyouk Choi and Isao Mochida, Characterization Of Particulate Matter Emitted From Diesel Engine, Fuel Chemistry Division Preprints 2002, 47(2), 776
- Christine Esangbedo, Andre´ L. Boehman, Joseph M. Perez, Characteristics of diesel engine soot that lead to excessive oil thickening, Tribology International 47 (2012) 194–203
- Howard L. Fang, Michael J. Lance, Influence of Soot Surface Changes on DPF Regeneration, SAE 2004-01-3043
- J. Rodríguez-Fernandez, F. Oliva, and R. A. Vazquez, Characterization of the Diesel Soot Oxidation Process through an Optimized Thermogravimetric Method, Energy Fuels 2011, 25, 2039–2048
- 312. Songtam Laosuwan, Preechar Karin, and Chinda Charoenphonphanich, Katsunori Hanamura, Thermo-gravimetric Analysis of Biodiesel Diffusion Flame's Particulate Matter, The Second TSME International Conference on Mechanical Engineering, 19-21 October, 2011, Krabi
- Kwang Chul Oh, Chun Beom Lee, Eui Ju Lee, Characteristics of soot particles formed by diesel pyrolysis, Journal of Analytical and Applied Pyrolysis 92 (2011) 456–462

- 314. Paul Lindsey Rounce, Engine Performance And Particulate Matter Speciation For Compression Ignition Engines Powered By A Range Of Fossil And Biofuels, University of Birmingham, PhD Thesis
- 315. P. Rounce, A. Tsolakis, A.P.E. York, Speciation of particulate matter and hydrocarbon emissions from biodiesel combustion and its reduction by aftertreatment, Fuel, Volume 96, June 2012, Pages 90–99
- P. R. Ryason, M. J. Hillyer, and T. P. Hansen, Infrared Absorptivities of Several Diesel Engine Soots; Application to the Analysis of Soot in Used Engine Oils, SAE 942030
- 317. Maurin Salamanca, Fanor Mondragon, Jhon Ramiro Agudelo, Pedro Benjumea, Alexander Santamaria, Variations in the chemical composition and morphology of soot induced by the unsaturation degree of biodiesel and a biodiesel blend, Combustion and Flame 159 (2012) 1100–1108
- 318. Alexander G. Sappok and Victor W. Wong, Impact of Biodiesel on Ash Emissions and Lubricant Properties Affecting Fuel Economy and Engine Wear, Deer Conference 2007
- Juhun Song, Mahabubul Alam and André L. Boehman, Characterization Of Diesel And Biodiesel Soot, Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem. 2004, 49(2),767
- 320. Juhun Song, Mahabubul Alam, Jinguo Wang and André Boehman, Fuel Impacts on Soot Nanostructure and Reactivity, Deer 2005 Conference Presentation
- 321. Juhun Song, Mahabubul Alam and André Boehman, Effect of Alternative Fuels on Soot Properties and Regeneration of Diesel Particulate Filters, Deer 2005 Conference Presentation
- 322. G.A. Stratakis, A.M. Stamatelos, Thermogravimetric analysis of soot emitted by a modern diesel engine run on catalyst-doped fuel, Combustion and Flame 132 (2003) 157–16
- 323. G A Stratakis, G S Konstantas and A M Stamatelos, Experimental investigation of the role of soot volatile organic fraction in the regeneration of diesel filters, Proc. Instn Mech. Engrs Vol. 217 Part D: J. Automobile Engineering
- 324. Aaron Williams, Robert L. McCormick, R. Robert Hayes, John Ireland, Howard L. Fang, Effect of Biodiesel Blends on Diesel Particulate Filter Performance, Presented at the Powertrain and Fluid Systems, Conference and Exhibition, October 2006, Toronto, Canada

- 325. Kent Froelund, Leandro A. Menezes, Hal R. Johnson and Wolfgang O. Rein, Real-Time Transient and Steady-State Measurement of Oil Consumption for Several Production SI-Engines, SAE Technical Paper 2001-01-1902
- 326. Magin Lapuerta, Octavio Armas, Jose Rodriguez-Fernadez, Effect of biodiesel fuels on diesel engine emissions, Progress in Energy and Combustion Science 34 (2008) 198–223
- 327. Jana Moldanova, Erik Fridell, Olga Popovicheva, Benjamin Demirdjian, Victoria Tishkova, Alessandro Faccinetto, Cristian Focsa, Characterisation of particulate matter and gaseous emissions from a large ship diesel engine, Atmospheric Environment 43 (2009) 2632–2641
- 328. Bruno Argueyrolles, Stephan Dehoux, Patrick Gastaldi Lysiane Grosjean, Franck Levy, Alexandre Michel, Daniel Passerel, Influence of injector nozzle design and cavitation on coking phenomenon, SAE Technical Paper 2007-01-1896, 2007
- 329. Angela Leedham, Rinaldo Caprott, Olaf Graupner, Thomas Klaua, Impact of Fuel Additives on Diesel Injector Deposits, SAE Technical Paper 2004-01-2935, 2004
- Michael C. Mendoza, Qin Zhang, Alan C. Hanse, John F. Reid, Injector Nozzle Coking With Oxygenated Diesel, SAE Technical Paper 2001-01-2016, 2001
- Carwood Motor Units Ltd of Birmingham, <u>http://www.carwood.co.uk</u>, 2013-05-26
- 332. Masato Ikemoto, Kazuhiro Omae, Kyoko Nakai, Reiko Ueda, Nobuhisa Kake- hashi, and Kazuo Sunami. Injection nozzle coking mechanism in common-rail diesel engine. 2011. doi: 10.4271/2011-01-1818. 48
- 333. Jens Tang, Stefan Pischinger, Matthias Lamping, Thomas Körfer, Marek Tatur, and Dean Tomazic. Coking phenomena in nozzle orifices of DI-diesel engines. SAE Int. J. Fuels Lubr., 2(1):259–272, 2009. doi: 10.4271/2009-01-0837. 49
- Gerhard Lepperhoff and Michael Houben. Mechanisms of deposit formation in internal combustion engines and heat exchangers. 1993. doi: 10.4271/931032
- 335. Avinash Agarwal, Dhananjay Srivastava, Gayatri Dwivedi, Gaurav Kawatra, Prem Kumar, OP Bhardwaj, Mathew Abraham, and Arun Jaura, Field trials of biodiesel (B100) and diesel fuelled common rail direct injection

euro-iii compliant sports utility vehicles in Indian conditions. 2008. doi: 10.4271/2008-28-0077

- Ejaz M. Shahid, Younis Jamal, A review of biodiesel as vehicular fuel, Renewable and Sustainable Energy Reviews 12 (2008) 2484–2494
- 337. Fangrui Maa, Milford A. Hanna, Biodiesel production: a review, Bioresource Technology 70 (1999)
- 338. Ayhan Demirbas, Biodiesel fuels from vegetable oils via catalytic and noncatalytic supercritical alcohol transesterifications and other methods: a survey, Energy Conversion and Management 44 (2003) 2093–2109
- 339. Ayhan Demirbas, Biodiesel production from vegetable oils via catalytic and non-catalytic supercritical methanol transesterification methods, Progress in Energy and Combustion Science 31 (2005) 466–487
- 340. Wards Auto World Engine Update 1999, personal printed copy
- 341. UK Government VCA Website Car and Fuel consumption downloads page, May 2004 data (Euro III and Euro IV), <u>http://carfueldata.direct.gov.uk/downloads/default.aspx</u>, 2013-05-26
- 342. UK Government VCA Website Car and Fuel consumption downloads page, August 2011 data (Euro IV, Euro V, Euro VI), <u>http://carfueldata.direct.gov.uk/downloads/default.aspx</u>, 2013-05-26
- Wards Engine & Vehicle Technology Update & <u>www.wardsauto.com</u>,
 2011 Light Vehicle Engines Availability and Specification
- Heywood J.B., Internal Combustion Engine Fundamentals. *McGraw-Hill* International Editions. 1988. ISBN 0-07-100499-8, pp. 134
- Lowell, S., Shields, J.E., Thomas, M.A., Thommes, M., Characterisation of Porous Solids and Powers: Surface Area, Pore Size and Density. *Springer*, 2004. ISBN-10: 1402023022, pp. 111-112
Bibliography

- Challen, B., Baranescu, R., Diesel Engine Reference Book, 2nd Edition. SAE international. 1999 ISBN 0-7680-0403-9
- Cummins, L., Internal Fire The Internal Combustion Engine, 1673-1900, 3rd Edition. *Carnot Pres.* 2000 ISBN 0-917308-05-0
- Cummins, L., Diesel's Engine, Volume One From Conception to 1918. Carnot Pres. 1993 ISBN 0-917308-03-4
- Handbook. Ready Reference for Lubricant and Fuel Performance. The Lubrizol Corporation. 1998
- Haycock R.F., Hillier J.E. Automotive Lubricants Reference Book, 2nd Edition. SAE International. 2004 ISBN 0-7680-1251-1
- Heisler, H., Vehicle and Engine Technology, 2nd Edition. Arnold. 1999 ISBN 0-340-69186-7
- > Heisler, H., Advanced Engine Technology. Arnold. 1995 ISBN 0-340-56822-4
- Heywood J.B., Internal Combustion Engine Fundamentals. *McGraw-Hill* International Editions. 1988 ISBN 0-07-100499-8
- Hsu B.D., Practical Diesel-Engine Combustion Analysis. SAE International. 2002 ISBN 0-7680-0914-6
- Mang T., Dresel W., Lubricants and Lubrication, 2nd Edition. Wiley-VCH. 2007 ISBN 978-3-527-31497-3
- Mortier R.M., Orszulik S.T. Chemistry and Technology of Lubricants, 2nd Edition. *Blackie Academic & Professional*. 1997 ISBN 0-7514-0246-X
- Philips, E.M., Pugh, D.S., How to Get a PhD. Third Edition Open University Pres. 2003 ISBN 0-335-20551-X
- Plint M., Martyr A. Engine Testing Theory and Practice, 2nd Edition. Butterworth-Heinemann. 2004 ISBN 0-7506-4021-9
- Robert Bosch GmbH. Automotive Handbook, 4th Edition. Robert Bosch GmbH. 1996 ISBN 1-56091-918-3
- Robert Bosch GmbH. Diesel-Engine Management, 4th Edition. Wiley. 2005 ISBN 0-470-02689-8
- Rogers, C., Automotive Diesel Engine Service Guide. Haynes. 1997 ISBN 1-85960-286-X
- Vincent, J.H., Aerosol Sampling: Science, Standards, Instrumentation and Applications. *Wiley*. 2007 ISBN 978-0-470-02725-7

