Source and Characterization of Particulate Matter from a Pilot-Ignited Natural Gas Fuelled Engine

by

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Abstract

With growing concern over particulate matter and gaseous emissions and stringent new emissions standards upcoming in 2007 for heavy duty transport vehicles, it has become essential to study the parameters that affect heavy duty vehicle emissions. At the University of British Columbia emissions from a heavy-duty engine running with Westport Innovations' high pressure direct injection of natural gas (HPDI) technology are studied. In this engine, a small quantity of diesel pilot fuel is injected prior to a main natural gas injection event to provide ignition. This study focuses on the effects of pilot fuel quantity, overall equivalence ratio and exhaust gas recirculation on particle mass, particle size, particulate soot fraction and on gaseous emissions. With HPDI, there is the question of how much of the particulate matter is pilot-derived; this question is addressed by using carbon-14 ($^{14}$C) tracing of biodiesel pilot fuel derived soot.

It was found that EGR, equivalence ratio and pilot quantity play an important role in particulate matter emissions, where the emissions increase by increasing any of these quantities. Particulate matter mass concentration is an order of magnitude higher at 25% EGR and high equivalence ratio than at low equivalence ratio without EGR. Particulate matter from this engine generally contains a larger fraction of soluble organic species than that from a typical diesel engine. The percentage of black carbon in particulate samples was found to range from approximately 5% at low load conditions without EGR to approximately 60-80% at high load with 25% EGR.

Particle structure can generally be described as agglomerates consisting of spherical primary particles of average size 10 - 25 nm. Particle size distributions definitely show evidence of a nucleation mode of particle formation (many small particles) and also a large number of larger particles likely formed due to particle-particle interaction (coagulation). EGR results in a larger average particle size.

Fossil fuels contain no $^{14}$C so using a biodiesel pilot fuel, naturally containing current carbon ($^{14}$C/C = $1.2 \times 10^{-12}$), enabled us to apportion the pilot fuel derived soot mass. The pilot fuel was found to contribute between 4 and 40% to soot emissions under the measured operating conditions. The highest contribution is found at low load without EGR. A very significant finding is that the pilot fuel is promoting black carbon formation from other sources within the combustion chamber (most likely natural gas). An increase in pilot fuel flow of 75%
causes an increase in soot emissions not derived from the pilot fuel of somewhere between 25% and 45% depending upon the engine operating condition. While the pilot-derived soot does not increase a large amount with increasing pilot fuel quantity, the soot derived from fossil sources does. This indicates that pilot fuel amount should be minimized and kept under tight control in HPDI combustion.
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Nomenclature and Acronyms

UBC: University of British Columbia
EPA: US Environmental Protection Agency
HPDI: High Pressure Direct Injection
SCRE: Single Cylinder Research Engine
TEOM: Tapered Element Oscillating Microbalance
TEM: Transmission Electron Microscopy
DMA: Differential Mobility Analyzer
SMPS: Scanning Mobility Particle Sizer
LII: Laser Induced Incandescence
FID: Flame Ionization Detector
NDIR: Non-Dispersive Infra-Red
CPC: Condensation Particle Counter
CNG: Compressed Natural Gas
TDC: Top Dead Center
DI: Direct Injection
CI: Compression Ignition
CA: Crank Angle
HRR: Heat Release Rate
EGR: Exhaust Gas Recirculation
\( \phi \): Equivalence Ratio
DOC: Diesel Oxidation Catalyst
DPF: Diesel Particulate Filter
STP: Standard Temperature and Pressure
PM: Particulate Matter
SOL: Solid Fraction of Particulate Matter Containing Elemental Carbon and Ash
EC: Elemental Carbon
BC: Black Carbon
Soot: Solid Fraction of Particulate Matter Containing Mainly Elemental Carbon
SOF: Soluble Organic Fraction of Particulate Matter
VOF: Volatile Organic Fraction
VF: Volatile Fraction
NVF: Non-Volatile Fraction
NO\(_2\): Nitrogen Oxides
tHC: Total Hydrocarbons
nmHC: Non-Methane Hydrocarbons
CO: Carbon Monoxide
O$_2$: Oxygen
CO$_2$: Carbon Dioxide
DR: Dilution Ratio
PDR: Primary Dilution Ratio
SDR: Secondary Dilution Ratio
AMS: Accelerator Mass Spectrometry
IRMS: Isotope Ratio Mass Spectrometry
$^{14}$C: Carbon-14 Isotope
$^{13}$C: Carbon-13 Isotope
$^{12}$C: Carbon-12 Isotope
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1. Introduction

Background
With increased vehicle traffic, if vehicle emission levels are not reduced, levels of atmospheric pollution will reach epic proportions. Some of the more polluted cities in the world (eg. Mexico city, Seoul, Buenos Aires, Santiago de Cuba, and Los Angeles) typically have frequent smog alerts making the living conditions almost unbearable for some residents. Mexico City experienced 327 days in 1996 that ozone levels exceeded Mexico standards and 182 days that PM$_{10}$ levels exceeded standards [1]. The city of Los Angeles experienced 68 days in 2003 that ozone levels exceeded US EPA one hour standards [2]. Air pollution is a global problem and will require global solutions.

Heavy duty transport vehicles contribute significantly to particulate and nitrogen oxide emissions. Particulate emissions have been associated with major health effects; acute effects such as respiratory problems and reduced visibility and chronic effects such as cancer, asthma, and severe respiratory diseases. Particle composition and size have been found to be large factors in their toxicology. Smaller particles can find their way through respiratory pathways into the lungs easier than larger particles. Certain particulate chemical compositions (in particular polycyclic aromatic hydrocarbons) have been shown to be carcinogenic and mutagenic [3].

Changes in vehicle design and operation are necessary to reduce these harmful emissions; governments have realized the pollution problem and committed to some drastic regulations over the next few years. By 2007 the EPA US2007 regulations call for a ten-fold decrease in particulate emissions and similarly drastic decreases in nitrogen oxides and hydrocarbons from heavy-duty on-road vehicles. Achieving these standards will require novel engine design and comprehensive research to determine effects of engine operation on emissions.

One of these novel engine concepts is under development by Westport Innovations Inc. The high pressure direct injection (HPDI) concept injects high pressure natural gas into the cylinder of an unmodified commercial heavy-duty diesel engine and a small quantity of diesel pilot fuel to initiate combustion, both through a single injector. This concept has been shown to reduce particulate matter emissions by 65% and nitrogen oxide emissions by 40% over an equivalently fuelled diesel engine. Unfortunately, even this large reduction in emissions will be insufficient to meet the US2007 standards without exhaust aftertreatment. Only certain pollutants can be removed with aftertreatment. Some semi-volatile particulate matter com-
pounds can be removed with diesel oxidation catalysts (DOC) and remaining particles can be removed to some degree with diesel particulate filters (DPF). NO\textsubscript{x} can be reduced by the use of a NO\textsubscript{x} catalyst. It is important to determine what portion of the particulate matter emissions are semi-volatile. It is also important to determine the size of particles that are emitted to be able to determine suitable pollutant treatment methods. Further work must be done to characterize emissions under a range of engine operating conditions to aid in the understanding of engine operation on emissions and to lead to possible strategies to reduce emissions.

Particulate Matter Background
Particulate matter is one general term that lumps together any type of particle in the liquid or solid phase coming from combustion exhaust gas. Particulate matter consists of a solid fraction (SOL), a soluble organic fraction (SOF) and a fraction of sulphate particulates. Particles leaving the engine prior to dilution consist mainly of solid particles. This solid fraction is often referred to as soot and consists of elemental carbon (EC) and ash. Elemental carbon is also often called black carbon (BC) or carbon black. The SOF consists mainly of unburned fuel and oil. The SOF is obtained by a specific process called Soxhlet extraction. If this process is not used to determine SOF it is not appropriate to call it SOF and it is more appropriately called volatile organic fraction (VOF). The SOF/VOF portion of total PM varies greatly from engine to engine and with engine operating condition. Typically SOF is the highest under low load and speed conditions and the lowest under high load and low engine speed [4].

Particle size distributions have been of great interest recently. Many studies in the past 10 years have determined that although new technology has reduced particulate emissions significantly, the number of smaller particles has increased significantly. It is these smaller particles that are of greater health concern [5]. The classification of particle size is as follows:

- PM\textsubscript{10} - particles less than 10 μm
- PM\textsubscript{2.5} - particles less than 2.5 μm
- Ultrafine particles - particles less than 100 nm
- Nanoparticles - particles less than 50 nm

Particles are formed by nucleation. These particles are said to be in the nuclei mode. Nuclei mode particles are all in the nanoparticle size range. Particles grow through coagulation and condensation/adsorption and are said to be in the accumulation mode during growth. The accumulation mode extends from the ultrafine particle range to the PM\textsubscript{10} range. Particle size
distributions have typically two peaks, one in the nuclei mode and one in the accumulation mode. The largest number of particles are typically found in the nuclei mode but these contribute least to the total particle mass. Particle counts from diesel engines range from $1 \times 10^6$ to $1 \times 10^9$ particles/cm$^3$. These numbers will vary widely from different engines and under different simulated dilution conditions and due to insufficient regulation on measurement methods it may not be possible to compare to other reported data [6].

**Previous Work by UBC Research Group**

Previous work by students at UBC showed interesting particulate matter emissions results. In 2001 Anne-Marie Baribeau studied the effects of injection pressure, timing and diesel fuel quantity on particulate matter emissions [7]. Particle mass emissions were characterized and the volatile organic fraction of filter-borne particulate matter was analyzed for “fuel-like” and “oil-like” components. Baribeau was unable to draw any conclusions on pilot fuel quantity effects on PM emissions. The VOF of total PM mass was found to be between 34 and 54% over the tested operating conditions. The effect of timing was inconclusive and it was found that increasing injection pressure reduced PM emissions.

In 2002, Tom Brakel studied the correlation between the tapered element oscillating microbalance (TEOM) and gravimetric filter analysis for measuring PM total mass [8]. It was found that the TEOM underestimated the mass by a factor of 1.43. Brakel also studied the effects of EGR on emissions and found that PM emissions did not increase significantly until an EGR fraction of approximately 15% is exceeded.

Anil Kumar Nair studied particulate matter structure using transmission electron microscopy in 2001 [9]. Peculiar grape-like particle agglomerates were imaged as well as more usual long-chain agglomerates.

**Goals of this Research**

This work builds on the research of these previous students by adding a more in depth look at particulate matter emissions. Particle size and mass were measured by several means to ensure accuracy and completeness. The effect of the pilot fuel was closely examined.

The main goals of this research were to:

1. Quantify the pilot fuel contribution to soot emissions
2. Establish repeatability in particulate matter data sampling. This includes addressing the poor TEOM/filter correlation that Brakel found.
3. Determine the effect of equivalence ratio, exhaust gas recirculation and pilot fuel quantity on particle mass, particle size and on gaseous emissions
4. Determine the soot fraction of total particulate matter under a range of engine operating conditions

This thesis has been organized into three main chapters, each of which are designed to be independent documents.

Chapter 2 presents research that establishes the independence of the particulate sampling system from the experimental results. This is a very important set of experiments that must be done to ensure that the dilution conditions are not affecting the measured particulate matter mass concentrations or size distributions.

Chapter 3 presents a set of experiments where the effects of different engine operating parameters on particulate matter mass emissions, particulate matter size distributions and gaseous emissions are investigated. The effects of equivalence ratio, exhaust gas recirculation and pilot fuel amount are investigated.

Chapter 4 presents research that has been done to quantify the pilot fuel contribution to soot emissions under different engine operating conditions. The diesel pilot fuel has been replaced with a biodiesel pilot fuel and the carbon-14 isotope in the biodiesel has been traced through to the soot using accelerator mass spectrometry.

Finally, Chapter 5 summarizes the main points in each of the three main chapters and attempts to tie all of the information together.
References


2. Effect of Dilution Ratio on Particulate Matter Measurement

2.1 Abstract

Determining the impact of dilution ratio on particle mass and size measurements is critical to the analysis of particulate matter data. The effect of dilution ratio ranging from 10 to 20 on particle mass and size was tested at four different engine-operating conditions. This research was carried out on the UBC Single Cylinder Research Engine (SCRE). The SCRE is fuelled by direct-injected natural gas; a small quantity of diesel pilot fuel initiates the combustion. The mass of particulate matter is measured with a Tapered Element Oscillating Microbalance (TEOM), an Aethalometer, and by gravimetric filter analysis. Particle size was determined with a Transmission Electron Microscope and with a Differential Mobility Analyzer.