- Willeke, K., Baron, P.A., Aerosol Measurement: Principles, Techniques and Applications. Van Nostrand Reinhold, New York. 1993 ISBN: 978-0-470-38741-2
- Wight, G.D., Fundamentals of Aerosol Sampling. Lewis Publishers, CRC Press. 1994
- Zhao H., Ladammatos N. Engine Combustion Instrumentation and Diagnostics. SAE International. 2001 ISBN 0-7680-0665-1



<u>Appendix 1</u>: Experimental Fuel Property Summary

Property	Unit	EN590	PC9	B100 (19.5:1)	B100 (16.5:1)
Density @ 15 deg C	kg/m3	827.75	845.1	883.2	880.4
Viscosity, kinematics @ 40 deg C	mm2/s	2.1905	2.5	4.488	4.72
Flashpoint	deg C	74.75	63.3	>171	178
Cloudpoint	deg C	-26	-12.2	-	-
Cold Filter Plugging Point	deg C	-27	-23.3	-14	0
Cetane Index		51.15	47.1	-	-
Cetane Number		54.65	46	58	55
Copper Corrosion (3hrs @50 deg C)	scale	1	1A	-	1
Oxidation Stability	g/m3	10	-	9.4	6.62
CCR (on 10% residue)	wt %	0.05	-	-	-
Total Aromatics	vol %	19.25	32.6	-	-
Ester Content	wt %	-	-	97.8	97.8
Linolenic acid methylester content C18:3	wt %			8	2.87
Olefins	vol %	-	5.6	-	-
Saturates	vol %	-	61.8	-	-
pH-Value	-	6.85	-	-	-
Neutralisation Number (TAN)	mg KOH/g	0.07	0.007	0.1	1.27
Lubricity @ 60 deg C	um	417.5	-	-	-
Conductivity @ 2 deg C	pS/min	550	-	-	-
Distillation @ 250 deg C	vol %	53.05	-	-	-
Distillation @ 310 deg C	vol %	96.8	-	-	-
Carbon Residue	wt %	0.01	-	< 0.3	0.1
Hydrogen	wt %	-	13.1	-	-
Carbon	wt %	-	86.9	-	-
Net Heat of Combustion	MJ/kg	-	42.9	-	-
Sulphur	ppm	5.5	497	<10	4.5
Chlorine	ppm	3	-	-	-
Water	ppm	17.5	-	222	395
Particulate Matter	ppm	3.5	2.2	1	3
Ash	wt %	0.001	-	< 0.01	0.002
Methanol	wt %	-	-	0.01	0.01
Na + K	ppm	-	-	0.5	2.25
Ca + Mg	ppm	-	-	<1	1.3
Р	ppm	-	-	<1	0.5
Monoglyceride	wt %	-	-	0.63	0.31
Diglyceride	wt %	-	-	0.17	0.01
Triglyceride	wt %	-	-	0.11	0.01
Free Glyceride	wt %	-	-	0.005	0.02
Total Glyceride	wt %	-	-	0.19	0.1

Table A1.1: Experimental Fuel Property Summary



Figure A1.1: B100 Fuel Batch Elemental Contaminate Comparison

<u>Appendix 2</u>: Experimental Lubricant Property Summary

Element	(ppm)	(% of total)
Ca	1181	30.7
Cu	0	0.0
Fe	0	0.0
Mg	4	0.1
Mn	0	0.0
Na	3	0.1
Р	508	13.2
S	1614	41.9
Si	5	0.1
Zn	533	13.8
AI	3	0.1
Cd	0	0.0

Table A2.1: Lubricant Elemental Composition Summary¹⁸

¹⁸ Due to confidentiality; the listed elements are limited to those which were also investigated for soot.

<u>Appendix 3</u>: Production Engine Compression Ratio Survey

Engine Description	Compression Ratio
Alfa Romeo 155 1.9	19.2
AM General Corp Hummer	20.2
Audi A6 1.9	19.5
Audi A8	19.5
BMW 318tds 1.7	22
BMW 325td 2.5	22.1
BMW 325tds 2.5	22.2
Citroen Saxo 1.5	23
Citroen Xanti 1.9	23
Citroen Xanti 1.9	21.8
Citroen Xm 2.1	21.5
Citroen Xm 2.4	20
Daihatsu Hijet Van 1.2	23
Daihatsu Rocky 2.8	21.2
Daimlerchrysler 3.0 E300	22
Daimierchrysler 6.6 V8 120BHP	20.9
Daimierchrysler 6.6 V8 215BHP	19.5
Daimierchrysier Grand Cherokee 3.1	21
Daimierchrysier Ram 5.9	10.2
Fiat Ducato 1.9	19.2
Fiat Ducato 2.5 Eist Marango 1.0	22.5
Fiat Punto Van 1 7	20.7
Fiat Punto Van 1.7	19
Fiat Scudo 1.9	23
Fiat Scudo 1.9	21.8
Fiat Siena 1.7	20.3
Fiat Uno 1.7	20.5
Ford F-1000 2.5	19.5
Ford F-1000 4.3	15.9
Ford Fiesta 1.8	21.5
Ford Focus 1.8	19.4
Ford Galaxy 1.9	19.5
Ford Super Duty F-Series V8 7.3	17.5
General Motors Astra 1.7	22
General Motors GMT800 6.5	19.5
General Motors P-truck 6.5	20.9
General Motors Vectra 2.0	18.5
Honda Accord 2.0	19.5
Kia Sportage 2.2	22
Lancia Delta 1.9	19.2
Lancia K 2.4	18.5 21 F
Ldiilid Z Z.U Mazda Brawow 2 0	21.5
Mazda Brawlly 5.0 Mazda Canella 2.2	21.0
Mazda Cronos 2.2	21.1
Mazda Eamilia 1.7	21.7
Mazda Titan 2.2	22.9
Mazda Titan 3.0	21
Mazda Titan 3.5	17.5
Mazda Titan 3.5	17
Mazda Titan 4.0	18
Mazda Titan 4.6	18
Mercedes A 170	19.5
Mercedes C 200 CDI	19
Mercedes C 250	22
Mercedes E 290	19.5
Mercedes E 300	22
Mercedes V 230	22
Mitsubishi Delica 2.5	21

Table A3.1: 1999 Engine Compression Ratio Data (part 1) [340]

Engine Description	Compression Ratio
Mitsubishi Jeep 2.7	21.5
Mitsubishi Libero 2.0	22.4
Mitsubishi Pajero 2.8	21
Nissan Caravan 2.7	22.2
Nissan Datsun 3.2	21.9
Nissan Largo 2.0	22.2
Nissan Laurel 2.8	22.4
Nissan Mistral 2.7	22.3
Nissan Regulus 3.2	22
Nissan Safari 2.8	21.8
Nissan Safari Wagon 4.2	22.8
Nissan Terrano 3.2	22
Peugeot 106 1.5	23
Peugeot 205 D Turbo 1.8	22
Peugeot 306 1.9	23
Peugeot 306 1.9	21.8
Peugeot 406 2.1	21.5
Peugeot Boxer 2.4	24
Peugeot Boxer 2.4	22
Renault Clio 1.9	21.5
Renault Laguna 2.2	23
Renault Laguna 2.2	22
Rover Discovery 2.5	19.5
Rover Range Rover	22
Rover Rover 100 1.5	23
Rover Rover 200 2.0	19.5
Rover Rover 800	22
Seat Cordoba 1.9	22.5
Seat Inca 1.7	19.5
Seat Toledo 1.9	22.5
Skoda Octavia 1.9	19.5
Toyota 1.5	22
Toyota Coaster 3.4	20
Toyota Corolla 2.0	23
Toyota Crown 2.4	21
Toyota Dyna 4.1	18.4
Toyota Hilux 2.8	22.2
Toyota Land Cruiser 3.0	21.2
Toyota Land Cruiser 4.2	22.7
Toyota Land Cruiser 4.2	18.6
Toyota Lucida 2.2	22.6
Toyota Mega Cruiser 4.1	17.8
Volvo \$40 1.9	20.5
Volvo 580 2.5	20.5
VW Lupo 1.7	19.5
VW Passat 1.9	22.5
VW Passat 2.5	19.5
V W POIO 1.9	22.5
Average:	20.9

Table A3.2: 1999 Engine Compression Ratio Data (part 2) [340]

Engine Description	Compression Ratio	
BMW 1 series 118d	17	
BMW 1 series 120d	17	
BMW 3 series 320d	17	
BMW 5 series 525d	17.5	
BMW 5 series 530d	17	
Chevrolet Silverado	17.5	
Chrysler Jeep Cherokee 2.8	17.5	
Citroen C3 1.4 Hdi	18	
Citroen C5 2.0 HDi (110 bhp)	17.6	
Dodge Ram	17.2	
Ford F350	18	
Ford Fiesta 1.4 TDCi	18	
Ford Focus 1.8 TDCi (115bhp)	18.5	
Ford Mondeo 2.0 TDCi (115 ps)	19.5	
Honda Accord 2.2 i-CTDi	16.7	
Hummer H1 6.5 V8	20.2	
Hyundi Matiz 1.5 TD	19	
Mazda 2.0 TD (121 ps)	18.3	
Mercedes-Benz C-Class C200 Cdi	18	
Mercedes-Benz C-Class C220 Cdi	18	
Mercedes-Benz E-Class E320 Cdi	18	
Peugeot 1.4 Hdi	17.9	
Peugeot 2.0 HDi (136 bhp)	18	
Renault 1.5 dci	18.8	
Renault 1.9 dci	18.3	
Renault 2.2 dci	18	
SAAB 9-3 1.9 TID (16 valve)	15.5	
SAAB 9-3 1.9 TID (8 valve)	18.1	
Toyota Avensis 2.0 D4-D	17.8	
Toyota Landcruiser 3.0 D4-D	18.4	
Toyota Yaris 1.4 D4-D	18.5	
Vauxhall 1.3 CDTi	18	
Vauxhall 1.7 CDTi	18.4	
Vauxhall 1.9 CDTi	17.5	
Volvo 2.0 D	18.5	
VW Group 1.9 TDI	19.5	
VW Group 2.0 TDI	19.5	
VW Group 2.5 V6	17.8	
VW Group 3.0V6	17	
VW Group Lupo 1.2	19.5	
VW Group 1.9 TDI	18	
VW Group 2.0 TDI	18.5	
Average:	18.0	