Test results indicate that at dilution ratios below 10, the measured particle mass concentration varies significantly with dilution ratio but at dilution ratios between 10 and 20, particle mass concentration shows no significant variation. Dilution ratio does not have a significant effect on particle size in the nanoparticle range. Particle size and mass were found to be strongly dependent on equivalence ratio.

2.2 Introduction

Recent research showing the adverse health effects of small particles (< 100nm) has resulted in growing awareness within governmental agencies that emitted particulate matter size and mass must be measured and regulated. The United States Environmental Protection Agency (US EPA) has established procedures that researchers and automobile manufacturers must follow when sampling particulate matter [1]. One requirement is that enough dilution air must be mixed with the exhaust so that the sampling temperature is at or below 52°C. No mention of the actual dilution ratio (volume of diluted flow/volume of exhaust) is included in the regulation. Agencies strive to make regulations that should make a fair comparison between different applications and different engines. However, the current regulation may
Particulate matter (PM) is comprised of insoluble particles (mainly black carbon particles or “soot”) and a soluble organic fraction (SOF) consisting mainly of unburned fuel, engine oil and other products of incomplete combustion. It is this soluble fraction that can be influenced by the dilution process that occurs when the exhaust gas leaves the tailpipe and enters the atmosphere.

Filter sample mass may be affected by filter temperature and dilution ratio. MacDonald et al. [2] reported independent effects of dilution ratio and sampling temperature on sampled exhaust particulate mass concentration. MacDonald reported that either increasing the filter temperature at fixed dilution ratio or increasing the dilution ratio at a fixed filter temperature results in a decrease in total particulate mass collected. In addition to particle mass being affected by dilution ratio it has also been proven that the particle size distribution is also affected. Kittelson et al. [3] [4] have shown that one dilution ratio may promote particle nucleation and growth where another one may suppress it. This paper focuses on particle size and mass variations at dilution ratios ranging from 10 to 20 at constant sampling temperature.

2.3 Apparatus and Procedures

2.3.1 Engine

This research was carried out on UBC’s single-cylinder research engine (SCRE), a Cummins ISX series heavy-duty six-cylinder, four-stroke, direct-injection engine, modified by the manufacturer to operate on only one cylinder as described by McTaggart-Cowan et al. [5]. The engine’s rated speed is 1800 RPM; the single firing cylinder has a 19:1 compression ratio and a displacement of 2.5 L (bore=137 mm, stroke=169 mm). The combustion geometry was not modified from the stock Cummins ISX diesel engine design. Fuelling is provided by Westport Innovations Inc.’s HPDI natural gas direct-injection system [6] [7]. In the HPDI system, approximately 95% of the energy is supplied from the non-premixed combustion of natural gas, injected into the cylinder shortly before the piston arrives at Top Dead Center (TDC). A diesel ‘pilot’, injected shortly before the natural gas, initiates the combustion. The fuelling system provides natural gas and diesel to the dual-fuel, concentric-needle injector via the engine’s internal fuelling rails at pressures up to 25 MPa. The engine is configured to provide cooled exhaust gas recirculation (EGR).

The SCRE’s air supply is provided (at up to 300 kPa) by an industrial-style rotary-screw compressor. Exhaust gas is recirculated between the high-pressure intake and exhaust streams.
2.3. Apparatus and Procedures

through an EGR cooler and a variable flow-control valve. To maintain a positive pressure
gradient in the EGR loop, as well as to reproduce the back-pressure normally exerted by
a turbocharger, the exhaust line pressure is maintained approximately 10 kPa above the
intake pressure by a remote-control butterfly valve. The EGR flow is determined from the
measurement of the CO\textsubscript{2} concentration in the intake and exhaust streams using separate
NDIR instruments. Gaseous emissions are measured using NDIR (CO\textsubscript{2}, CO, CH\textsubscript{4}), FID
(tHC), paramagnetic (O\textsubscript{2}) and chemiluminescent (NO\textsubscript{x}) analyzers. In-cylinder pressure is
measured with a flush-mounted, water-cooled piezoelectric transducer. This measurement
is used to quantify the engine's load in terms of gross indicated quantities (eg. GIMEP,
GISFC). Brake-performance parameters are not representative of load due to high internal
friction exerted by the five non-firing cylinders.

Tests were carried out without EGR and with 25% (by mass) recirculated exhaust. The
engine speed was 1200rpm for all tests, while two gross-indicated mean-effective pressures
(GIMEP: a measure of the work done over the compression and power strokes only) (850 kPa
and 1200 kPa), and two equivalence ratios (\(\Phi = 0.4\) and 0.6) were tested. For this testing the
equivalence ratio is defined as the ratio of the actual and stoichiometric fuel to oxidizer ratios
in the combustion chamber, where the oxidizer includes the oxygen in both the ingested fresh
air and in the recirculated exhaust. By specifying the EGR fraction, the GIMEP, and (\(\Phi\)),
the engine's operating condition (fuel, air, EGR flows) is fully defined [8]. Throughout these
tests, the combustion timing was held constant by varying the timing of the diesel injection
so that 50% of the total heat release occurred at 10°ATDC. The timing of the natural gas
injection was fixed relative to the diesel injection.

2.3.2 Dilution System

A schematic of the dilution system is shown in Figure 2.1. A portion of the engine exhaust
branches off from the main exhaust duct and travels through a short transfer tube (transfer
tube 1 - flow rate \(\approx 35\) lpm). Most of this exhaust flow then bypasses the main dilution
system and travels through a back pressure regulated line. The portion of exhaust remaining
travels again through a short transfer tube (transfer tube 2 - flow rate \(\approx 3\) lpm) and then
passes through an orifice that is designed to give a high pressure drop so that the entire
sample line downstream of the orifice is at approximately atmospheric pressure (the pressure
drop in the piping is less than 30 kPa). A back-pressure regulator controls the pressure
upstream of the orifice and removes the influence of engine back-pressure from the sampling
system. After the exhaust sample passes through the orifice it is mixed with a diluent (nitro-
gen in this case) at a fixed flow rate of approximately 30 slpm. Control of the dilution ratio
is achieved by changing the pressure drop across the orifice with the back-pressure regulator.
The dilution ratio (DR) is determined by measuring the CO\textsubscript{2} concentrations in the exhaust
gas, the bottled N\textsubscript{2}, and the diluted flow.
The sample line has multiple ports where a portion of the diluted sample is drawn into each of the particulate matter measurement instruments. There is approximately two meters of mixing length, after diluent is mixed with raw exhaust, until a sample is drawn from the sample line. The entire system is heated and fully insulated to minimize thermophoretic particle losses to the walls. Particle mass was measured with a Tapered Element Oscillating Microbalance (TEOM, R&P series 1105) and an Aethalometer (Magee Scientific). The TEOM measures total particulate mass via a tapered element with a small filter connected to the end. The cantilever element oscillates at its natural frequency and this natural frequency can be related to the total mass collected on the filter. The Aethalometer measures black carbon on a filter tape by optical means. The TEOM inlet temperature was controlled between 50°C and 55°C for all test conditions. In addition to these two instruments for mass measurement, gravimetric analysis was also performed. Two teflon-coated quartz filters (Pallflex Emfab TX40H120-WW) in series collected particulate matter at a constant temperature of 45°C. The filters were weighed in a temperature (22±1°C) and humidity (35±2%) controlled room.
before and after sampling and allowed to equilibrate for at least 24 hours. The back-up filter mass collected was treated as a sampling artifact and subtracted from the primary filter mass.

Particle size was determined with a long-column Differential Mobility Analyzer (DMA) of similar design to that described by Knutson and Whitby [9], combined with a Grimm ultra-fine Condensation Particle Counter (CPC). Particle size distributions in the diameter range of 10 nm and 800 nm were measured. Fuchs' charging theory was used to calculate charging probabilities for the Po-210 neutralizer. Data inversion was performed including multiple charging of up to four charges and the inverted distribution was constrained to be positive. Count efficiency of the particle counter is nearly 100% for all particle sizes above 10 nm. However, the diffusional losses within the DMA column are significant for particle sizes below 20 nm [9] [10].

In addition to determining particle size with the DMA, Transmission Electron Microscopy (TEM) was used to image typical particles. Samples were collected on lacy carbon TEM grids (Ted Pella Inc, part no. 01881-FX1). Diluted exhaust was sampled at approximately 100 ml/min through the grid for 1 min at equivalence ratio of 0.6 (with and without EGR), for 5 min at equivalence ratio of 0.4 with EGR and for 10 min at equivalence ratio of 0.4 without EGR. The objective was to get a single layer of particles so that the structure could easily be examined with the microscope.

2.4 Results - Particle Mass

Black carbon (BC) fraction of the total particulate matter measured by the Aethalometer ranged from 15% at low equivalence ratio without EGR to approximately 40% at high equivalence ratio with EGR. In a later set of experiments, the aethalometer data was corrected using the method given in Appendix A. A broader range of black carbon fractions were found; BC ranged from 5% at low equivalence ratio (0.4) without EGR to 65% at high equivalence ratio (0.6) and 25% EGR. Exhaust particulate matter from diesel engines typically contains a much higher fraction of BC.
2.4. Results - Particle Mass

(a) DR = 1-10, $\Phi = 0.5$, no EGR.

(b) DR = 10-20

**Figure 2.2**: PM MC as a Function of Dilution Ratio
Particle mass concentration increases with increasing equivalence ratio and increasing EGR fraction. The measured particle mass concentration was approximately 20 times higher at $\Phi = 0.6$ and 25% EGR compared to $\Phi = 0.4$ without EGR as shown in Figure 2.2(b). The particulate mass concentrations have been corrected for dilution ratio and reported as per unit volume of raw exhaust (undiluted) at STP (21.1°C, 101.3 kPa).

Initial testing showed that measurements by the TEOM (held at 50°C) were very sensitive to dilution ratio (Figure 2.2(a)). TEOM reliability was an issue during the initial testing (it was found that there were some leaks) and the issues were consequently resolved. Results at very low dilution ratio may have been affected by water adsorption and are far from typical sampling conditions. In addition, particulate matter emissions vary greatly from injector to injector. Due to these issues, particulate matter mass concentrations can not be compared between Figures 2.2(a) and 2.2(b).

The results of the present study, which focused on more conventional dilution ratios of 10-20, are shown in Figure 2.2(b). No significant variation with dilution ratio at constant TEOM temperature was observed for any of the operating conditions tested. These results suggest that as long as the dilution ratio is somewhere in the range of 10-20, the measured particulate matter mass concentrations will not be affected by dilution ratio.

2.5 Results - Particle Size

Figure 2.3 shows the effect of dilution ratio and equivalence ratio on the measured particle size. Particle size is given as “Mobility Diameter”; this is the diameter of a spherical particle with the same electrical mobility. Further investigation is required into the effects of EGR fraction on particle size. Particle number concentration has been corrected by the total dilution (primary and secondary) and is reported as number of particles per cubic centimeter of raw exhaust gas at STP.
Particle number concentration is approximately 3 to 4 times greater at an equivalence ratio of 0.6 than at an equivalence ratio of 0.4. The largest number of particles is found at the smallest particle size. The results show that particle size and number in the ultrafine particle range (< 100 nm) is not highly dependent upon the dilution process for this HPDI engine operation. This suggests that particles are formed and coagulate in the combustion chamber or exhaust line and are mixed with enough exhaust gases and excess air that coagulation ceases shortly after combustion. Since the particulate matter contains a large fraction of semi-volatile particulate matter it was expected that a difference in particle number concentration due to dilution ratio would only be observed at very small particle sizes, due to particle nucleation. Since particle number was not affected by dilution ratio, we may conclude that either particle formation is not occurring in the dilution tunnel or that these particles are smaller than 10 nm and hence are not being detected.

In the particle size range of 100 nm to 300 nm there were some differences in particle number distribution: whether this is due to dilution ratio or some other effect is not clear. There is a possibility of contamination in the larger particle size range (> 300 nm) as the raw particle counts were insensitive to dilution ratio and equivalence ratio; this is still under...
investigation. There is a possibility that the larger particles are artifacts caused by arcing in the DMA column. Interestingly, this result is contradictory to the results reported by Kittelson et al. [3], who reported a significant effect of dilution ratio on particle size in the ultrafine particle range (< 100 nm) and little or no effect for particles larger than 100 nm. Whether this difference is due to the primary fuel (Kittelson’s results are for a diesel-fuelled engine) requires further study.

**Figure 2.4:** TEM images for two grid samples

Figure 2.4 shows two TEM images for $\Phi = 0.4$ without EGR for high and low dilution ratio. The webbing that can be seen is the lacey carbon on the TEM grid. Both of the images show a number of large particle agglomerates consisting of many spherical primary particles. Although the primary particle size is different for each of these different agglomerates, each agglomerate consists mainly of primary particles of the same size. The primary particle size ranges from about 10 nm to 50 nm in these images. The collection efficiency of the TEM grid is not high for small particles, which may explain why many small single particles or shorter agglomerate chains are not collected on the grid.
2.6 TEOM Correlation with Gravimetric Measurements

The TEOM and gravimetric measurements showed excellent agreement, with a linear regression: 

$$m_{TEOM}[mg/m^3] = 1.05m_{filter} - 0.91, \quad R^2 = 0.983.$$ 

It is believed that the good correlation between the TEOM mass and the filter mass is due to heating the TEOM inlet to approximately 55°C and to the method of filter treatment that was used. As outlined in the procedure, a back-up filter was used to sample all vapors that are trapped in the filters and the mass of this filter was subtracted from the primary filter. Many papers suggest that the TEOM underestimates the particulate mass by approximately 10% - 30% due to moisture, temperature and pressure effects [11] [12] [13] [14] [15]. Here we find that the TEOM overestimates the particulate mass by approximately 5%.

![Figure 2.5: TEOM Correlation with Gravimetric Measurements](image)
2.7 Conclusions

1. At very low dilution ratios there was a large effect of dilution ratio on measured particulate matter mass concentration; however, dilution ratios in the range of 10 and 20 were not sensitive to this effect.

2. Dilution ratio did not have a significant influence on overall particulate matter size in the ultrafine particle range (< 100 nm).

3. Particle mass concentration was strongly dependent on equivalence ratio and EGR fraction; the mass concentration increased significantly by increasing either of these parameters.

4. The number of particles of a given size increased with increased equivalence ratio. The size distribution remained proportional. The effect of EGR on particle size distribution is still under investigation.

5. Based on TEM images, primary particle size varies between agglomerates from the same sample but appears to be nearly the same in each agglomerate chain.

References


3.1 Abstract

Growing health concern over emissions from heavy duty compression ignition engines has resulted in stringent future emissions regulations. By 2007 the EPA US2007 regulations call for a ten-fold decrease in particulate emissions and similarly drastic decreases in nitrogen oxides and hydrocarbons from heavy-duty on road vehicles. To achieve these standards, comprehensive research must be done to determine effects of engine operation on emissions.

In this work, the effects of equivalence ratio, exhaust gas recirculation and pilot fuel type and quantity on particulate matter and gaseous emissions were investigated on a modern heavy-duty, direct-injection, natural gas fuelled engine. The main objective was to characterize the effects of these engine operating parameters on total particulate matter (PM) mass, PM structure, PM size distribution, black carbon fraction of PM, and on gaseous emissions. This research was carried out on the UBC Single Cylinder Research Engine (SCRE). The SCRE is fuelled by direct-injected natural gas; a small quantity of diesel pilot fuel initiates the combustion. The mass of particulate matter is measured with a Tapered Element Oscillating Microbalance (TEOM), an Aethalometer, and by gravimetric filter analysis. Particle size was determined with a Transmission Electron Microscope and with a Differential Mobility Analyzer.

Particulate matter and carbon monoxide mass increase with increasing equivalence ratio, exhaust gas recirculation and with increasing pilot fuel amount. Dramatic increases in PM and CO were observed going from low equivalence ratio without EGR to high equivalence ratio with EGR. EGR reduces NO\textsubscript{x} but increases hydrocarbons emissions. Particle structure can generally be described as agglomerates consisting of spherical primary particles. Average primary particle size was found to be around 10 - 25 nm. Particle size distributions definitely show evidence of a nucleation mode of particle formation (many small particles) and also a large number of larger particles likely formed due to particle to particle interaction (coagulation). EGR causes particles in the range of 100 nm - 300 nm range to increase.
3.2. Introduction

This is believed to be due to particle growth through coagulation with recirculated exhaust particles. It was found that the amount of black carbon in the particulate sample (found from taking the ratio of Aethalometer measured mass to TEOM measured mass) ranges from approximately 5% at low load conditions without EGR to approximately 60-80% at high load with 25% EGR.

3.2 Introduction

With growing concern over particulate matter and gaseous emissions and with stringent emissions standards upcoming in 2007 for heavy duty transport vehicles, it has become essential to study the parameters that affect heavy duty vehicle emissions. Table 3.1 shows the US EPA emissions regulations for the period of 2007-2010 compared with the current standards.

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>2004 g/bhp-hr (g/kWh)</th>
<th>2007 - 2010 g/bhp-hr (g/kWh)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM</td>
<td>0.1 (0.13)</td>
<td>0.01 (0.013)</td>
</tr>
<tr>
<td>NOx</td>
<td>4.0 (5.36)</td>
<td>0.2 (0.268)</td>
</tr>
<tr>
<td>NMHC</td>
<td>1.3 (1.75)¹</td>
<td>0.14 (0.188)</td>
</tr>
<tr>
<td>CO</td>
<td>15.5 (20.78)</td>
<td>15.5 (20.78)</td>
</tr>
</tbody>
</table>

Table 3.1: Upcoming and Current Emission Regulations for Heavy-Duty On-road Vehicles

¹ Total Hydrocarbons

The particulate matter standard is to be fully implemented in 2007 and the NO_x and HC standards are to begin implementation in 2007 and be fully implemented by 2010. The NO_x and HC standards will be phased in at 50% for the first three years (i.e. 50% of new on-road heavy duty vehicles must meet the standard) and then 100% in 2010.

By 2007 the EPA US2007 regulations call for a ten-fold decrease in particulate emissions; from 0.13 g/kWh to 0.013 g/kWh. Not only does the absolute amount of particulate emitted provide cause for concern but also the size and type of particles that are emitted. Recent studies suggest that smaller particles in the ultrafine particle range (< 100 nm) are the most harmful to human beings because they are so small that they can easily travel through the respiratory pathways to the lungs. Studies have shown one chemical class to be particularly harmful, Polycyclic Aromatic Hydrocarbons (PAH) [1]. PAH’s can be in particle or gaseous
form. PAH's have been found to be carcinogens and mutagens [2].

Two other types of emissions from heavy duty compression ignition engines are a source of concern; nitrogen oxides (NO\textsubscript{x}) and hydrocarbons (tHC). Nitrogen oxides and hydrocarbons in combination through photochemical reactions form ozone (one component of smog). Smog in densely populated areas has been responsible for severe respiratory problems, vegetation damage and building damage. In addition to being smog producers, hydrocarbons are also greenhouse gases. Nitrogen oxides themselves are acute irritants, can affect visibility, can affect textile strength and have been known to suppress growth of plants [3].

Particulate matter (PM) can be classified as consisting of a solid fraction consisting mainly of elemental carbon (EC) or black carbon (BC) otherwise known as “soot” and a soluble organic fraction (SOF). The SOF includes any semivolatile organic compounds that condense during the atmospheric dilution process. Typically these compounds are associated with unburnt lubricating oil and unburnt fuel. The soot fraction is mainly pure carbon developed in fuel-rich pockets during combustion. Soot particles are generally aggregates consisting of nearly all spherical primary particles.

In this work, the effects of equivalence ratio, exhaust gas recirculation and pilot fuel type and quantity on particulate matter and gaseous emissions were investigated on a modern heavy-duty direct injection natural gas fuelled engine. The main objective was to characterize the effects of these engine operating parameters on particulate matter structure, PM size distribution, black carbon fraction of PM, total PM mass and on gaseous emissions.

### 3.3 Apparatus and Procedures

#### 3.3.1 Engine

This research was carried out on UBC’s single-cylinder research engine (SCRE), a Cummins ISX series heavy-duty six-cylinder, four-stroke, direct-injection engine, modified by the manufacturer to operate on only one cylinder as described by McTaggart-Cowan et al. [4]. The engine’s rated speed is 1800 RPM; the single firing cylinder has a 19:1 compression ratio and a displacement of 2.5 L (bore=137 mm, stroke=169 mm). The combustion geometry was not modified from the stock Cummins ISX diesel engine design. Fuelling is provided by Westport Innovations Inc.’s HPDI natural gas direct-injection system [5] [6]. In the HPDI system, approximately 95% of the energy is supplied from the non-premixed combustion of natural gas, injected into the cylinder shortly before the piston arrives at Top Dead Center (TDC). A diesel ‘pilot’, injected shortly before the natural gas, initiates the combustion. The
fuelling system provides natural gas and diesel to the dual-fuel, concentric-needle injector via the engine’s internal fuelling rails at pressures up to 25 MPa. The engine is configured to provide cooled exhaust gas recirculation (EGR).

The SCRE's air supply is provided (at up to 300 kPa) by an industrial-style rotary-screw compressor. Exhaust gas is recirculated between the high-pressure intake and exhaust streams through an EGR cooler and a variable flow-control valve. To maintain a positive pressure gradient in the EGR loop, as well as to reproduce the back-pressure normally exerted by a turbocharger, the exhaust line pressure is maintained approximately 10 kPa above the intake pressure by a remote-control butterfly valve. The EGR flow is determined from the measurement of the CO₂ concentration in the intake and exhaust streams using separate NDIR instruments. Gaseous emissions are measured using NDIR (CO₂, CO, CH₄), FID (tHC), paramagnetic (O₂) and chemiluminescent (NOₓ) analyzers. In-cylinder pressure is measured with a flush-mounted, water-cooled piezoelectric transducer. This measurement is used to quantify the engine's load in terms of gross indicated quantities (eg. GIMEP, GISFC). Brake-performance parameters are not representative of load due to high internal friction exerted by the five non-firing cylinders.

### 3.3.2 Gaseous Emission Instruments

Gaseous emissions are measured using non-dispersive infra-red (CO₂, CO, CH₄), flame ionization detector (tHC), paramagnetic (O₂) and chemiluminescent (NOₓ) analyzers. Table 3.2 gives a summary of the gaseous emission instruments.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Analyzer</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>Beckman 880</td>
</tr>
<tr>
<td>CO₂</td>
<td>California Analytical Model 100</td>
</tr>
<tr>
<td>CO</td>
<td>Siemens 21P</td>
</tr>
<tr>
<td>CH₄</td>
<td>Siemens 22P</td>
</tr>
<tr>
<td>tHC</td>
<td>Ratfisch RS55</td>
</tr>
<tr>
<td>O₂</td>
<td>Siemens Oxymat 5E</td>
</tr>
<tr>
<td>NOₓ</td>
<td>Advanced Pollution Instrumentation Model 200AH</td>
</tr>
</tbody>
</table>

**Table 3.2: Gaseous Analyzers**

Each of the analyzers were calibrated before testing and the calibration was verified after testing to ensure good data collection. Raw exhaust is sampled via a heated and fully insulated sample line directly from the engine during testing. Total hydrocarbon sample is first
taken from the sample line and heated in the analyzer the remaining gas passes through a condenser to remove water and is then directed to the other instruments. All emissions are reported in gross indicated specific terms.

### 3.3.3 Dilution System

A schematic of the dilution system is shown in Figure 3.1. A fraction of the engine exhaust is separated from the main exhaust stream and travels through a short transfer tube. It then passes through an orifice that is designed to give a high pressure drop so that the entire sample line downstream of the orifice is at approximately atmospheric pressure (the pressure drop in the piping is less than 30 kPa). A back-pressure regulator controls the pressure upstream of the orifice and removes the influence of engine back-pressure from the sampling system. After the exhaust sample passes through the orifice it is mixed with a clean dry diluent (nitrogen in this case) at a fixed flow rate of approximately 30 slpm. Control of the dilution ratio is achieved by changing the pressure drop across the orifice with the back-pressure regulator.

The sample line has multiple ports where a portion of the diluted sample is drawn into each of the particulate matter measurement instruments. There is approximately two meters of mixing length, after diluent is mixed with raw exhaust before a sample is drawn from the sample line. The entire system is heated and fully insulated to minimize thermophoretic particle losses to the walls. The residence time before a sample is taken from the main sample line is 3 s as recommended by European Commission (Directorate General Transport and Environment) [7].
3.3. Apparatus and Procedures

3.3.4 Particle Instruments

Particle mass was measured with a Tapered Element Oscillating Microbalance (TEOM, R&P series 1105), an Aethalometer (AE21 Magee Scientific), and by gravimetric filter analysis. Particle size was determined by a Differential Mobility Analyzer (DMA) combined with a Condensation Particle Counter (CPC) and by using transmission electron microscopy (TEM) to view particles collected on TEM grids.