 Table A3.3: 2005 Engine Compression Ratio Data [341]

Alfa Romeo Giulietta 2.0 JTDM 16.5 Alfa Romeo MiTo 1.3 ITDM 16.8	
Alfa Romeo MiTo 1.3 ITDM 16.8	
Alfa Romeo MiTo 1.6 JTDM 16.5	
Audi A4 2.7 TDI 190BHP 17	
Audi A4 3.0 V6 TDI 240BHP 16.8	
Audi A7 3.0 TDI Quattro S 16.8	
Audi A8 4.2 TDI Quattro 16.5	
Audi Q7 6.0 TDI V12 16	
BMW Series 1 2.0 116D M Sport 16	
BMW Series 1 2.0 118D Sport 16.5	
BMW Series 1 2.0 120D Sport 16.5	
BMW Series 1 2.0 123D M Sport 16	
BMW Series 3.3.0.330D SE 16.5	
BMW Series 3 3.0 335D M Sport Auto 17	
BIMW Series 5 3.0 530D SE 16.5	
BINIW Series 5 3.0 535D M Sport Auto 16.5	
Chauralat Cruza 2.01T	
Chevelor 6 7 17 3	
Citroon Parlingo 1 6 HDI 75HD 18 5	
Citroop C2 1 4 HDI 70HD 17 0	
Citroen C/1 6 E-HDI 110PS 18	
Citroen C5 2 0 HDI 160HP 17 6	
Citroen DS3 1 6 HDI 90HP 18	
Fiat Bravo 1 6 120BHP 16 5	
Fiat Punto Evo 1.3 75BHP 16.8	
Ford 6.7 16.2	
Ford Fiesta 1.4 TDCI 18.1	
Ford Focus Hatchback 1.6 TDCI 115PS 16	
Ford Focus Hatchback 1.6 TDCI 95PS 16	
Ford Focus Hatchback 2.0 TDCI 115PS 18	
Ford Ka 1.3 TDCI 75PS 17.6	
Ford Mondeo 2.0 TDCI 140PS 18.5	
Ford Mondeo 2.0 TDCI 140PS 18.5	
General Motors 6.6 V8 260BHP 16.8	
General Motors 6.6 V8 397BHP 16	
Honda Accord 2.2 I-DTEC Type S 16.3	
Hyundi i30 1.6 CRDI 90BHP 17.3	
Hyundi i40 Estate 1.7 CRDI 17	
Hyundi ix35 2.0 CRDI 184BHP 16	
Hyundi Santa Fe 2.2 CRDI 196BHP 16	
Jaguar XF 2.2D 15.8	
Jaguar XF 3.0D V6 16	
Kia Rio 1.5 CRDI TX 17.8	
Kia Carens 2.0 CRDI 17.3	
Kia Carnival MPV 2.9 GSE 18	
Kia Sorento 2.2 CRDI 16	
Kia Soul 1.6 TX 17.3	
Kia Sportage 1.7 D 17	
KIA Venga 1.4 CRDI TX ISG 17	
Land Rover Discovery 4 3.0 SDV6 16.1	
Land Rover Freelander 2.2 ED4 15.8	
Land Kover Kange Kover 3.0 IDV6 16	
Land Kover Kange Kover 4.4 IDV8 16.1	
LEXUS IS 2.2 2000 15.8	
IViazua UX-7 Z.2 IVIZK-UU 10.3	
IVIdZUG IVIdZUG3 1.00 SPOTT 10	
IVIAZUA IVIAZUAD Z. ZU IZYBER 10.1	
Mercedes C-Class 2.1 C250 CDI 16.2	

Table A3.4: 2011 Engine Compression Ratio Data (part 1) [342, 343]

Engine Description	Compression Ratio	
Mercedes E-Class 3.0 E350 CDI Blueteo	15.5	
Mercedes GL-Class 4.0 GL 450 CDI	17	
Mercedes Viano 3.0 CDI	18	
Mini 1.6 D	16.5	
Mini 2.0 SD	16.5	
Mini Countryman	18	
Mitsubishi Grandis MPV 2.0 DI-D	18	
Mitsubishi Lancer 1.8 DI-D	14.9	
Mitsubishi Outlander 2.2 DI-D	16.6	
Mitsubishi Pajero 3.2 DI-D	17	
Nissan Juke 1.5 DCI	15.2	
Nissan Murano 2.5 DCI	15	
Nissan Note 1.5 DCI	15.2	
Nissan X-Trail 2.0 DCI 173BHP	15.6	
Opel Antara 2.0 CDTI	17.5	
Opel Astra 1.7 CDTI 125PS	18.4	
Opel Astra 2.0 CDTI 160PS	16.5	
Opel Corsa 1.3 CDTI 75BHP	18	
Opel Meriva 1.7 CDTI 130HP	16.5	
Opel Zafira 1.9 CDTI 120PS	18	
Opel Zafira 1.9 CDTI 150PS	17.5	
Peugeot 207 1.4 HDI 70BHP	17.9	
Peugeot 207 Estate 1.6 HDI 92BHP	18.1	
Peugeot 308 1.6 HDI 112BHP	18	
Peugeot 508 2.0 HDI 163BHP	17.6	
Renault Clio 1.5 DCI 90	17.9	
Renault Laguna 2.0 DCI 175	16	
Renault Laguna III 2.0 DCI 180	16	
Renault Megane 1.5 DCI 110	15.2	
Saab 9-3 1.9 TTID 180BHP	16.5	
Saab 9-5 2.0 TTID 190BHP	16.5	
Subaru Legacy 2.0 TD	16.3	
Suzuki Swift 1.25 DDIS GLX	16.8	
Suzuki SX4 2.0 DDIS	16.5	
Toyota Auris 1.4 D-4D DPF	17.8	
Toyota Avensis 2.0 D-4D DPF 125BHP	15.8	
Toyota Avensis 2.2 D-4D 150BHP	15.7	
Toyota iQ 1.4 D-4D	16.5	
Toyota Landcruiser 3.0 D-4D	17.9	
Toyota Landcruiser 4.5 V8 D-4D	16.8	
Toyota Yaris 1.4 D4-D	17.9	
Volvo C30 1.6 D2 115PS	18.3	
Volvo C30 2.0 D3 150PS	16.5	
Volvo S60 2.0 D3 163PS	16.5	
Volvo S60 2.4 D5 215PS	16.5	
Volvo XC90 2.4 DS 200PS	17.3	
VW Golf 1.6 TDI 105BHP Bluemotion	16.5	
VW Golf 2.0 TDI 140BHP Edition R	16.5	
VW Golf 2.0 TDI GTD	18.5	
VW Polo 1.2 TDI 75BHP Bluemotion	16.5	
VW Polo 1 6 TDI DSG 90 RHP	16.5	
VW Touareg 3 0 V6 Blue motion	16.8	
	16.8	

Table A3.5: 2011 Engine Compression Ratio Data (part 2) [342, 343]

<u>Appendix 4</u>: Steady-State Speed-Torque Operating Points

Reference	Speed	% Max. Torque	Injection Duration (deg CA)	Torque Group Definition
1	1400	20	7.5	Α
2	1400	75	12.8	С
3	1600	65	12.8	С
4	1700	60	12.2	В
5	1700	75	14.3	С
6	1800	55	12.2	В
7	1800	75	14.3	С
8	1900	50	11.7	В
9	1900	100	19.9	E
10	2000	75	15.8	С
11	2100	75	15.8	С
12	2500	40	10.7	В
13	2500	65	15.7	С
14	2500	90	19.3	D
15	2700	70	15.6	С
16	2700	90	19.5	D
17	3000	65	15.3	С
18	3000	90	20.4	D
19	3000	100	22.9	E
20	3500	65	16.3	С
21	3500	90	21.7	D
22	3500	100	24.5	E
23	4000	65	16.4	С
24	4000	90	22.1	D
25	4000	100	25.5	E

Table A4.1: Steady-State Speed-Torque Operating Points for Emissions and

 Performance Parameterisation

<u>Appendix 5</u>: Computation of VW 1.9I TDI Engine Geometry

Input Data:					
Displacement (Stated):	1896 cm^3	1.896 dm^3	0.001896 m^3		
Compression Ratio Rv (Stated):	19.5				
Bore (Stated):	79.5 mm	7.95 cm	0.0795 m		
Stroke (Stated):	95.5 mm	9.55 cm	0.0955 m		
Measured Piston Bowl Vol. Vpb:	22338.49 mm^3	22.33849 cm^3	2.23385E-05 m^3		
Single Cylinder Displacement:	474 cm^3	0.474 dm^3	0.000474 [°] m^3		
Swept Volume Vs: Vs = (((bore)^2xpi)/4)xstroke	17 1052 6660 12	474 0505550 40	0.00017405 0.10		
Vs	4/4053.6669 mm^3	4/4.0536669 cm^3	0.000474054 m^3		