Tapered Element Oscillating Microbalance (TEOM)
The TEOM measures total particulate mass via a tapered element with a small filter connected to the end. The cantilever element oscillates at its natural frequency and this natural frequency can be related to the total mass collected on the filter by,

\[
\Delta m = \frac{k_0}{F_1^2 - F_0^2} \tag{3.1}
\]
3.3. Apparatus and Procedures

where,

- $k_0$ is a calibration constant
- $F_0$ is the frequency of oscillation of the tapered element at the last measured time
- $F_1$ is the current frequency of oscillation of the tapered element

From this equation, the change in mass over a certain time step is obtained. Dividing this by the volumetric sample flow rate into the TEOM, the mass concentration can be obtained in real time.

The TEOM inlet temperature was kept between 50°C and 58°C during testing, resulting in a TEOM head temperature (internal) of between 48°C and 50°C.

Aethalometer
The Aethalometer measures black carbon on a filter tape by optical means. Model AE21, Magee Scientific, has two light channels: one to measure black carbon and one UV channel. The UV channel is supposed to measure oily matter on the filter paper as well as black carbon but this has proved to be problematic in the past. Therefore the UV channel was turned off for all of the experiments. Light of wavelength 880 nm is passed through a quartz filter paper. Two detectors monitor the light transmission through the filter; one monitors the light passing through a spot with collected particulate and one monitors a clean spot on the filter paper to establish a zero reference point (so the measurement is not affected by fluctuations in light intensity). The factory set optical cross section is 16.6 m²g⁻¹ for this instrument and this was not altered.

Obtaining an accurate mass concentration of black carbon is complicated with the Aethalometer. Typically investigators apply two different correction factors to the mass reading: one to correct for multiple scattering of the light beam at the filter fibers in the unloaded filter, and the other to correct for an underestimation of black carbon due to excess loading on the filter paper ("Shadowing Effect"). Refer to papers by Weingartner et al. [8], and Niessner et al. [9] [10]. The raw data obtained here from the Aethalometer was corrected for multiple scattering of the light beam at the filter fibers and for the Shadowing Effect. Details of the correction are in Appendix A.

Gravimetric Analysis
Two teflon-coated quartz filters (Pallflex Emfab TX40H120-WW) in series (one primary and one back-up filter) collected particulate matter at a constant temperature of 45°C. The filters were weighed in a temperature (22 ± 1°C) and humidity (35± 2%) controlled room before and after sampling and allowed to equilibrate for between 24 and 48 hours.
The problem with using quartz filters for sampling is that they have a large specific surface area upon which adsorption of gases can occur. The amount of adsorbed organic vapor on the sampling filter is often estimated by placing a second filter in series with the first. The first filter samples the total mass; the particulate matter and adsorbed organic vapor and the second filter only represents the adsorbed organic vapor. The mass collected on the back-up filter in this experiment was treated as a sampling artifact and subtracted from the primary filter mass. Many researchers take this approach as discussed in the review article by Turpin et al. [11].

**Differential Mobility Analyzer (DMA)**

Particle size was determined with a long-column Differential Mobility Analyzer (DMA) of similar design to that described by Knutson and Whitby [12], combined with a Grimm Ultrafine Condensation Particle Counter (CPC).

The purpose of the DMA is to separate particles of a known size from the incoming aerosol stream. The incoming aerosol first passes through a Po-210 neutralizer in which the aerosol particles are exposed to a large concentration of bipolar ions. The particles and ions reach a state of equilibrium and the particles also carry a bipolar charge distribution [13] [14]. These particles then enter the DMA (Electrostatic Classifier).

Figure 3.2 shows a schematic of the DMA. The polydisperse aerosol enters at the top of the column along with a particle free sheath air stream. The particles travel at the same velocity as the sheath air streamlines. There is a rod in the center of the column that is charged with a voltage ranging from 10-10000 V. The positively charged particles will tend to migrate toward the negatively charged rod depending upon their electrical mobility (which depends upon particle size and its' charge). There is a slot near the end of the rod where a narrow particle size range will be entrained into. These particles travel to the CPC to be counted.

As the aerosol enters the CPC it is saturated with alcohol as it passes over a hot alcohol bath. The vapor saturated aerosol then enters a condenser where the alcohol condenses onto the particles and the particles are grown into droplets large enough to be detected optically by lasers.

Each scan (voltage increased from 10 V to 10000 V) of the DMA takes approximately 6.5 min. At least two complete scans were performed at each of the test points. The repeatability between different scans at the same operating condition was excellent. Relative standard error in number concentration between scans at the same test point was at most 7%.
Particle size distributions in the diameter range of 10 nm and 800 nm were measured. Fuchs’ charging theory was used to calculate charging probabilities for the Po-210 neutralizer [14] [13] [15]. Data inversion was performed including multiple charging of up to four charges and the inverted distribution was constrained to be positive. Count efficiency of the particle counter is nearly 100% for all particle sizes above 10 nm. However, the diffusional losses within the DMA column are significant for particle sizes below 20 nm [12] [15].

**Transmission Electron Microscopy**

In addition to determining particle size with the DMA, Transmission Electron Microscopy (TEM) was used to image typical particles. Samples were collected on lacey carbon TEM grids (Ted Pella Inc, part no. 01881-FX1). The TEM grid was placed inside a 1/8” Swagelok tube fitting and attached to a 1/8” sample port taken off of the main diluted exhaust sample line. A low-flow suction pump was placed after the grid to draw a flow of approximately 100 ml/min through the grid. Sample time was varied according to particulate emission
rates in order to achieve a single layer of particles on the grid where possible. Sample times ranged from 10 seconds to 10 minutes.

This sample method was chosen over the more traditional method of thermophoretic deposition on a cool grid because the temperature gradient between the grid and the diluted exhaust was not very large (at most 40°C). Traditionally, undiluted exhaust at high temperature is sampled where there is a large gradient between the exhaust and the grid surface. During the dilution process, particles grow due to condensation or coagulation and new particles nucleate. Therefore sampling raw exhaust is an unrealistic representation of the actual particle structure in the atmosphere.

There are two problems with the TEM collection/analysis method. Firstly, the grid is placed inside the column of the microscope where it is subjected to a vacuum. This may drive off any semivolatile species that were near their vapor pressure at atmospheric pressure and hence create another artifact of the method [16]. The other issue is the collection efficiency of the grid. Particles are collected onto the grid via three mechanisms: diffusion, interception and impaction. Small particles are transported mainly by diffusion whereas larger particles are transported mainly by interception and impaction. Calculations show that due to the geometry of the grid, the efficiency of collecting small particles (5-100 nm) is very small, < 5% (primary mechanism: diffusion). Therefore we do not expect to see any particles less than 100nm collected on the grid. Larger particles will not diffuse to the carbon webbing on the grid fast enough to be collected by this mechanism but they will be collected by interception and impaction with the grid. Transmission Electron Microscopy is not a very robust method for determining actual particle size distributions. However, it provides excellent qualitative insight into primary particle size and agglomerate structure.

3.3.5 Testing Conditions and Procedures

This section describes the operating points tested and the dilution conditions.

Experimental Design
Testing was performed with biodiesel and diesel pilot fuels with the goal of comparing the emissions generated by using different pilot fuels. The testing was broken down into 4 blocks: blocks 1 and 4 with diesel pilot fuel and blocks 2 and 3 with biodiesel pilot fuel. To check whether there would be injector deterioration, blocks 1 and 4 are compared to characterize any changes. Table 3.3 gives the complete test matrix. The experiment consisted of a full factorial set of tests with 3 factors: equivalence ratio, EGR, and pilot fuel mass flow. There are 8 operating points and each point was repeated 3 times per block. Test points were randomized within blocks. In total 96 test points were taken.
3.3. Apparatus and Procedures

<table>
<thead>
<tr>
<th></th>
<th>Φ</th>
<th>EGR (%)</th>
<th>$\dot{m}_{\text{pilot}}$ (kg/hr)</th>
<th>Speed (rpm)</th>
<th>IMEP (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.4</td>
<td>0</td>
<td>0.15</td>
<td>1200</td>
<td>850</td>
</tr>
<tr>
<td>2</td>
<td>0.4</td>
<td>25</td>
<td>0.15</td>
<td>1200</td>
<td>850</td>
</tr>
<tr>
<td>3</td>
<td>0.4</td>
<td>0</td>
<td>0.25</td>
<td>1200</td>
<td>850</td>
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<tr>
<td>4</td>
<td>0.4</td>
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<td>0.25</td>
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<td>0.15</td>
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<td>1200</td>
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<td>6</td>
<td>0.6</td>
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<td>1200</td>
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<td>0.6</td>
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<td>0.25</td>
<td>1200</td>
<td>1200</td>
</tr>
<tr>
<td>8</td>
<td>0.6</td>
<td>25</td>
<td>0.25</td>
<td>1200</td>
<td>1200</td>
</tr>
</tbody>
</table>

Table 3.3: Operating Conditions Tested

Engine Operation
Tests were carried out without EGR and with 25% (by mass) recirculated exhaust. The engine speed was 1200 rpm for all tests, while two gross-indicated mean-effective pressures (GIMEP: a measure of the work done over the compression and power strokes only) (850 kPa and 1200 kPa), and two equivalence ratios (Φ) (0.4 and 0.6) were tested. The equivalence ratio is defined here as the ratio of the actual and stoichiometric fuel to oxidizer ratios in the combustion chamber, where the oxidizer includes the oxygen in both the ingested fresh air and in the recirculated exhaust.

The biodiesel used was World Energy's soy-based biodiesel and it was mixed at UBC with diesel (43% by volume biodiesel mixture). Table 3.4 shows the composition and properties of the biodiesel.

| Cetane number | 52.9 |
| Flash point   | 113°C |
| Kinematic viscosity | 3.887 cSt @ 40°C (3.887x10^-6 m^2/s) |
| Gross Heat of Combustion | 17081.7 Btu/lb (39648.7 kJ/kg) |
| Elemental Analysis (% mass) | 77.84% C, 11.90% H |

Table 3.4: Biodiesel Properties - B100 World Energy

By specifying the EGR fraction, the GIMEP, and Φ, the engine's operating condition (fuel, air, EGR flows) is fully defined [17]. Throughout these tests, the combustion timing was held constant by varying the timing of the diesel injection so that 50% of the heat release occurred at 10° ATDC. The diesel pilot was injected 1.8 ms before the natural gas, hence the timing of the natural gas injection was fixed relative to the diesel injection. The natural gas composition is given in Table 4.2.
3.3. Apparatus and Procedures

<table>
<thead>
<tr>
<th>Compound</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Butane (C₄H₁₀)</td>
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</tr>
<tr>
<td>i-Butane (C₄H₁₀)</td>
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</tr>
<tr>
<td>i-Pentane (C₅H₁₂)</td>
<td>0.03</td>
</tr>
<tr>
<td>n-Pentane (C₅H₁₂)</td>
<td>0.02</td>
</tr>
<tr>
<td>Hexane (C₆H₁₄)</td>
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<td>Heptane (C₇H₁₆)</td>
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<tr>
<td>Octane (C₈H₁₈)</td>
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</tr>
<tr>
<td>Nitrogen (N₂)</td>
<td>1.91</td>
</tr>
<tr>
<td>Methane (CH₄)</td>
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</tr>
<tr>
<td>Carbon Dioxide (CO₂)</td>
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<td>Ethane (C₂H₆)</td>
<td>1.85</td>
</tr>
<tr>
<td>Propane (C₃H₈)</td>
<td>0.48</td>
</tr>
</tbody>
</table>

Table 3.5: Natural Gas Composition

**Dilution Ratio**

All instruments sample exhaust that has been diluted by either a primary dilution or a primary plus secondary dilution. The TEOM, filters for gravimetric analysis, and TEM grids sample primary diluted exhaust. The Aethalometer and the DMA have sample streams diluted further by a secondary dilution. Whether the instrument samples more dilute exhaust is just determined by the levels of particulate that each of these instruments can measure.

Dilution ratio is defined as,

\[
DR = 1 + \frac{n_{\text{diluent}}}{n_{\text{exhaust}}} \tag{3.2}
\]

Where \( n_{\text{diluent}} \) is the molar flow rate of diluent (in this case bottled nitrogen) and \( n_{\text{exhaust}} \) is the molar flow rate of exhaust.

The primary dilution ratio (PDR) is determined by measuring the CO₂ concentrations in the exhaust gas, the bottled N₂, and in the diluted flow,

\[
PDR = \frac{[CO₂]_{\text{exh,wet}} - [CO₂]_{\text{diluent,wet}}}{[CO₂]_{\text{total,wet}} - [CO₂]_{\text{diluent,wet}}} \tag{3.3}
\]

The secondary dilution ratio (SDR) was determined by measuring the dilution flow rate with a primary standard flow meter. Knowing the volumetric flow rate of the dilution air and the flow rates into the Aethalometer and the DMA, the secondary dilution ratio can be
determined. This method is not as robust as measuring the difference in CO₂ concentrations but was the only available method as the CO₂ analyzers were dedicated to measuring concentration of CO₂ in the primary diluted exhaust.

The primary dilution ratio was fixed at approximately 12 for all tests and the secondary dilution ratio was approximately 10, resulting in a total dilution ratio of approximately 120 for the flow going to the Aethalometer and the DMA. The total dilution ratio was kept low to minimize background noise in the DMA readings.

3.4 Results and Discussion

3.4.1 Particulate Matter Mass Emissions

Figure 3.3 shows the total particulate matter mass concentration for each of the operating conditions and Figure 3.4 shows the black carbon mass concentration. Black carbon mass concentration has been corrected according to the procedure in Appendix A.
3.4. Results and Discussion

Figure 3.3: Total Particulate Mass Concentration

With the exception of the BC biodiesel data, each bar represents the average of 6 data points and the error bar represents + (maximum-average) and - (average-minimum). The reported error is due to the correction method and the variability between repeated data points. The biodiesel BC bars are an average of only 3 data points as one of the data sets was discarded due to unacceptable errors. The secondary dilution system was not operating correctly for block 2 of testing so the Aethalometer readings were incorrect.
3.4. Results and Discussion

Effect of Equivalence Ratio
It can be seen from Figure 3.3 that there is larger amount of total particulate matter at higher equivalence ratio. Particulate matter is formed in the fuel-rich areas inside the combustion chamber. Richer overall mixtures will tend to increase the number of fuel rich pockets inside the cylinder. An increase in equivalence ratio also reduces the amount of excess oxygen in the cylinder available to oxidize the soot. We see the total PM increase from approximately 0.02 g/GikWh to 0.05 g/GikWh going from $\Phi = 0.4$ to 0.6 without EGR and with EGR we see total PM changing from 0.03 g/GikWh to 0.15 g/GikWh. Total PM without EGR approximately doubles going from low to high equivalence ratio on a g/GikWh basis but the absolute emissions actually go up by a factor of approximately 3.5. With EGR the PM emissions on a g/GikWh basis increase five-fold going from low to high equivalence ratio but the actual absolute mass emissions increase by nearly a factor of 7.

Black Carbon Fraction
The amount of black carbon in the particulate sample ranges from approximately 5% at low
load conditions without EGR to approximately 60-80% at high load with 25% EGR. This trend can be seen in Figure 3.5. It should be mentioned that this data can not be compared to the data in Chapter 2 as the aethalometer data was not corrected in Chapter 2 and the operating conditions were different.

![Figure 3.5: Black Carbon Fraction (Comparison Between TEOM and Aethalometer Mass Measurements)](image)

The error bars on the Aethalometer black carbon data represent a minimum and maximum based upon error that may have been introduced in the correction method. To test whether the correction method used was reliable, twelve quartz filters were analyzed for elemental carbon (EC) and organic carbon (OC) at Natural Resources Canada (NRCan). The comparison between the EC/OC analysis and the Aethalometer vs. TEOM mass is presented in Table 3.6. The correlation is not good for one of the data points: $\Phi = 0.4, 25\%$EGR, high pilot flow. However, it is apparent that the correlation is reasonable for the other data points and therefore it can be concluded that the method used to correct the Aethalometer data is effective.
3.4. Results and Discussion

<table>
<thead>
<tr>
<th>Test Point</th>
<th>EC/TC</th>
<th>BC/TPM</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Phi=0.4, 0%$EGR, Low pilot</td>
<td>8.7</td>
<td>7.3</td>
</tr>
<tr>
<td>$\Phi=0.4, 25%$EGR, Low pilot</td>
<td>32.5</td>
<td>33.3</td>
</tr>
<tr>
<td></td>
<td>23.2</td>
<td>25.8</td>
</tr>
<tr>
<td>$\Phi=0.4, 25%$EGR, High pilot</td>
<td>37.5</td>
<td>60.1</td>
</tr>
<tr>
<td>$\Phi=0.6, 0%$EGR, Low pilot</td>
<td>46.5</td>
<td>55.3</td>
</tr>
<tr>
<td></td>
<td>50.3</td>
<td>49.9</td>
</tr>
<tr>
<td>$\Phi=0.6, 0%$EGR, High pilot</td>
<td>55.8</td>
<td>59.9</td>
</tr>
<tr>
<td></td>
<td>52.8</td>
<td>56.8</td>
</tr>
<tr>
<td>$\Phi=0.6, 25%$EGR, Low pilot</td>
<td>72.8</td>
<td>75.2</td>
</tr>
<tr>
<td></td>
<td>73.7</td>
<td>73.0</td>
</tr>
<tr>
<td>$\Phi=0.6, 25%$EGR, High pilot</td>
<td>79.3</td>
<td>75.1</td>
</tr>
<tr>
<td></td>
<td>77.7</td>
<td>75.8</td>
</tr>
</tbody>
</table>

Table 3.6: EC/TC Results Compared to Aethalometer/TEOM (BC/TPM) Measurements

Previous testing by Baribeau on a six-cylinder version of the Cummins ISX400 engine operating on natural gas resulted in a VOC fraction of between 34 and 58% [18]. Baribeau tested according to the AVL-8 test mode on a 6-cylinder turbocharged engine and we have tested on a single cylinder version of the same engine with independent intake air control and under different operating conditions. Baribeau determined the VOC fraction by heating the filter in an oven at 325°C and weighing the filter before and after. It is difficult to compare SOF or VOC fraction results found using different engines and analysis methods. Therefore it is difficult to determine if these results agree well with Baribeau’s or not.

Effect of EGR

As we would expect, there is an increase in particulate matter with increasing EGR fraction. There is a dramatic increase in PM of approximately 0.15g/kWh (about a 300% increase) at high equivalence ratio ($\Phi = 0.6$) with EGR over the non-EGR case. At low equivalence ratio the effect of EGR was less pronounced but still significant; PM increased approximately 75% with the addition of 25% EGR. One significant contributing factor to this is that EGR lowers the intake oxygen concentration more at high equivalence ratio than at low equivalence ratio. Desantes et al. [19] found that the engine operating condition that produced the largest change in particulate matter with increasing EGR fraction was moderate speed (1200rpm) and high load ($\Phi = 0.62$). They reported more than a 300% increase in particulate matter going from 0% EGR to 25% EGR. At low loads they also found a much smaller effect of EGR on PM emissions when changing the EGR amount. Nitu et al. [20] reported no change in smoke number (BSN) between non-EGR and 25% EGR test points at low load and high engine speed. It is evident from the current findings and from previous work that engine operating condition plays a significant role in the effect of EGR addition.
3.4. Results and Discussion

Effect of Pilot Fuel
There is no significant difference in PM with the type of pilot fuel used. One might expect this result; the biodiesel was mixed with diesel 43% by volume so that the properties and composition were not much different from diesel and the total fuel contribution by the pilot is typically only around 5% on an energy basis.

Table 3.7 shows the percentage increases in total particulate matter and black carbon at each operating condition going from low to high pilot fuel flow. These increases are based upon the average of 9 test points for each operating condition. It can be seen that as the amount of pilot fuel is increased the amount of particulate matter also increases. This effect is more significant with exhaust gas recirculation.

<table>
<thead>
<tr>
<th>Operating Condition</th>
<th>$\text{TPM}<em>{\text{high}}/\text{TPM}</em>{\text{low}}$ $%$</th>
<th>$\text{BC}<em>{\text{high}}/\text{BC}</em>{\text{low}}$ $%$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Phi = 0.4, 0% \text{ EGR}$</td>
<td>1.08</td>
<td>1.73</td>
</tr>
<tr>
<td>$\Phi = 0.4, 25% \text{ EGR}$</td>
<td>1.30</td>
<td>1.82</td>
</tr>
<tr>
<td>$\Phi = 0.6, 0% \text{ EGR}$</td>
<td>1.17</td>
<td>1.19</td>
</tr>
<tr>
<td>$\Phi = 0.6, 25% \text{ EGR}$</td>
<td>1.25</td>
<td>1.48</td>
</tr>
</tbody>
</table>

Table 3.7: Change in Particulate Matter Mass Going From Low to High Pilot Flow

There is about a 25-30% increase in total particulate matter going from a pilot fuel flow rate of 0.15 kg/hr to 0.25 kg/hr with EGR and without EGR an increase of between 8 and 17% is observed. The increase in PM is not proportional to the increase in pilot fuel. A 75% increase in pilot fuel causes an increase in total particulate matter of between 8 and 30%. Similar results were found by McTaggart-Cowan et al. [21] where a 75% increase in pilot fuel produced approximately a 40% increase in particulate matter.

The black carbon mass concentration increases with increasing pilot fuel amount for those test points with EGR. This would tend to suggest that the pilot fuel is forming black carbon and not just condensing as unburnt fuel onto the recirculated particles. If it were condensing onto recirculated particles the SOF would increase not the soot fraction with increasing pilot fuel flow. There is between a 19 and 82% increase in black carbon mass emissions going from low to high pilot flow. This increase is generally more substantial than the total particulate matter increase with pilot flow. This also is evidence that the pilot fuel is causing soot to form during combustion.
3.4. Results and Discussion

TEOM vs. Gravimetric Filter Analysis

The TEOM mass measurements agree well with the gravimetric analysis as seen in Figure 3.6. The data was corrected by removing data points where the TEOM and filter mass measurements differed by more than a factor of 2. These points were considered outliers and in total 7 points were removed from the data set (out of a total of 70, so 10% were removed). After removing the outliers the TEOM mass correlates well with the collected media mass on the filters; a linear regression gives: $m_{TEOM} = 0.9643m_{filter} - 0.3491$, $R^2=0.9777$. It is believed that the good correlation between the TEOM mass and the filter mass is due to heating the TEOM sample inlet to approximately 55°C and to the method of filter treatment that was used. As outlined in the procedure section, a back-up filter was used to sample all vapors that are trapped in the teflon coated quartz filters (Emfab) and the mass of this filter was subtracted from the primary filter. Many papers suggest that the TEOM underestimates the particulate mass by approximately 10 - 30% due to moisture, temperature and pressure effects [22] [23] [24] [25] [26]. We see about a 5-10% underestimation by the TEOM in our current results.

![Graph showing the correlation between TEOM and gravimetric measurements.](image-url)

Figure 3.6: TEOM Correlation with Gravimetric Measurements
3.4. Results and Discussion

3.4.2 Particle Size Distribution and Number Concentration

Particle size distributions are represented as a function of "mobility diameter". Particles are generally chain-like agglomerates and so plotting a graph against particle diameter does not fully describe the situation. Mobility diameter is the diameter of a sphere with the same electrical mobility as the agglomerate. The electrical mobility can be obtained by performing a force balance on the particle; it is the ratio of the drag on the particle to the electrical force that is applied to it [27].

Effect of Pilot Fuel

Figures 3.7 and 3.8 show the effect of pilot fuel amount on particle number and size. Each point is an average of 6 data points and the error bars represent ± one standard error (standard deviation divided by the square root of the number of data points). Figure 3.7 is without EGR and Figure 3.8 is with EGR.

There are two different modes in which particles are formed: an accumulation mode and a nuclei mode. The accumulation mode typically consists of large agglomerates of primarily solid carbon particles. These particles grow primarily due to coagulation of primary carbon particles formed during combustion. The nuclei mode is where nanoparticles (<20nm) are formed by nucleation. Referring to Figures 3.7 and 3.8 it can be seen that there is always a nuclei mode present (many small particles).

Kittelson et al. [28] state that the composition of these nuclei mode particles is uncertain. Many researchers believe that these particles are due to semi-volatile organic vapors condensing as the exhaust is cooled (including Kittelson in a previous paper [29]. Kittelson et al. [28] suggest that a significant fraction of these particles are solid (possibly due to lube oil additives).