Clearance Volume:	Vc = Vs/(Rv-1)		
Rv	Vc	Vc	Vc
15	33860.97621 mm^3	33.86097621 cm^3	3.3861E-05 m^3
15.5	32693.35634 mm^3	32.69335634 cm^3	3.26934E-05 m^3
16	31603.5778 mm^3	31.6035778 cm^3	3.16036E-05 m^3
16.5	30584.10754 mm^3	30.58410754 cm^3	3.05841E-05 m^3
17	29628.35418 mm^3	29.62835418 cm^3	2.96284E-05 m^3
17.5	28730.52527 mm^3	28.73052527 cm^3	2.87305E-05 m^3
18	27885.50982 mm^3	27.88550982 cm^3	2.78855E-05 m^3
18.5	27088.78097 mm^3	27.08878097 cm^3	2.70888E-05 m^3
19	26336.31483 mm^3	26.33631483 cm^3	2.63363E-05 m^3
19.5	25624.52254 mm^3	25.62452254 cm^3	2.56245E-05 m^3
20	24950.193 mm^3	24.950193 cm^3	2.49502E-05 m^3
20.5	24310.44446 mm^3	24.31044446 cm^3	2.43104E-05 m^3
21	23702.68335 mm^3	23.70268335 cm^3	2.37027E-05 m^3

Clearance Height Estimation	Hc = ((Vc-Vpb)x4)/(bore^2xpi)	(Maximum	Possible Values)
Rv	Нс	Нс	Hc
15	2.321250757 mm	0.232125076 cm	0.002321251 m
15.5	2.086029082 mm	0.208602908 cm	0.002086029 m
16	1.866488852 mm	0.186648885 cm	0.001866489 m
16.5	1.661112508 mm	0.166111251 cm	0.001661113 m
17	1.468572185 mm	0.146857219 cm	0.001468572 m
17.5	1.287700973 mm	0.128770097 cm	0.001287701 m
18	1.117469244 mm	0.111746924 cm	0.001117469 m
18.5	0.956965042 mm	0.095696504 cm	0.000956965 m
19	0.805377741 mm	0.080537774 cm	0.000805378 m
19.5	0.661984347 mm	0.066198435 cm	0.000661984 m
20	0.526137975 mm	0.052613797 cm	0.000526138 m
20.5	0.397258083 mm	0.039725808 cm	0.000397258 m
21	0.274822185 mm	0.027482219 cm	0.000274822 m

Table A5.1: Computation of Clearance Height for 15:1 to 21:1 Compression

Ratio Range

Additional 'Ring Groove' in the Top Land (Height = 6mm)						
Specified Dims Depth						
R2	39.37	mm	3.936	5 cm	0.03936	5 m
Height	6.00	mm	0.0	5 cm	0.00	6 m
Volume of	Piston Mat	terial for Re	emoval	(Cv at m	odified Rv - Cv at orig	inal Rv)
Rv				Volum	e	
15	8236.45	mm^3	8.236	cm^3	0.00008236	m^3
15.5	7068.83	mm^3	7.069	cm^3	0.000007069	m^3
16	5979.06	mm^3	5.979	cm^3	0.000005979	m^3
16.5	4959.59	mm^3	4.960	cm^3	0.000004960	m^3
17	4003.83	mm^3	4.004	cm^3	0.000004004	m^3
17.5	3106.00	mm^3	3.106	cm^3	0.000003106	m^3
18	2260.99	mm^3	2.261	cm^3	0.000002261	m^3
18.5	1464.26	mm^3	1.464	cm^3	0.000001464	m^3
19	711.79	mm^3	0.712	cm^3	0.000000712	m^3
19.5	0.00	mm^3	0.000	cm^3	0.000000000	m^3
20	NA	mm^3	NA	cm^3	NA	m^3
20.5	NA	mm^3	NA	cm^3	NA	m^3
21	NA	mm^3	NA	cm^3	NA	m^3
Calculated	Inner Rad	ius roquiro	d for Groov	0		
Rv	miler Nau	ius require		R1		
15	33.356	mm	3.336	cm	0.033356	m
15.5	34.272	mm	3.427	cm	0.034272	m
16	35.106	mm	3.511	cm	0.035106	m
16.5	35.868	mm	3.587	cm	0.035868	m
17	36.568	mm	3.657	cm	0.036568	m
17.5	37.213	mm	3.721	cm	0.037213	m
18	37.811	mm	3.781	cm	0.037811	m
18.5	38.366	mm	3.837	cm	0.038366	m
19	38.882	mm	3.888	cm	0.038882	m
19.5	39.365	mm	3.937	cm	0.039365	m
20	NA	mm	NA	cm	NA	m
20.5	NA	mm	NA	cm	NA	m
21	NA	mm	NA	cm	NA	m
Creative D-	oth _ D4 D	2	(This is the	double of t	he 'out' into the nictor	top lend)
R2 -R1	pui = K1-K	2	(This is the	depth of t	ne cui into the pistor	r top land)
15	6.0087	mm	0.6009	cm	0.006009	m
15.5	5.0927	mm	0.5093	cm	0.005093	m
16	4.2594	mm	0.4259	cm	0.004259	m
16.5	3.4973	mm	0.3497	cm	0.003497	m
17	2.7973	mm	0.2797	cm	0.002797	m
17.5	2.1518	mm	0.2152	cm	0.002152	m
18	1.5542	mm	0.1554	cm	0.001554	m
18.5	0.9994	mm	0.0999	cm	0.000999	m
19	0.4826	mm	0.0483	cm	0.000483	m
19.5	0.0000	mm	0.0000	cm	0.000000	m
20	NA	mm	NA	cm	NA	m
20.5	NA	mm	NA	cm	NA	m
21	NA	mm	NA	cm	NA	m

Table A5.2: Ring Groove Incision (R_2 - R_1), D = 6 mm

Appendix 6: Summary of Soot Analysis Methods &

References

Rank	Analysis Method	Acronym
1	Transmission Electron Microscopy	(TEM)
2	Surface Area Analysis (isotherm and BET analysis, surface area)	(BET)
3	Thermogravimetrical Analysis	(TGA)
4	X-ray Photoelectron Spectroscopy	(XPS)
5	Boehm Titration (Surface Acid Functionality)	-
6	High Resolution Transmission Electron Microscopy	(HRTEM)
7	Gas Chromatography (PAH Analysis)	(GC)
8	Gas Chromatography Mass Spectrometry (PAH analysis)	(GC-MS)
9	High Resolution Transmission Electron Microscopy	(HRTEM)
10	Scanning Electron Microscopy	(SEM)
11	X-ray Diffraction	(XRD)
12	Fourier Transform Infrared Spectroscopy	(FT-IR)
13	Energy Dispersive Spectrometer	(EDS or EDX)
14	Pycnometry (Nitrogen or helium adsorption)	-
15	Scanning Mobility Particle Sizing	(SMPS)
16	BET-Equivalent Primary Particle Diameter	-
17	Electron Energy Loss Spectra	(EELS)
18	High-pressure Liquid Chromatography (PAH analysis)	(HPLC)
19	Scanning Transmission Electron Microscopy	(STEM)
20	Surface Porosity Analysis (isotherm and BET analysis, porosity)	(BJH)
21	Diffuse Reflectance Infrared Fourier Transform Spectra	(DRIFT)
22	Inductively Coupled Plasma Mass Spectroscopy	(ICP-MS)

Table A6.1: Popular Soot Analysis Methods Determined by Literature Survey¹⁹

Soot Characteristic	Analysis Method
Surface Elemental Analysis	X-Ray Photoelectron Spectroscopy (XPS)
Bulk Elemental Analysis	Inductively Charged Plasma Mass Spectroscopy (ICP-MS)
Surface Area	Brunsuer Emmett and Teller (BET)
Surface Area	Adsorption Isotherm Analysis
Porocity	Barrett-Joyner-Halenda (BJH) Adsorption
Forosity	Isotherm Analysis
Density	N2 Pycnometry
Primary Particle Diameter	Spherical non-porous particle assumption based BET surface area and density
Surface Acid Functionality	Boehm Titration
Poly Aromatic Profile	Gas Chromatography-Mass Spectrometry (GC-MS).
Soot Residue, Carbonaceous Content and Ash	Thermogravimetrical Analysis (TGA)

Table A6.2: Soot Characterisation Analysis Methods Utilised in this Work

¹⁹ Methods highlighted in **bold** in Table A6.1 and Table A6.2 are those utilised in this work.

Soot Analysis Method	References								
	Albers_2000 [248], Antusch_2010 [249], Bardasz_1995 [117],								
	Boehm_2001 [118], Chang_1974 [250], Clague_1999 [233], Collura_2002								
	[251], Collura_2004 [134], Kirchner_2003 [252], Liu_2010 [253],								
(XPS) X-ray	Muller_2006 [254], Muller_2007 [255], Nguyen_2006 [124], Patel_2012								
photoelectron	[256], Rausa_1998 [257], Ruiz_2006 [258], Smith_2001 [259], Wal_2009								
000000000000000000000000000000000000000	[63], Wal_2011 [260], Bardasz_1995 [119], Bardasz_1996 [115],								
	Bardasz_1997 [212], Saathoff_2003 [261], Stanmore_1999 [139],								
	Lamharess_2011 [112], Setiabudi_2004 [262]								
	Lyyranen_2002 [263], Okada_2003 [264], Ulrich_2003 [234],								
	Vlasankova_1999 [265], Wang_2003 [220], Ripple_1990 [165],								
(ICP-MS) Inductively	Agarwal_2010 [87], Gangwar_2011 [266], Szynkowsha_2008 [232],								
coupled plasma mass spectroscopy	Maricq_2007 [182], Clague_1999 [233], Arai_1992 [267], Bardasz_1995								
	[117], Bardasz_1996 [115], Bardasz_1997 [212], Bardasz_1997_2 [211],								
	Stanmore_1999 [139], Ghzaoui_2003 [268], Collura_2004 [134],								
	Covitch_1988 [138], Lombaert_2003 [221]								
	Aubin_2003 [269] , Bau_2010 [151] , Chen_2010 [270] , Chughtai_1999 [46] ,								
	Fernandes_2003 [271], Ghzaoui_2003 [268], Harris_1985 [272],								
	lshiguro_1991 [131], Lamharess_2011 [112], Lapuerta_2010 [136],								
	Levitt_2007 [273], Levitt_Thesis_2007 [274], Lu_2011 [142], Liu_2010								
	[253], Muckenhuber_2004 [116], Nguyen_2006 [124], Patel_2012 [256],								
(BET) Surface Area Analysis (isotherm and	Popovitcheva_2000 [166], Popovitcheva_2003 [275], Pott_1991 [276],								
BET analysis, surface	Rockne_1999 [277], Ruiz_2006 [258], Setiabudi_2004 [262], Silva_1999								
area)	[278], Smekens_2005 [155], Zerda_1999 [137], Thiele_Case_Study [236],								
	Otto_1980 [135], Mueller_2004 [237], Wegner_2002 [279],								
	Johannessen_2000 [280], Covitch_1988 [210], Kandas_2005 [147],								
	Mueller_2004 [237], Stanmore_1999 [139], Yu_2005 [140], Collura_2004								
(BJH) Surface Porosity Analysis (isotherm and BET analysis, porosity)	[134]								
	Barrett_1951 [148], Bau_2010 [151], Lapuerta_2010 [136], Nguyen_2006								
	[124], Song_2007 [17], Groen_2003 [282], Groen (Delft Solid Solutions)								
	[283], Popovicheva_2000 [166], Kaneko_1994 [141], Zerda_1999 [137],								
	Rockne_1999 [277] , Yu_2005 [140]								