The amount of volatile organic matter is completely dependent upon the type of engine and the fuel used. In the SCRE it is believed that the amount of non-black carbon particulate matter varies from about 95% at low load without EGR to about 35% at high load with EGR (based upon Aethalometer and TEOM comparisons).
3.4. Results and Discussion

![Graph showing the effect of the pilot fuel amount on particle size and number - no EGR.](image)

(a) $\Phi = 0.4$, 0\%EGR

(b) $\Phi = 0.6$, 0\%EGR

**Figure 3.7:** Effect of the pilot fuel amount on particle size and number - no EGR
3.4. Results and Discussion

Figure 3.8: Effect of the pilot fuel amount on particle size and number - with EGR
3.4. Results and Discussion

Particle size and number concentration are not significantly affected by the amount of pilot fuel injected in the small particle size range (less than about 80 nm) or in the large particle size range (greater than 500 nm). However, in the mid-size range a noticeable trend can be observed. With more pilot fuel there are more particles in the 150 nm to 300 nm size range at $\Phi = 0.6$ and in the 80 nm to 200 nm size range at $\Phi = 0.4$. The difference in emissions with increasing pilot fuel amount is more distinct at $\Phi = 0.4$ than at $\Phi = 0.6$.

All of the particle size distributions show a gap in data between 300 and 500 nm. Interestingly, few particles were found in this size range. This warrants further research.

Figure 3.9 shows two TEM images; one for low pilot fuel flow and one for high pilot fuel flow. From the images the observations made from the particle size distributions can not be verified. The resolution of the TEM is not high enough to see minor differences in particulate structure.
Figure 3.9: TEM images of PM with low pilot (a) and high pilot (b)
Effect of Equivalence Ratio

Equivalence ratio has a large effect on particle number and size. Higher equivalence ratio produces more particles of all sizes. However, there is not a proportional change in the distribution. There are approximately twice as many very small (around 10 nm) and large (> 500nm) particles with the increase in equivalence ratio and approximately 100 times more particles at 100 nm size. Figure 3.10 shows this effect for biodiesel and for diesel. Each point is an average of 3 data points. There is no significant difference between biodiesel and diesel particle size emissions except at low equivalence ratio between about 100 and 200 nm. Diesel tends to give a slightly higher number of particles in this range but the trend may be confounded with a small amount of experimental error since there were only 3 size distributions at each test condition. The data in this figure do not include EGR and the pilot flow is fixed, i.e. this effect is solely due to the equivalence ratio. Higher equivalence ratio produces many more particles (about 5 times more) in the range of 50 - 200 nm but not a large amount more in the very small range or in the very large range. This would suggest that the natural gas is mainly producing particles during combustion that quickly coagulate either inside the cylinder or in the exhaust piping before dilution (accumulation mode). At higher equivalence ratio the injection duration is longer and the diffusion flame lasts longer therefore more particulate matter can form. Higher equivalence ratio also means less oxidizer is available at the end of combustion to oxidize the soot particles.
Figure 3.10: Effect of equivalence ratio on particle size and number

Figure 3.11 shows two x-ray images obtained from the TEM. They are both at the same magnification. The basic structure of the particulate matter is agglomerate chains consisting of many primary spherical particles; well known structure of diesel particulate found in literature [30]. It is difficult to make concrete conclusions from these two images about effects of equivalence ratio. It appears that the agglomerate size is larger on average at $\Phi = 0.6$, consistent with the DMA results. The primary particle size appears to be in the range of 10-25 nm and similar size is observed for each of the equivalence ratios. As stated previously, most of the small particles are not captured by this TEM sampling method. It is therefore not possible to speculate on the total particulate mass, volatility of the sample or the number and structure of particles in the nuclei mode.
3.4. Results and Discussion

Figure 3.11: TEM images of low $ \Phi $ (a) and high $ \Phi $ (b)
3.4. Results and Discussion

**Effect of EGR.**
Figure 3.12 shows the effect of EGR on particle size distribution at high and low equivalence ratio. One very interesting effect is that with EGR at the high equivalence ratio we actually see the curve cross over the non-EGR curve at around 40 nm particle size. The number of particles less than 40 nm actually decreases with 25% EGR at high equivalence ratio. Particles in the nuclei mode are likely joining the recirculated exhaust particles. This cross-over is not observed at low equivalence ratio.

![Figure 3.12: Effect of EGR on particle size and number](image)

EGR tends to increase the average particle size. The peak particle size is approximately 50nm at $\Phi = 0.6$ without EGR and with EGR it is approximately 70-80 nm. Smallwood et al. [31] studied the effects of EGR on a light-duty TDI engine using a Scanning Mobility Particle Sizer (SMPS) and Laser Induced Incandescence (LII). Consistent with our results, they found that at low speed (1100 rpm) the peak particle diameter increased with increasing EGR amount.
3.4. Results and Discussion

There are two different mechanisms by which the average particle size is growing: condensation/adsorption and coagulation. The results from this testing are contrary to what was found by Niemi et al. [32] where they observed a proportional increase in all particle sizes with a larger fraction of EGR. Kreso et al. [33] report a reduction in total number of particles with EGR but an increase in the total volume of particles. They found results very similar to the results presented here; the number of accumulation mode particles increased with increasing EGR and the number of nuclei mode particles decreased with increasing EGR. The discrepancy in reported data may be in the engine speed. With lower engine speeds, there is more time in the cylinder for coagulation to occur. Smallwood et al. [31] also found little change in peak particle diameter with increasing EGR at higher engine speed (1500 rpm). It should be mentioned that the comparison with other experiments may not be possible because of different dilution conditions.

It would be interesting to determine if the increase in particle number is solely due to the introduction of recirculated exhaust particles into the cylinder or due to other effects such as manifold pressure and cylinder temperature. Filtering recirculated exhaust before introducing it into the combustion chamber would allow this to be determined and would be very interesting for future work.

Figure 3.13 shows two TEM images comparing PM with and without EGR. With EGR we have a higher fraction of black carbon than without and so we would expect to see longer agglomerate chains consisting of mainly black carbon primary particles (spherical) and this can be observed in the figure. Some of the particulate appears to be covered in a film in the EGR image (these particles have been circled). The primary carbon particles are spheres so any "smearing" of these spheres may be condensed semi-volatile matter. Condensed SOF will tend to look lighter on the TEM images because the material is not as dense. However, it must be noted that the actual difference in color between the two images can not provide insight into the particulate composition as the images have been altered to provide the clearest picture.
Figure 3.13: TEM images of PM without EGR (a) and with EGR (b)
With EGR there are many more particles in the size range of 100 - 400 nm at the high equivalence ratio and at the low equivalence ratio we see a large increase in the number of particles in the range of 20 - 200 nm. There is possibly a significant difference between the mechanisms by which particles are formed and grow at different equivalence ratio. At high equivalence ratio, many particles are formed during combustion and less oxygen is available to oxidize them. It is likely that these newly formed particles are joining recirculated exhaust particles via coagulation and therefore increasing the total number of larger particles while reducing the number of smaller particles. At low equivalence ratio, there are not as many particles formed during combustion and there is more oxygen available to oxidize the particles that do form. The proportional increase in number of particles of all sizes may be solely due to the addition of recirculated exhaust particles in the combustion chamber.

**TEM Comparison to Previous Results**

Previous work done by Kumar where particulate from a similar engine (Cummins QSK60 running with HPDI) was sampled by thermophoretic means onto TEM grids showed very strange grape-like agglomerates [34]. These grape-like agglomerates were seen at high load and speed (75% of the rated load and 1800 rpm). By contrast, none of these grape-like structures were observed in the current work. Testing done by Kumar [34] at lower load and speed (21% load and 730 rpm) on a six-cylinder version of the SCRE (Cummins ISX400 running with HPDI) resulted in chain-like agglomerates; very similar to the TEM grid images presented here. This suggests that particulate emissions are very different from different engines and under different operating conditions (speed, load, etc.) and the results appear to be extremely dependent upon the sampling method (thermophoretic, diffusion, impaction).

### 3.4.3 Gaseous Emissions

The effects of equivalence ratio, exhaust gas recirculation, and pilot fuel type and quantity on nitrogen oxide (NO\textsubscript{x}), total hydrocarbon (tHC) and carbon monoxide (CO) emissions will be examined in this section.

**Carbon Monoxide**

Figure 3.14 shows the effect of the varied engine operating parameters on carbon monoxide emissions. The bars represent the average of 6 data points each and the error bars are ± one standard error. Basically, CO emissions correlate well with particulate matter emissions as far as general trends but actual increases on a percent basis do not correlate well. Increasing EGR or equivalence ratio tends to increase carbon monoxide emissions. Pilot fuel amount has little or no effect on carbon monoxide emissions.
3.4. Results and Discussion

25% EGR increases the CO emissions by a factor of approximately 1.6 over the non-EGR test point regardless of equivalence ratio. Particulate matter emissions increase with EGR as well but the amount of increase is not independent of equivalence ratio. PM emissions increase by about a factor of 1.8 at $\Phi=0.4$ and by about a factor of 3 at $\Phi=0.6$ over the non-EGR test point.

Table 3.8 shows the effect of increasing the equivalence ratio on PM and CO emissions. It can be seen that PM and CO correlate well with EGR but without EGR CO increases about 5 or 6 times going from low to high equivalence ratio but the corresponding PM increase is only by about a factor of 3.
3.4. Results and Discussion

<table>
<thead>
<tr>
<th>Change due to increase in $\Phi$ (high/low$\Phi$)</th>
<th>no EGR</th>
<th>no EGR</th>
<th>25% EGR</th>
<th>25% EGR</th>
</tr>
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<td>low pilot</td>
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<td>6.0</td>
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<td>5.8</td>
</tr>
<tr>
<td>high pilot</td>
<td>2.9</td>
<td>3.2</td>
<td>5.0</td>
<td>5.6</td>
</tr>
</tbody>
</table>

Table 3.8: Correlation Between CO and PM

Nitrogen Oxides

Figure 3.15 shows the effect of EGR and $\Phi$ on nitrogen oxide emissions. The bars represent the average of 6 data points each and the error bars are ± one standard error. Pilot fuel amount or type does not appear to affect NO$_x$ emissions.

![Figure 3.15: Nitrogen Oxide Emissions](image)

EGR lowers the intake oxygen mass fraction and the combustion temperature and therefore lowers the amount of thermally formed nitrogen oxides. EGR will have a greater impact
on reducing NO\textsubscript{x} emissions at higher equivalence ratio. The intake oxygen mass fraction (g O\textsubscript{2}/ g net charge) is lower at higher equivalence ratio because the total intake charge increases with increasing equivalence ratio when EGR is added (parameters fixed are equivalence ratio, GIMEP, and EGR mass fraction). Adding 25\% EGR tends to reduce NO\textsubscript{x} by approximately a factor of 3 at $\Phi = 0.4$ and by a factor of 3.5 at $\Phi = 0.6$ over the non-EGR case. McTaggart-Cowan et al. \cite{35} found that NO\textsubscript{x} emissions are almost exclusively a function of two parameters: intake oxygen mass fraction and injection timing.

Interestingly, higher equivalence ratio gives slightly lower NO\textsubscript{x} emissions on a g/GikWh basis. The NO\textsubscript{x} emission is approximately 4.8 g/GikWh at $\Phi = 0.4$ and approximately 4.4 g/GikWh at $\Phi = 0.6$. This result is statistically significant; the error bars do not overlap. This result may be somewhat misleading since the emissions on a g/hr basis were 127 g/hr at $\Phi = 0.6$ and 98 g/hr at $\Phi = 0.4$.

**Hydrocarbons**

Hydrocarbon emissions vary with equivalence ratio, EGR, and with pilot fuel amount as shown in Figure 3.16. The bars represent the average of 6 data points each and the error bars are ± one standard error.

Higher equivalence ratio tends to give lower hydrocarbon emissions. This can be attributed to a higher combustion temperature and a more flammable mixture; more of the hydrocarbons are burned. When the natural gas is injected early in the injection process some of the fuel mixes with air to a point that it is non-flammable before combustion starts (over-leaning). With higher equivalence ratio, the combustion duration is longer and some of the over-mixed fuel may be burned later in the combustion process when it comes into contact with hot combustion products whereas at lower equivalence ratio this overlean mixture does not have time to burn.
3.4. Results and Discussion

Exhaust gas recirculation tends to increase the total hydrocarbon emissions over the non-EGR case. EGR addition delays ignition and more inert gas tends to reduce the flammability of the mixture. Heywood [36] shows a correlation between hydrocarbon emissions and ignition delay (longer ignition delay leads to higher hydrocarbon emissions).

At low equivalence ratio, $\phi = 0.4$, we see that adding more pilot fuel in fact lowers the hydrocarbon emissions. This is reasonable because more pilot fuel will produce more burning zones within the combustion chamber and hence a larger ignition surface for the natural gas to be ignited from. With too low of a pilot fuel flow more of the natural gas will escape the cylinder without being burned because it has been mixed out beyond the flammability limits before a flame reaches it. We don’t see an effect of pilot fuel amount on hydrocarbon emissions at $\phi = 0.6$.

A comparison in the heat release rate between $\phi = 0.4$ and $\phi = 0.6$ is shown in Figure 3.17. From the heat release rate it can be seen that the combustion duration is longer at higher equivalence ratio and combustion starts sooner.
3.5 Conclusions

Black Carbon Fraction

1. The amount of black carbon in the particulate sample ranges from approximately 5% at low load conditions without EGR to approximately 60-80% at high load with 25% EGR.

Figure 3.17: Heat Release Rate Comparison at Different Equivalence Ratio
3.5. Conclusions

**Effect of Pilot fuel Amount**

2. There is an increase in particulate matter mass with increase in pilot flow but this increase is not proportional, i.e. a 50% increase in pilot flow does not produce a 50% increase in PM. A 75% increase in pilot fuel produces only about a 10-30% increase in particulate matter. There is an increase in BC mass concentration with increasing pilot flow, suggesting that the pilot fuel is forming soot and not just condensing and adsorbing onto recirculated exhaust particles.

3. Size and number concentration of particles is not significantly affected by pilot amount without EGR. However, with EGR, more pilot fuel causes an increase in the number of particles in the 100-300 nm range. Smaller particles appear to be unaffected by EGR addition.

4. There is no significant effect of pilot fuel type on emissions.

5. Pilot fuel amount does not affect CO or NO\(_x\) significantly but may slightly affect tHC emissions at low equivalence ratio where higher pilot amount appears to decrease tHC emissions.

**Effect of EGR**

6. EGR increases PM dramatically at high \(\Phi\) (nearly a 300% increase at \(\Phi = 0.6\) going from no EGR to 25% EGR. At low equivalence ratio PM emissions increased approximately 75% with the addition of 25% EGR.

7. There is a larger average particle size with EGR and many more particles in the range of 100-400 nm for \(\Phi = 0.6\) and more particles in the range of 20-200 nm at \(\Phi = 0.4\).

8. The number of particles less than 40 nm decreases with 25% EGR at high equivalence ratio. Particles in the nuclei mode are likely joining the recirculated exhaust particles.

9. Adding 25% EGR tends to reduce NO\(_x\) by approximately a factor of 3 at \(\Phi = 0.4\) and by a factor of 3.5 at \(\Phi = 0.6\) over the non-EGR case.
Effect of Equivalence Ratio

10. There is a larger amount of particulate matter at higher equivalence ratio.

11. Total PM approximately doubles without EGR and increases five-fold with EGR going from low to high equivalence ratio.

12. As equivalence ratio increases there are more particles of all sizes but this is not a uniform increase. Particles around 100 nm experience an increase in number of about 2 orders of magnitude and particles around 20 nm only double in number approximately.

13. At $\Phi = 0.6$, peak particle size is larger than at $\Phi = 0.4$.

14. Higher equivalence ratio gives slightly lower NO$_x$ and tHC's but increases CO emissions on a g/GikWh basis. NO$_x$ emissions are approximately 4.8 g/GikWh at $\Phi = 0.4$ and approximately 4.4 g/GikWh at $\Phi = 0.6$.

15. CO and PM do not correlate well without EGR but with EGR the correlation is reasonable.
References


4. Source Apportionment of Particulate Matter from a Diesel Pilot Ignited Natural Gas Fuelled Heavy Duty DI Engine

4.1 Abstract

In recent years there has been a growing awareness that particulate matter, especially fine diesel particulate is a health concern. Epidemiological studies have found particulate matter to have contributed to a wide range of pulmonary and cardiovascular health problems and there is also evidence leading researchers to believe that certain particulate compounds are carcinogenic and mutagenic [1]. It is this evidence that has stimulated research to develop new technologies to reduce these harmful particulate emissions without increasing nitrogen oxide (NO\textsubscript{x}) emissions or fuel consumption.

Westport Innovations has developed a concept called high pressure direct injection (HPDI) of natural gas where an existing heavy-duty diesel engine has been converted to natural gas. This combustion concept requires an ignition source (a diesel pilot in this case) as natural gas does not ignite fast enough without engine compression ratio modification. To further reduce emissions it is necessary to understand the origin of the particulate matter (PM); natural gas, lubricating oil or diesel pilot fuel can all contribute. This study quantifies the contribution of the diesel pilot to PM emissions under different engine operating conditions.

It has been found that the pilot fuel contribution to soot ranges from 4-40% over the tested operating conditions; correspondingly, the contribution by natural gas and lubricating oil combined ranges from 60-96%. The highest fraction of soot from the pilot source is at low load without exhaust gas recirculation. The lowest fraction of soot from the pilot source is at high load with exhaust gas recirculation.
4.2 Introduction

Particulate matter forms in fuel-rich areas within the combustion chamber and these fuel-rich areas can be plentiful in compression ignition (CI) engines. Growing concern over the health effects of PM and other pollutants motivated adoption of more stringent emissions regulations and has prompted research and development of new engine technologies to reduce emissions. One of the new engine technologies is being developed by Westport Innovations; a heavy duty engine converted to run with high pressure direct-injection (HPDI) of natural gas. This concept uses a diesel pilot fuel to provide ignition since natural gas ignites too slowly under typical engine operation.

HPDI technology has been found to reduce PM emissions by 65% over an equivalently fuelled diesel engine. However, upcoming heavy-duty on-road PM emissions regulations for 2007 (US EPA) will require much greater reductions. To be able to further reduce PM emissions from this type of engine, it is important to understand the origin of the particulate matter. Possible sources include natural gas, diesel pilot fuel, and engine lubricating oil. The lubricating oil contribution should, in theory, depend upon engine speed and load. It is more important to discover how much of the pilot fuel (only about 5% of the total fuel by mass) is producing particulate matter during combustion. The work presented here will quantify the pilot fuel contribution to PM emissions over a range of engine operating conditions.

4.3 Methods to Trace the Origin of Particulate Matter

4.3.1 Trace Elements

Researchers have tracked engine lubricating oil consumption for decades. Typically, the “S-Trace” method has been used where experiments were conducted with sulfur-free diesel fuel and the sulfur in the lubricating oil was traced to SO$_2$ in the exhaust [2] [3]. This method does not in any way link sulphates in the particulate matter to engine oil and actually would not predict lube oil consumption well if the sulphates in the particulate were not quantified.

To determine the particulate matter due to lubricating oil consumption, elements present in the oil may be traced to the particulate. Currently, a common analysis method is Proton Induced X-ray Emission (PIXE). Trace elements present only in the lubricating oil and not in the fuel may be traced. Common elements that are plentiful in typical lubricating oil are Zinc, Calcium, and Magnesium. Particulate matter is collected on teflon filters and subsequently analyzed.
The challenge with estimating lubricating oil contribution with the trace element method is in the assumption that all components of the lubricating oil behave the same as the trace element. This is in fact only a good assumption if the lubricating oil was vaporizing and re-condensing/nucleating into particles of the same original composition. If the lubricating oil is burned or pyrolyzed to any degree during combustion this method fails.

Trace element analysis can only give insight into the lubricating oil contribution to particulate matter. It is not possible with this method to apportion particulate matter sources when more than one fuel is injected into the combustion chamber. The objective of the research is mainly to determine the contribution of the diesel pilot fuel in this HPDI engine.

**4.3.2 Carbon Isotopes**

Carbon isotopes can be used as tracers as all fuels and oils usually contain carbon. There are three naturally occurring carbon isotopes: $^{12}$C (98.9%), $^{13}$C (1.19%) and $^{14}$C (1.2×10⁻¹₀%). An element, such as carbon, is characterized by how many protons its nucleus contains. Carbon contains 6 protons. The number of neutrons in the nucleus determines which isotope of the element is present. $^{13}$C contains 6 protons and 7 neutrons and carbon 12 contains 6 protons and 6 neutrons. $^{13}$C and $^{12}$C are “stable” isotopes because they do not radioactively decay. $^{14}$C, on the other hand, is not stable because it does radioactively decay. Two possible tracers arise from these three carbon isotopes: $^{13}$C/$^{12}$C and $^{14}$C/$^{12}$C.

**Carbon-13**

Rare stable isotopes are potential natural tracers that are present in all organic matter including fuels and lubricating oils. Every fuel or oil contains a unique ratio of $^{13}$C isotope to $^{12}$C isotope ($^{13}$C/$^{12}$C). $^{13}$C/$^{12}$C is commonly reported as a $\delta^{13}$C - value. $\delta^{13}$C - values are reported in parts per thousand (‰) and compared always to a standard. $\delta^{13}$C - values are calculated by:

$$\delta^{13}C(‰) = \left( \frac{R_x}{R_s} - 1 \right) \times 1000$$

(4.1)

$R_x$ is the ratio of $^{13}$C to $^{12}$C in the sample and $R_s$ is the ratio of $^{13}$C to $^{12}$C in the standard [4]. According to the Vienna Pee-Dee Belemnite (vpdb) standard, $R_s$ is 1.1237×10⁻². This is the average terrestrial abundance ratio of $^{13}$C/$^{12}$C. $R_x$ is determined with Isotope Ratio Mass.
4.3. Methods to Trace the Origin of Particulate Matter

Spectrometry (IRMS); using common equipment available at most universities.

To use this method for source apportionment, the $^{13}\text{C}/^{12}\text{C}$ ratio of each fuel and oil component source must be determined for reference end points. Due to fractionation of the sample, the isotope ratio must be determined by treating the fuel and oil components just as they would behave within the combustion chamber (i.e. each fuel must be heated and burned under the same conditions as it would in cylinder in order to minimize effects of lighter hydrocarbons boiling off earlier than heavier ones). In the case of lube oil, does it burn or just vaporize? Questions about the behavior of the fuel and oils within the combustion chamber make this method of tracing carbon extremely complex.

At UBC this method was attempted and the results were inconclusive. Each fuel and oil component $^{13}\text{C}/^{12}\text{C}$ ratio was found but there was a repeatability problem. The ratios of the different fuel and oil components turned out to be very similar and hard to distinguish from one another; $\delta^{13}\text{C}$ - values ranged from -25 to -32%. It was decided that an additional doping of $^{13}\text{C}$ of one of the fuel components would be necessary to obtain a strong enough signal to make the PM sample distinguishable. The cost of a $^{13}\text{C}$ tracer was found to be very high (> 20000 USD). As stated previously the main drawback of the method is in the possible artifacts due to compound fractionation; fuels and oils factionate under different combustion and heating conditions [5] [6].

Carbon-14

Determining PM source has been of research interest for more than 2 decades now. Before AMS was available as a tool to aid in the analysis of isotopes, Homan and Robbins in the early 80's labelled specific diesel fuel component carbon with $^{14}\text{C}$ and counted radioactive decays in PM collected from a diesel engine [7]. Another group of researchers (Mayer et al.) in 1980 added radioactive carbon tracers to the engine lubricating oil and counted decays [8]. These were landmark experiments, being that they were the first times anyone tried to determine the particulate matter source using isotope tracing, but this method of decay counting was an extreme radiation hazard.

Cosmic rays collide with nitrogen atoms in the atmosphere to form $^{14}\text{C}$. This $^{14}\text{C}$ combines with oxygen to form carbon dioxide and plants absorb this carbon dioxide through photosynthesis. Since bio-derived fuels and oils are recently produced from plants they contain $^{14}\text{C}$. $^{14}\text{C}$ decays with a half life of 5730 years (Cambridge half-life) so fossil fuels buried deep in the earth for >60,000 years are essentially carbon free. Since cosmic rays enter the earth's atmosphere at nearly a constant rate, bio-derived fuels will be labelled uniformly with the $^{14}\text{C}$ isotope. Contemporary naturally occurring $^{14}\text{C}$ isotope levels are 103 amol $^{14}\text{C}/\text{mg C}$. This level can easily be detected by accelerator mass spectrometry (AMS) and the carbon
4.3. Methods to Trace the Origin of Particulate Matter

originates from a natural source and is not at a level where it is considered harmful. This makes it an excellent choice for a tracer.