Table A6.3: Literature Examples for the Analysis Methods Utilised in this Work

(Part 1)

Soot Analysis Method	References								
Pycnometry (Nitrogen	Bau_2010 [151], Choi_1995_2 [239], McMurry_2002 [283], Song_2007								
or helium adsorption)	[17], Coudray_2008 [150], Hanel_1977 [284], Park_2004 [152],								
papers related to this	Maricq_2004 [154], Stanmore_1999 [139], Rockne_1999 [277]								
BET-Equivalent	Mueller_2004 [237], Virtanen_2004 [32], Harris_2001 [285], Ishiguro_1991								
Primary Particle	[131], Schraml_1999 [34], Wegner_2002 [279], Johannessen_2000 [280],								
Diameter	Thiele_Case_Study [236], Lapuerta_2010 [136]								
	Lopez_Ramon_1999 [286], Chiang_2002 [245], Boehm_1994 [156],								
	Goertzen_2010 [243], Oickle_2010 [244], Kim_2012 [287], Kim_2012_1								
	[288], Matsumura_1972 [167], Yu_2005 [140], Boehm_2001 [118],								
Boehm Titration	Boehm_1964_2 [242], Muckenhuber_2005 [289], Muckenhuber_2004								
(Surface Acid Functionality)	[116], Setiabudi_2004 [262], Levitt_2007 [274], Kirchner_2000 [106],								
, , , , , , , , , , , , , , , , , , , ,	Levitt_Thesis_2007 [274], Manjo_2012 [290], Popovicheva_2003 [275],								
	Popovicheva_2000 [291], Moldonova_2009 [105], Ghzaoui_2003 [268],								
	Collura_2004 [134]								
	Barbella_1989 [292], Barbella_1989_2 [293], Barbella_1988_2 [294],								
	Ciajolo_2001 [295], Collura_2002 [251], Collura_2004 [134], Dobbins_2007								
/	[25], Lin_2006 [296], Lombaert_2003_2 [221], Lombaert_2007 [297],								
(GC-MS) Gas Chromatography Mass	Henderson_1984 [298], Popovicheva_2009 [299], Yang_1998 [300],								
Spectrometry (PAH	Poster_2003 [183], Rhead_1996 [175], Lu_2011 [142], Williams_1989 [28],								
analysis)	EPA_Method_610 [246], Brandenberger_2005 [301], Moldonova_2009								
	[105], Lemaire_2009 [302], Allouis_2002 [303], Arai_1992 [267],								
	Gotze_1991 [171], Jin_1983 [304], Bagley_1996 [79]								
	Al_Qurashi_2008 [305], Al_Qurashi_2011 [113], Bardasz_1995 [117],								
	Boehman_2005 [306] , Braun_2005 [307] , Chen_2010 [270] , Choi_2002								
	[308], Clague_1999 [233], Collura_2002 [251], Collura_2004 [134],								
	Esangbedo_2011 [309], Fang_2004 [310], Fernandez_2011 [311],								
(TCA)	Laosuwan_2011 [312] , Oh_2011 [313] , Rausa_1998 [257] ,								
Thermogravimetrical	Rounce_2011_PhD [314], Rounce_2012 [315], Ryason_1994 [316],								
Analysis	Salamanca_2011 [317], Sappok_2007 [318], Setiabudi_2004 [262],								
-	Song_2004 [319], Song_2004_2 [320], Song_deer_2005 [321], Song_2006								
	[16], Song_2007 [17], Stratakis_2003 [322], Stratakis_2003_2 [323],								
	Williams_2006 [324], Covitch_1985 [210], Ripple_1990 [165],								
	Lapuerta_2010 [136], Stanmore_1999 [139], Rockne_1999 [277]								

Table A6.4: Literature Examples for the Analysis Methods Utilised in this Work

(Part 2)

Appendix 7: Method Flow Diagram for Chapter 4





<u>Appendix 8</u>: Correction of Soot Bulk Inorganic Results (ICP-MS)

A8.1 Introduction

Following careful examination of the original ICP-MS results, it became clear that there were a series of inconstancies which pointed to several of the soot samples being contaminated with elements which either had no identifiable source (i.e. foreign to the experiment) or were attributable to known uncontrollable factors that could not be avoided when the soot was experimentally collected from the engine.

All original ICP-MS results for the soot collected in the fuel, compression ratio and sample position experiments (Section 3.1.5.3) are presented in Table A8.1 in the form of % weight of the sample. In Table A8.2 the results of Table A8.1 have been calculated as a percentage of the total % weight of inorganics in each soot sample.

Table A8.1: 19.5:1 and 16.5:1 Ceramic Thimble Soot and DPF Soot Bulk Elemental

 Composition (% weight), Original ICP-MS Results²⁰

		#1269 ICP: Bulk Inorganic Contaminants by Acid-digestion ICP (wt%)												
Description	%Ca	%Cu	%Fe	%Mg	%Mn	%Na	%Р	%S	%Si	%Zn	%AI	%Cd	Total wt%	
19.5:1 CT, EN590	0.083	0.003	0.034	0.002	0.012	0.656	0.016	0.001	0.001	0.033	0.000	0.000	0.841	
16.5:1 CT, EN590	0.250	0.000	0.066	0.023	0.000	0.000	0.043	0.000	0.087	0.056	0.000	0.000	0.525	
16.5:1 DPF, EN590	0.990	0.080	3.420	0.064	< 0.001	0.060	0.690	0.250	0.080	2.870	0.130	0.060	8.694	
19.5:1 CT, PC9	0.078	0.002	0.043	0.002	0.006	1.050	0.002	0.282	0.001	0.028	0.000	0.000	1.494	
16.5:1 CT, PC9	0.320	0.000	0.110	0.021	0.000	0.000	0.072	1.060	0.160	0.077	0.000	0.000	1.820	
16.5:1 DPF, PC9	0.990	0.080	4.680	0.068	< 0.001	0.080	0.510	0.320	0.080	2.250	0.130	0.060	9.248	
19.5:1 CT, B100	0.277	0.015	0.171	0.005	0.010	0.083	0.051	0.330	0.017	0.105	0.000	0.000	1.064	
16.5:1 CT, B100	2.880	0.000	1.080	0.350	0.000	0.450	1.030	0.014	0.110	0.560	0.000	0.000	6.474	
16 5·1 DPF B100	5 2 5 0	0.840	9 620	0 7 3 0	<0.001	0.890	2 300	1 500	0.080	5 300	0 2 1 0	1 2 3 0	27 950	

 Table A8.2: 19.5:1 and 16.5:1 Ceramic Thimble Soot and DPF Soot Bulk Elemental

 Composition (% weight/total % weight), Original ICP-MS Results

			#12	269 ICP: Bul	k Inorganic (Contaminant	s by Acid-di	gestion ICP (% of Total w	vt% Inorgani	ics)		
Description	%Ca	%Cu	%Fe	%Mg	%Mn	%Na	%P	%S	%Si	%Zn	%AI	%Cd	Total %
19.5:1 CT, EN590	9.869	0.357	4.043	0.238	1.427	78.002	1.902	0.119	0.119	3.924	0.000	0.000	100.000
16.5:1 CT, EN590	47.619	0.000	12.571	4.381	0.000	0.000	8.190	0.000	16.571	10.667	0.000	0.000	100.000
16.5:1 DPF, EN590	11.387	0.920	39.337	0.736	0.000	0.690	7.937	2.876	0.920	33.011	1.495	0.690	100.000
19.5:1 CT, PC9	5.221	0.134	2.878	0.134	0.402	70.281	0.134	18.876	0.067	1.874	0.000	0.000	100.000
16.5:1 CT, PC9	17.582	0.000	6.044	1.154	0.000	0.000	3.956	58.242	8.791	4.231	0.000	0.000	100.000
16.5:1 DPF, PC9	10.705	0.865	50.606	0.735	0.000	0.865	5.515	3.460	0.865	24.330	1.406	0.649	100.000
19.5:1 CT, B100	26.034	1.410	16.071	0.470	0.940	7.801	4.793	31.015	1.598	9.868	0.000	0.000	100.000
16.5:1 CT, B100	44.486	0.000	16.682	5.406	0.000	6.951	15.910	0.216	1.699	8.650	0.000	0.000	100.000
16.5:1 DPF, B100	18.784	3.005	34.419	2.612	0.000	3.184	8.229	5.367	0.286	18.962	0.751	4.401	100.000

Within the following section, the data from Table A8.1 and Table A8.2 is examined to identify contaminates in the original samples which grossly mask the

²⁰ In Table A8.1 and A8.2; CT denotes Ceramic Thimble (soot collected at the exhaust manifold) and DPF denotes soot collected in a DPF in the exhaust system (refer to Section 3.5).

underlying soot bulk inorganic changes that were effected by the factors experimentally investigated. The data in Table A8.1 and Table A8.2 will then be corrected for these identified contaminates and this revised/corrected data then forms the basis of the results discussion presented in the main body of this work.

A8.2 Identification of Foreign Contaminate

Considering first the ceramic thimble data presented in Table A8.1 and Table A8.2, it was observed that the range in total percentage weight of inorganic contaminant across the three fuels at the exhaust manifold for 19.5:1 was 0.841 to 1.494% and for the 16.5:1 samples this range was a broader 0.525 to 6.474%. The other interesting feature of this data was that for the 19.5:1 data set, it was the PC9 fuel which had the most significant level of inorganic contaminates but that this dramatically shifted to the RME B100 soot sample for the 16.5:1 samples. These observations are illustrated in Figure A8.1.



Figure A8.1: Exhaust Manifold Soot Total (% Weight) of Inorganics, Original ICP-MS Results

<u>Hypothesis</u>: It is intuitive to believe that the concentration of inorganic material in the soot dry carbonaceous fraction sampled at the exhaust manifold was principally a function of the fuel consumption rate, oil consumption rate and the concentration of carbonaceous soot produced in combustion during a given engine cycle. Other metallic elements (principally iron) originate from the engine.

Considering the results summarised in Figure A8.1, it was clear that the B100 inorganic concentration observed in the 16.5:1 sample when compared to the EN590 and the PC9 at the same compression, conformed to what would be expected if the hypothesis for explaining the concentration is valid. i.e. the B100

fuel was observed to have a (>80%) reduction in exhaust soot concentration relative to the other two fuels (Table 4.10) and therefore the concentration of inorganics should have been significantly higher in this sample as was observed. At 19.5:1 this was not the case however. Indeed, in the case of the PC9 fuel, the exhaust carbonaceous soot concentration was the highest of the three fuels in all experiments and thus this fuel should have resulted in soot with generally the lowest inorganic contaminate level if sulphur is ignored.

A8.2.1 Sodium (Na)

The first step in deconstructing these anomalies was the observation that there was a very high concentration of sodium in the 19.5:1 EN590 and PC9 samples, constituting 78 and 70% of the total inorganics in each sample respectively, Table A8.2. So significant was this single element contamination for these two samples, that no other samples were observed to have any single element contribute more than 50% in all of the other tests. These two mineral fuel derived samples were from the first two soot collection experiments performed in this work which indicated a possible association. The concentration of sodium was negligible in all other soot samples from these two mineral fuels, Figure A8.2, indicating it was very unlikely the sodium originated from either of the two mineral fuels.





One plausible explanation for this sodium was that it may have originated from the biodiesel fuel which was being investigated as part of the engine performance and emissions baseline experiments conducted prior to the soot collection experiments (Section 3.1.5.2). One of the catalysts commonly used in the transesterification process for biodiesel is NaOH (sodium hydroxide) and it is possible a residual amount was present in the B100 fuel which was used originally during the development phase of the experimental system. As an example of the plausibility of this, Gangwar et al. [266] reported a similar finding when investigating the soot produced from a vegetable oil. Indeed, the fuel physiochemical summary in Appendix 1 (Table A1.1 and Figure A1.1) details the presence of sodium in the original B100 fuel.

The main issue with this explanation however is the fact that if the sodium was contaminate from the B100 fuel alone, then it would also be expected to be a significant contaminate in the B100 soot, and likely more so. Although, sodium was observed in all B100 soot samples, which is consistent with sodium being present in the B100 fuel, it was only 3-7% of the total inorganic contaminate.

It is believed therefore that the only plausible explanation for the high concentration of sodium in the two 19.5:1 mineral diesel soot samples was contamination of the samples occurring following sample collection i.e. during sample handling and preparation prior to the ICP-MS soot bulk analysis (Section 3.6.3). How this may have occurred is not known as the sample analysis was coordinated by Lubrizol and undertaken by a third party.

The non-contaminated base level of sodium in the two afflicted original soot samples is not known but can be inferred from the other mineral diesel soot samples and these indicate that the normal sodium concentration should be negligible, i.e. the 16.5:1 results shown in Figure A8.2. These results reveal that there was no sodium detected in these samples and thus the best method to address the sodium contamination is to take the data presented in Table A8.1 and to simply negate the sodium from these two samples. The result from this is presented in Table A8.3 and Table A8.4.

 Table A8.3: 19.5:1 and 16.5:1 Ceramic Thimble Soot and DPF Soot Bulk Elemental

 Composition (% weight), Original ICP-MS Results with Sodium Contaminate Negated

			#1269 ICP: Bulk Inorganic Contaminants by Acid-digestion ICP (wt%)												
	Description	%Ca	%Cu	%Fe	%Mg	%Mn	%Na	%Р	%S	%Si	%Zn	%Al	%Cd	Total wt%	
	19.5:1 CT, EN590	0.083	0.003	0.034	0.002	0.012	0.000	0.016	0.001	0.001	0.033	0.000	0.000	0.185	
	16.5:1 CT, EN590	0.250	0.000	0.066	0.023	0.000	0.000	0.043	0.000	0.087	0.056	0.000	0.000	0.525	
	16.5:1 DPF, EN590	0.990	0.080	3.420	0.064	< 0.001	0.060	0.690	0.250	0.080	2.870	0.130	0.060	8.694	
	19.5:1 CT, PC9	0.078	0.002	0.043	0.002	0.006	0.000	0.002	0.282	0.001	0.028	0.000	0.000	0.444	
	16.5:1 CT, PC9	0.320	0.000	0.110	0.021	0.000	0.000	0.072	1.060	0.160	0.077	0.000	0.000	1.820	
	16.5:1 DPF, PC9	0.990	0.080	4.680	0.068	< 0.001	0.080	0.510	0.320	0.080	2.250	0.130	0.060	9.248	
	19.5:1 CT, B100	0.277	0.015	0.171	0.005	0.010	0.083	0.051	0.330	0.017	0.105	0.000	0.000	1.064	
	16.5:1 CT, B100	2.880	0.000	1.080	0.350	0.000	0.450	1.030	0.014	0.110	0.560	0.000	0.000	6.474	
Г	16.5:1 DPF. B100	5.250	0.840	9.620	0.730	< 0.001	0.890	2.300	1.500	0.080	5.300	0.210	1.230	27.950	

 Table A8.4: 19.5:1 and 16.5:1 Ceramic Thimble Soot and DPF Soot Bulk Elemental

 Composition (% weight/total % weight), Original ICP-MS Results with Sodium

 Contaminate Negated

		#1269 ICP: Bulk Inorganic Contaminants by Acid-digestion ICP (% of Total wt% Inorganics)											
Description	%Ca	%Cu	%Fe	%Mg	%Mn	%Na	%Р	%S	%Si	%Zn	%AI	%Cd	Total %
19.5:1 CT, EN590	44.865	1.622	18.378	1.081	6.486	0.000	8.649	0.541	0.541	17.838	0.000	0.000	100.000
16.5:1 CT, EN590	47.619	0.000	12.571	4.381	0.000	0.000	8.190	0.000	16.571	10.667	0.000	0.000	100.000
16.5:1 DPF, EN590	11.387	0.920	39.337	0.736	0.000	0.690	7.937	2.876	0.920	33.011	1.495	0.690	100.000
19.5:1 CT, PC9	17.568	0.450	9.685	0.450	1.351	0.000	0.450	63.514	0.225	6.306	0.000	0.000	100.000
16.5:1 CT, PC9	17.582	0.000	6.044	1.154	0.000	0.000	3.956	58.242	8.791	4.231	0.000	0.000	100.000
16.5:1 DPF, PC9	10.705	0.865	50.606	0.735	0.000	0.865	5.515	3.460	0.865	24.330	1.406	0.649	100.000
19.5:1 CT, B100	26.034	1.410	16.071	0.470	0.940	7.801	4.793	31.015	1.598	9.868	0.000	0.000	100.000
16.5:1 CT, B100	44.486	0.000	16.682	5.406	0.000	6.951	15.910	0.216	1.699	8.650	0.000	0.000	100.000
16.5:1 DPF, B100	18.784	3.005	34.419	2.612	0.000	3.184	8.229	5.367	0.286	18.962	0.751	4.401	100.000

Observe that for the PC9 soot in the ceramic thimble samples; the sulphur contribution with the sodium negated is now 63.5% which is closer to the 58.24% observed for the 16.5:1 sample. Thus, the correction for the sodium contaminate is essential to correctly interpreting the factor effects on the soot bulk chemistry.

A8.2.2 Silicon (Si)

The next foreign contaminate identified in the samples was silicon and this was revealed by the significant increase in the concentrations of silicon in the soot samples between the high and low engine compression experiments, Figure A8.3 (taken from the original uncorrected ICP-MS data, Table A8.2).





This was a relatively simple foreign contaminate to identify and explain as there was a clear source which was the silicon sealant (Loctite 5367) used to seal the head gasket on the 2nd of three attempts to seal the thicker head gasket assembly used for the low compression engine build, Section 3.3.4. This sealant was carefully removed from the engine but clearly traces of it remained which

was revealed by the very sensitive ICP-MS analysis. The fact that this silicon became entrained within the soot samples proved to be a very interesting if unintentional finding. What it highlighted was the very strict level of cleanliness and preparation required in the engine experiments to minimise the probability of foreign contaminates influencing the soot findings.

A further interesting observation was the very significant reduction in concentration of silicon in the soot sampled at the DPF. It is postulated that the soot therefore evolved in the exhaust in such a way as to preferentially remove this element. For example, it could have been entrained within the adsorbed SOF on the surface of the soot sampled at the exhaust manifold; the SOF should have been reduced as the soot moved through the oxidation catalyst prior to the DPF, thereby reducing the silicon in the soot sample.

As the silicon contaminate has been attributed to the sealant used in the 16.5:1 compression ratio modification and the observation made that it was present principally in the exhaust manifold soot samples; the most plausible method of removing its effects from the soot bulk inorganic data is to simply negate the silicon from all the 16.5:1 exhaust manifold soot samples. However, this would confuse later result analysis when the effect of sample location is considered, Chapter 6. Thus, to avoid confusion, silicon has been negated from all 16.5:1 soot samples. This has been done by subtracting it from the data presented in Table A8.3 (i.e. the sodium corrected results) and the result of this is presented in Table A8.5 and Table A8.6.

 Table A8.5: 19.5:1 and 16.5:1 Ceramic Thimble Soot and DPF Soot Bulk Elemental

 Composition (% weight), Original ICP-MS Results with Sodium & Silicon Contaminate

 Negated

		#1269 ICP: Bulk Inorganic Contaminants by Acid-digestion ICP (wt%)											
Description	%Ca	%Cu	%Fe	%Mg	%Mn	%Na	%P	%S	%Si	%Zn	%AI	%Cd	Total wt%
19.5:1 CT, EN590	0.083	0.003	0.034	0.002	0.012	0.000	0.016	0.001	0.001	0.033	0.000	0.000	0.185
16.5:1 CT, EN590	0.250	0.000	0.066	0.023	0.000	0.000	0.043	0.000	0.000	0.056	0.000	0.000	0.438
16.5:1 DPF, EN590	0.990	0.080	3.420	0.064	< 0.001	0.060	0.690	0.250	0.000	2.870	0.130	0.060	8.614
19.5:1 CT, PC9	0.078	0.002	0.043	0.002	0.006	0.000	0.002	0.282	0.001	0.028	0.000	0.000	0.444
16.5:1 CT, PC9	0.320	0.000	0.110	0.021	0.000	0.000	0.072	1.060	0.000	0.077	0.000	0.000	1.660
16.5:1 DPF, PC9	0.990	0.080	4.680	0.068	< 0.001	0.080	0.510	0.320	0.000	2.250	0.130	0.060	9.168
19.5:1 CT, B100	0.277	0.015	0.171	0.005	0.010	0.083	0.051	0.330	0.017	0.105	0.000	0.000	1.064
16.5:1 CT, B100	2.880	0.000	1.080	0.350	0.000	0.450	1.030	0.014	0.000	0.560	0.000	0.000	6.364
16.5:1 DPF, B100	5.250	0.840	9.620	0.730	< 0.001	0.890	2.300	1.500	0.000	5.300	0.210	1.230	27.870

Table A8.6: 19.5:1 and 16.5:1 Ceramic Thimble Soot and DPF Soot Bulk ElementalComposition (% weight/Total % weight), Original ICP-MS Results with Sodium & SiliconContaminate Negated

		#1269 ICP: Bulk Inorganic Contaminants by Acid-digestion ICP (% of Total wt% Inorganics)											
Description	%Ca	%Cu	%Fe	%Mg	%Mn	%Na	%P	%S	%Si	%Zn	%AI	%Cd	Total %
19.5:1 CT, EN590	44.865	1.622	18.378	1.081	6.486	0.000	8.649	0.541	0.541	17.838	0.000	0.000	100.000
16.5:1 CT, EN590	57.078	0.000	15.068	5.251	0.000	0.000	9.817	0.000	0.000	12.785	0.000	0.000	100.000
16.5:1 DPF, EN590	11.493	0.929	39.703	0.743	0.000	0.697	8.010	2.902	0.000	33.318	1.509	0.697	100.000
19.5:1 CT, PC9	17.568	0.450	9.685	0.450	1.351	0.000	0.450	63.514	0.225	6.306	0.000	0.000	100.000
16.5:1 CT, PC9	19.277	0.000	6.627	1.265	0.000	0.000	4.337	63.855	0.000	4.639	0.000	0.000	100.000
16.5:1 DPF, PC9	10.798	0.873	51.047	0.742	0.000	0.873	5.563	3.490	0.000	24.542	1.418	0.654	100.000
19.5:1 CT, B100	26.034	1.410	16.071	0.470	0.940	7.801	4.793	31.015	1.598	9.868	0.000	0.000	100.000
16.5:1 CT, B100	45.255	0.000	16.970	5.500	0.000	7.071	16.185	0.220	0.000	8.799	0.000	0.000	100.000
16.5:1 DPF, B100	18.837	3.014	34.517	2.619	0.000	3.193	8.253	5.382	0.000	19.017	0.753	4.413	100.000

A8.2.3 Sulphur (S)

The third and final ambiguity identified in the original ICP-MS results, was an unusually high concentration of sulphur in the 19.5:1 B100 exhaust manifold soot sample. This was identified as a suspect foreign contaminate as it comprised over 30% of the total inorganic contaminates of the sample and by contrast the sulphur in the 16.5:1 B100 sample was just 0.22% of the total inorganic contaminates, Table A8.6 (sodium and silicon corrected ICP-MS results). This is result is illustrated in Figure A8.4.





One plausible explanation for this excessive sulphur in the 19.5:1 B100 soot sample was contamination from residual sulphur that was carried over from the previous PC9 soot collection experiment; possibly picked up from residual sulphur in the fuel system, engine deposits or sample line from the exhaust manifold. This postulation derives from the PC9 fuel soot collection experiment being conducted immediately prior to the B100 collection experiment. Thus, although measures were taken such as flushing the fuel system and changing the engine oil (Section 3.2.1.6), sulphur contamination from the prior experiment occurred. Avoidance of such contamination in a practical engine experiments such as those in this work, would have necessitated a full engine disassembly and clean between each test which was impractical.

As per the methodology used for negating the sodium and silicon contaminates; the sulphur in the B100 19.5:1 exhaust manifold sample has been set to zero in the previously corrected data presented in Table A8.5 to remove its masking of the ICP-MS results for this sample. These final ICP-MS soot bulk inorganic corrected results are presented in Table A8.7 and Table A8.8.

Table A8.7: 19.5:1 and 16.5:1 Ceramic Thimble Soot and DPF Soot Bulk ElementalComposition (% weight), Original ICP-MS Results with Sodium, Silicon & SulphurContaminate Negated

		#1269 ICP: Bulk Inorganic Contaminants by Acid-digestion ICP (wt%)												
Description	%Ca	%Cu	%Fe	%Mg	%Mn	%Na	%P	%S	%Si	%Zn	%AI	%Cd	Total wt%	
19.5:1 CT, EN590	0.083	0.003	0.034	0.002	0.012	0.000	0.016	0.001	0.001	0.033	0.000	0.000	0.185	
16.5:1 CT, EN590	0.250	0.000	0.066	0.023	0.000	0.000	0.043	0.000	0.000	0.056	0.000	0.000	0.438	
16.5:1 DPF, EN590	0.990	0.080	3.420	0.064	< 0.001	0.060	0.690	0.250	0.000	2.870	0.130	0.060	8.614	
19.5:1 CT, PC9	0.078	0.002	0.043	0.002	0.006	0.000	0.002	0.282	0.001	0.028	0.000	0.000	0.444	
16.5:1 CT, PC9	0.320	0.000	0.110	0.021	0.000	0.000	0.072	1.060	0.000	0.077	0.000	0.000	1.660	
16.5:1 DPF, PC9	0.990	0.080	4.680	0.068	< 0.001	0.080	0.510	0.320	0.000	2.250	0.130	0.060	9.168	
19.5:1 CT, B100	0.277	0.015	0.171	0.005	0.010	0.083	0.051	0.000	0.017	0.105	0.000	0.000	0.734	
16.5:1 CT, B100	2.880	0.000	1.080	0.350	0.000	0.450	1.030	0.014	0.000	0.560	0.000	0.000	6.364	
16.5:1 DPF, B100	5.250	0.840	9.620	0.730	< 0.001	0.890	2.300	1.500	0.000	5.300	0.210	1.230	27.870	

Table A8.8: 19.5:1 and 16.5:1 Ceramic Thimble Soot and DPF Soot Bulk ElementalComposition (% weight/total % weight), Original ICP-MS Results with Sodium, Silicon &Sulphur Contaminate Negated

		#1269 ICP: Bulk Inorganic Contaminants by Acid-digestion ICP (% of Total wt% Inorganics)											
Description	%Ca	%Cu	%Fe	%Mg	%Mn	%Na	%P	%S	%Si	%Zn	%AI	%Cd	Total %
19.5:1 CT, EN590	44.865	1.622	18.378	1.081	6.486	0.000	8.649	0.541	0.541	17.838	0.000	0.000	100.000
16.5:1 CT, EN590	57.078	0.000	15.068	5.251	0.000	0.000	9.817	0.000	0.000	12.785	0.000	0.000	100.000
16.5:1 DPF, EN590	11.493	0.929	39.703	0.743	0.000	0.697	8.010	2.902	0.000	33.318	1.509	0.697	100.000
19.5:1 CT, PC9	17.568	0.450	9.685	0.450	1.351	0.000	0.450	63.514	0.225	6.306	0.000	0.000	100.000
16.5:1 CT, PC9	19.277	0.000	6.627	1.265	0.000	0.000	4.337	63.855	0.000	4.639	0.000	0.000	100.000
16.5:1 DPF, PC9	10.798	0.873	51.047	0.742	0.000	0.873	5.563	3.490	0.000	24.542	1.418	0.654	100.000
19.5:1 CT, B100	37.738	2.044	23.297	0.681	1.362	11.308	6.948	0.000	2.316	14.305	0.000	0.000	100.000
16.5:1 CT, B100	45.255	0.000	16.970	5.500	0.000	7.071	16.185	0.220	0.000	8.799	0.000	0.000	100.000
16.5:1 DPF, B100	18.837	3.014	34.517	2.619	0.000	3.193	8.253	5.382	0.000	19.017	0.753	4.413	100.000

With the principal contaminates identified and negated from the ICP-MS results, it is useful to return to the opening part of this appendix entry and compare how these corrections have adjusted the total percentage weight of inorganics for the exhaust manifold samples. Figure A8.5 illustrates this for the final corrected data from Table A8.8. When compared to Figure A8.1 it is clear that the corrected ICP-MS data now more closely aligns to the initial hypothesis in Section A8.2 concerning the concentration of inorganic material in the soot sample. i.e. the total percentage weight of inorganics in the samples is

proportional to the combination of measured exhaust soot concentration, fuel consumption rate and lubricant consumption rate of each respective soot collection test, Table 4.10. (This principal is outlined in more detail in the main body of this work where FSF, Section 4.3.2, is combined with the ICP-MS results e.g. Section 5.4 and Section 6.4)





A8.3 Concluding Remarks

The identification of the sodium, silicone and sulphur as foreign elements in specific soot samples, illustrated the high sensitivity of the bulk soot elemental analysis and the requirement to maintain high standards of cleanliness in the soot collection and sample handling to maximise result reliability/reproducibility. The final corrected ICP-MS results presented in Table A8.7 and Table A8.8 are the results presented and discussed in the main body of this work. These corrected results ensure that the developed models that explain the ICP-MS findings and associated conclusions are free from the influence of the ambiguities identified in this appendix entry.

<u>Appendix 9</u>: Injector Coking Observations and Investigation

A9.1 Introduction

Injector coking is the term used to describe the formation of deposits both within and at the exit of fuel injector nozzle holes and is a phenomenon commonly observed on modern diesel engines that employ high-pressure small nozzle-diameter fuel injection systems [328,329]. Injector coking can impact on engine performance by restricting the amount of fuel delivered to the combustion chamber and altering the spray pattern [330]. There are three factors that have been identified in literature as important in injector coking: 1) the fuel composition 2) the nozzle tip temperature and 3) the nozzle hole geometry [328]. One of the common engine test procedures used to quantify the susceptibility of an engine and fuel to coking is to run an engine at rated power for an extended period of time as this combines heavy fuelling with high cylinder and fuel injector tip temperatures [328].

A9.2 Injector Coking Issues Experienced in this Work

The most severe coking of the injector nozzles in the work reported herein occurred during both the RME B100 rated engine power soot collection tests with the problem being far more pronounced during the lower compression 16.5:1 experiment as illustrated in Figure A9.1.



Figure A9.1: 16.5:1 B100 Experiment Injector Coking Induced Torque Loss and Soot Concentration Reduction²¹

²¹ Discontinuities in the torque occur as a result of the experiment being conducted as a series of individual 2 hour segments to manage the ceramic thimble soot collection process (Section 3.5.1).

The torque loss observed during each soot collection experiment at rated conditions is summarised in Table A9.1 and reveals that for all experiments where torque loss could be assessed, there was a distinct difference between the mineral and biodiesel coking extent. In the case of the mineral fuels the power loss was consistent at 0.35 Nm per hour or 3.1-3.3% over the 20 hours of operation at maximum power. Whilst for the B100 fuel the loss was at least a factor of 1.86 greater. Importantly, in the case of the mineral fuels the reduction in compression ratio was observed to not accelerate the rate of power loss unlike observed for the B100. Additionally, it was clear that the coking did not worsen over time but was specific to each experiment configuration (note that the data in Table A9.1 is listed in experimental order).

Table A9.1: Summary of Injector Coking Induced Torque Loss for all Six Rated

 Condition Experiments²²

		Start Torque	End Torque	Period	Est. Rate	Torque Loss	
	Test	(Nm)	(Nm)	(hours)	(Nm/h)	(%)	
	19.5:1 EN590	NA	NA	NA	NA	Na	
	19.5:1 PC9	225	218	20	0.350	3.11	Original
	19.5:1 B100	216	203	20	0.650	6.02	Injectors
	16.5:1 B100	209	193	12	1.333	7.66	
	16.5:1 EN590	220	213	20	0.350	3.18	New
	16.5:1 PC9	210	203	20	0.350	3.33	Injectors

When the engine was stripped down to be adapted to the lower compression, the nozzles of the injectors were visually examined for any sign of coking issue. This visual inspection at the end of the 19.5:1 program of experimental work indicated that there was no significant visible build-up of external deposit on the surface of the injector tip apart from the cylinder 2 injector, Figure A9.2.





²² A reliable torque loss estimate for the first 19.5:1 experiment with EN590 was not available due to a forced turbocharger replacement which masked the coking based power loss.

The existing injectors were therefore not changed at this stage so as to avoid concerns over the impact injector change may have on the experimental results. The experiments continued with the first experiment at 16.5:1 but there was a very significant increase in the rate of torque loss observed compared to the prior 19.5:1 B100 experiment and this resulted in the exhaust soot concentration falling to the point where the soot collection experiment became unviable and thus the experiment was ceased at 12 hours, Table A9.1; 8 hours short of the planned duration (Section 3.1.5.3). The fuel injectors were then removed from the engine and investigated. A visual inspection of the injectors revealed that there was now significant external nozzle coking visible on the all the injector tips, Figure A9.3 (a), in contrast to Figure A9.2.



Figure A9.3: Comparison of Coked and Cleaned Injectors with B100 Fuel at 16.5:1

When the exhaust manifold was removed and checked at the end of the 16.5:1 B100 experiment, a white deposit was seen coating the inside of the manifold Figure A9.4.



Figure A9.4: 16.5:1 B100 Post Test Inspection - White Residue on the Inside of the Exhaust Manifold

Agarwal et al. [335] reported a similar observation and attributed this to traces of catalyst (NaOH - sodium hydroxide or KOH- Potassium hydroxide) remaining from the transesterification processing of the original biodiesel feedstock. This was therefore potentially an additional indicator as to the cause of the significant increase in coking for this experiment.

In order to confirm that the reduction in power and fuel consumption was caused by the suspected coking, the injectors were flow tested at Carwood Motor Units Ltd of Birmingham [331]. The injectors were first ultrasonically cleaned and then evaluated in a Hartridge AVM2-PC Unit Injector test bench using ISO 4113 fluid. The results were compared to a new injector (supplied by Lubrizol) and it was found that at the maximum fuelling test condition there was a lower total quantity per injection of 3.64%. A significant variability was also observed in the injector response times.

The cleaned injectors were subsequently re-fitted to the engine and the engine peak power checked with the B100 biodiesel fuel. It was observed that the torque had recovered from 192.90 Nm to 217 Nm, or an increase of 12.5%. However, the coefficient of variation IMEP was observed to be ~5% when previously it had been ~1% prior to the injector cleaning. Following these findings, new injectors were sourced from Lubrizol and the engine fuel system purged of the B100 biodiesel. The remaining tests were completed with the new set of injectors and this set experienced roughly the same rate of power loss compared to the equivalent 19.5:1 PC9 experiments Table A9.1.

A9.3 Causes of the Injector Coking

The torque loss for these two final experiments suggested that the increased rate of torque loss observed for the 16.5:1 B100 biodiesel experiment relative to the earlier 19.5:1 B100 biodiesel experiment; was not directly attributable to the reduction in compression ratio. This implied the reported increase in coking with increased injector nozzle temperature [332-334] was not responsible as the reduction in compression acted to reduce the baulk gas temperature and thus the temperature of the injector tip.

A review of literature revealed insights that helped to understand these observations. Argueyrolles et al. [328] and Leedham et al. [329] both identified that coking in general increased with zinc contamination from fuel. Indeed, Leedham et al. [329] found that trace amounts of zinc and copper in fuel as low as 1 ppm would accelerate the rate of injector coking. Further, Argueyrolles et al.

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[328] postulated that zinc dithiophosphate from the lubricant contributed to injector coking. Leedam et al. [329] specifically observed that the presence of zinc in fuel directly affected the area, volume and thickness of deposits that formed on the external surfaces of injector nozzle holes.

From the review of literature it was therefore concluded that the presence of zinc in the soot bulk inorganics was an indication that increased injector coking was more likely, it was also likely that the higher the level of zinc, the more significant the coking issue. Considering this, the ICP-MS results were combined with the exhaust soot concentration (Table 4.10) to estimate the mass of soot based zinc per engine cycle and the result is presented in Figure A9.5.



Figure A9.5: Estimated Mass of Z_n in the Cylinder Soot Per cycle for the Rated Condition Experiments (ICP-MS)

The results presented in Figure A9.5 suggest that at 19.5:1 compression, the mass of zinc found in the B100 soot was half that observed for both mineral fuels but that this increased significantly at 16.5:1 (this was thought to be through increased lubricant consumption). Thus, this agreed with the increase in the injector coking observed for this fuel. Unfortunately, the increase in zinc does not agree with the unchanged rate of power loss observed for the mineral fuels with the reduction in compression ratio. It is therefore concluded that the observed changes in soot bulk zinc with compression ratio reduction fail to explain all the observations (assuming that the exhaust manifold soot sample zinc concentration is representative of that in the cylinder). It is therefore postulated that the lower cylinder temperatures at 16.5:1 offset any increased coking potential from the zinc increase for the two mineral fuels, EN590 and PC9.

It is also possible these findings support the observations of Leedham et al. [329]. This is because the increase in soot zinc mass with compression reduction (illustrated in Figure A9.5) is believed to largely have come from increased lubricant consumption from blowby and the B100 lubricant fuel dilution at 16.5:1. Leedham et al. [329] concluded fuel borne zinc and not zinc from the lubricant caused accelerated coking.

A9.4 Concluding Remarks

Injector coking was observed to be 2-4 times more significant for the B100 fuel compared to the EN590 and PC9 fuels studied. Further, the B100 fuel sensitivity to coking increased with the reduction in compression ratio which was not the case for both mineral diesel fuels. It is concluded that the coking observations in this work for the B100 fuel must therefore be related principally to the fuel properties rather than any change in zinc concentration in the cylinder (whether fuel of lubricant borne). Argawal et al. [87] and others [330,336-339] state that the higher viscosity of biodiesel fuels causes the increased coking associated with such fuels and the viscosity of the B100 biodiesel used in this work was approximately double that of the mineral diesel fuels , Appendix 1 (Table A1.1).

Appendix			

'I am not discouraged because every wrong attempt discarded is a step forward.'

Thomas Edison

'When you are going through hell, keep on going.

Never, never, never give up.'

Winston Churchill