This tracer method has been used successfully by researchers at the University of California Berkley, Sandia National Laboratories, and the Lawrence Livermore National Laboratory to trace bioderived fuels within a diesel engine with the purpose of quantifying the lubricating oil contribution to particulate matter and understanding the mechanisms by which oxygenates reduce particulate emissions [9] [10] [11] [12].

The pros and cons of using $^{13}$C or $^{14}$C as tracers were weighed and it was decided to use $^{14}$C. The method developed at LLNL [9] for analyzing $^{14}$C within filter PM samples is very robust and accurate.

4.3.3 Accelerator Mass Spectrometry

Accelerator Mass Spectrometry (AMS) basically can be used as a method of detecting isotope ratios at levels of $< 1$ in $10^{15}$. The difference between traditional mass spectrometry (MS) and AMS is in the energies to which the ions are accelerated. MS works in the thousands of electron volts and AMS works in the millions of electron volts. AMS does not suffer from the inherent ambiguities in identifying ions with the same mass (eg. $^{14}$C and $^{14}$N) as MS does [13].

Basically, the procedure for determining the isotope ratio of a sample is as follows [13] [9]:

1. Sample atoms are ionized using a cesium ion sputter source. This creates negatively charged carbon atoms. Negative ions of nitrogen do not form so there is no chance of $^{14}$N masking the $^{14}$C signal.

2. Ions of 14 kg/kmol and 13 kg/kmol mass and charge of -1 are separated by momentum in a mass spectrometer.

3. The stable isotope current of ($^{13}$C), used to provide the isotope ratio ($^{14}$C/$^{13}$C), is measured using an off-axis Faraday cup between high energy magnets.

4. The negatively charged carbon beam is accelerated to high energies toward the accelerator terminal maintained at 6.5 MeV.

5. At the terminal a thin carbon foil is used to strip the negative charge from the ion beam and convert it to multiply-charged positive ions (+4 charge is the most plentiful). This destroys unwanted molecules (eg. $^{12}$CH$_2^-$, $^{13}$CH$^-$).
6. This beam is then repelled by the terminal and accelerated to 32.5 MeV.

7. This high energy beam then passes through two 90° analyzing magnets where carbon ions are separated according to their momentum, charge and energy.

8. Remaining ions are counted in a multiple anode gas ionization detector where rate of energy loss identifies the $^{14}\text{C}^+4$ with energy 32MeV.

4.4 Radiocarbon as a Tool for Particulate Matter Source Apportionment

For each sample, AMS directly measures the $^{14}\text{C} / ^{13}\text{C}$ ratio of carbon isotopes. The total amount of carbon present is the sum of $^{14}\text{C}$, $^{13}\text{C}$ and $^{12}\text{C}$ isotopes. In a pilot-ignited natural gas engine the $^{14}\text{C}$ concentration in an emission sample can be expressed as:

$$
\frac{^{14}\text{C}}{C_{\text{sample}}} = \frac{^{14}\text{C}_{\text{pilot}} + ^{14}\text{C}_{\text{CNG}} + ^{14}\text{C}_{\text{tube}} + ^{14}\text{C}_{\text{bk}}}{C_{\text{pilot}} + C_{\text{CNG}} + C_{\text{tube}} + C_{\text{bk}}}
$$

(4.2)

where $^{14}\text{C}_{\text{pilot}}$ and $C_{\text{pilot}}$ are the masses of carbon-14 isotope and total carbon mass from the diesel pilot fuel and $^{14}\text{C}_{\text{CNG}}$ and $C_{\text{CNG}}$ are the masses of carbon-14 isotope and total carbon mass from natural gas. Similarly, $^{14}\text{C}_{\text{tube}}$ and $C_{\text{tube}}$, and $^{14}\text{C}_{\text{bk}}$ and $C_{\text{bk}}$ are the masses of carbon-14 and total carbon from the engine lubricating oil and the background, respectively. The background component is the ambient carbon (organic vapors or CO$_2$) that is absorbed by the deposited particulate matter [9]. Isotope analysis is performed on each of the fuels, lubricating oil and background samples. Ultimately, it is the amount of carbon coming from the tracer that we are interested in. For this experiment, the pilot was the tracer. So subtracting the carbon-14 content of natural gas, lubricating oil and the background from the total carbon-14 gives the carbon-14 attributable to the tracer.

The measured quantity in AMS is $^{14}\text{C} / ^{13}\text{C}$; the desired quantity is $^{14}\text{C}/C$. The method used to convert the measured quantity to the desired quantity is as follows:

An unknown sample $^{14}\text{C} / ^{13}\text{C}$ isotope ratio is measured and compared to the measured $^{14}\text{C} / ^{13}\text{C}$ of a standard of known isotope ratio $^{14}\text{C}/C$. The sample signal measured by AMS is given by,
4.4. Radiocarbon as a Tool for Particulate Matter Source Apportionment

\[
S_{\text{sample}} = k \left( \frac{^{14}C}{^{13}C} \right)_{\text{sample}} \quad (4.3)
\]

and the standard measured signal,

\[
S_{\text{standard}} = k \left( \frac{^{14}C}{^{13}C} \right)_{\text{standard}} \quad (4.4)
\]

The proportionality constant \( k \) is an artifact of measurement and is constant as long as the equipment is the same. Therefore the two equations may be combined to give,

\[
\left( \frac{^{14}C}{^{13}C} \right)_{\text{sample}} = \frac{S_{\text{sample}}}{S_{\text{standard}}} \left( \frac{^{14}C}{^{13}C} \right)_{\text{standard}} \quad (4.5)
\]

Isotope ratio mass spectrometry (IRMS) can be used to find the ratio of carbon-13 to carbon-12 isotopes of a sample as detailed in the previous section. Knowing the \( \delta^{13}C \) value of the sample we can express the \( ^{14}C/^{12}C \) of the sample as,

\[
\left( \frac{^{14}C}{^{12}C} \right)_{\text{sample}} \approx \frac{\left( \frac{^{14}C}{^{12}C} \right)_{\text{standard}} S_{\text{sample}}}{S_{\text{standard}}(1 + \delta^{13}C)} \quad (4.6)
\]

and finally,

\[
\left( \frac{^{14}C}{C} \right)_{\text{sample}} \approx \left( \frac{^{14}C}{^{12}C} \right)_{\text{sample}} \quad (4.7)
\]

An average \( \delta^{13}C \) - value of -28‰ was used for this analysis. It was found previously that for all of the sources the range of \( \delta^{13}C \) - values was from -25 to -32‰ and using any value within this range affects the result by no more than 0.7%. 
4.5 Apparatus and Procedures

4.5.1 Engine and Fuel

This research was carried out on UBC’s single-cylinder research engine (SCRE), a Cummins ISX series heavy-duty six-cylinder, four-stroke, direct-injection engine, modified by the manufacturer to operate on only one cylinder as described by McTaggart-Cowan et al. [14]. The engine’s rated speed is 1800 RPM; the single firing cylinder has a 19:1 compression ratio and a displacement of 2.5 L (bore=137 mm, stroke=169 mm). The combustion geometry was not modified from the stock Cummins ISX diesel engine design. Fuelling is provided by Westport Innovations Inc.’s HPDI natural gas direct-injection system [15] [16]. In the HPDI system, approximately 95% of the energy is supplied from the non-premixed combustion of natural gas, injected into the cylinder shortly before the piston arrives at Top Dead Center (TDC). A diesel ‘pilot’, injected shortly before the natural gas, initiates the combustion. The fuelling system provides natural gas and diesel to the dual-fuel, concentric-needle injector via the engine’s internal fuelling rails at pressures up to 25 MPa. The engine is configured to provide cooled exhaust gas recirculation (EGR).

The SCRE’s air supply is provided (at up to 300 kPa) by an industrial-style rotary-screw compressor. Exhaust gas is recirculated between the high-pressure intake and exhaust streams through an EGR cooler and a variable flow-control valve. To maintain a positive pressure gradient in the EGR loop, as well as to reproduce the back-pressure normally exerted by a turbocharger, the exhaust line pressure is maintained approximately 10 kPa above the intake pressure by a remote-control butterfly valve. The EGR flow is determined from the measurement of the CO2 concentration in the intake and exhaust streams using separate NDIR instruments. Gaseous emissions are measured using NDIR (CO2, CO, CH4); FID (tHC), paramagnetic (O2) and chemiluminescent (NOx) analyzers. In-cylinder pressure is measured with a flush-mounted, water-cooled piezoelectric transducer. This measurement is used to quantify the engine’s load in terms of gross indicated quantities (eg. GIMEP, GISFC). Brake-performance parameters are not representative of load due to high internal friction exerted by the five non-firing cylinders.

The diesel pilot fuel was replaced with a blend of biodiesel and diesel fuel so that the $^{14}$C isotope tracing would be possible. Diesel and biodiesel were mixed at UBC to a mixture of 43% biodiesel by volume. The biodiesel fuel is a soy-based fuel purchased from World Energy. The biodiesel fuel composition is given in Table 4.1. The pilot fuel was not pure biodiesel as in the past this proved troublesome for the injector. A large amount of coking on the injector tip was the cause of early testing termination (perhaps due to the higher viscosity of the biodiesel). It was thought that a mixture of diesel/biodiesel would prolong the life of the injector and enable testing completion.
4.5. Apparatus and Procedures

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<tr>
<td>Kinematic viscosity</td>
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<tr>
<td>Gross Heat of Combustion</td>
<td>17081.7 Btu/lb (39648.7 kJ/kg)</td>
</tr>
<tr>
<td>Elemental Analysis (% mass)</td>
<td>77.84% C, 11.90% H</td>
</tr>
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</table>

Table 4.1: Biodiesel Properties - B100 World Energy

The density of diesel fuel was slightly lower than the density of biodiesel; \( \rho_{\text{diesel}} = 854 \text{ kg/m}^3 \) and \( \rho_{\text{biodiesel}} = 872 \text{ kg/m}^3 \). The composition of the diesel fuel was unavailable. The natural gas composition is given in Table 4.2.

<table>
<thead>
<tr>
<th>Component</th>
<th>Mass Fraction (%)</th>
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</thead>
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<td>n-Butane ((C_4H_{10}))</td>
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</tr>
<tr>
<td>i-Butane ((C_4H_{10}))</td>
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</tr>
<tr>
<td>i-Pentane ((C_5H_{12}))</td>
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<tr>
<td>n-Pentane ((C_5H_{12}))</td>
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<tr>
<td>Hexane ((C_6H_{14}))</td>
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<tr>
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<tr>
<td>Octane ((C_8H_{18}))</td>
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<tr>
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<tr>
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<tr>
<td>Propane ((C_3H_8))</td>
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</tr>
</tbody>
</table>

Table 4.2: Natural Gas Composition During Testing

4.5.2 Test Conditions

Tests were completed without EGR and with 25% (by mass) recirculated exhaust. The engine speed was 1200 rpm for all tests, while two gross-indicated mean-effective pressures (GIMEP: a measure of the work done over the compression and power strokes only) (850 kPa and 1200 kPa), and equivalence ratios \((\Phi)\) (0.4 and 0.6) were tested. The equivalence ratio has been defined here as the ratio of the actual and stoichiometric fuel to oxidizer ratios in the combustion chamber, where the oxidizer includes the oxygen in both the ingested fresh air and in the recirculated exhaust. Table 4.3 shows the eight tested operating points. Each operating point was repeated six times.
4.5. Apparatus and Procedures

<table>
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<tr>
<th></th>
<th>$\Phi$</th>
<th>EGR (%)</th>
<th>$\bar{m}_{\text{pilot}}$ (kg/hr)</th>
<th>Speed (rpm)</th>
<th>GIMEP (kPa)</th>
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<tr>
<td>1</td>
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</tr>
</tbody>
</table>

Table 4.3: Operating Conditions Tested

By specifying the EGR fraction, the GIMEP, and the ($\Phi$), the engine’s operating condition (fuel, air, EGR flows) is fully defined [17]. Fuel injection pressure was held at 19 MPa. Throughout these tests, the combustion timing was held constant by varying the timing of the diesel injection so that 50% of the heat release. The diesel pilot was injected 1.8 ms before the natural gas, hence the timing of the natural gas injection was fixed relative to the diesel injection.

4.5.3 Filter Sample Collection Method

Filter samples for isotope analysis were collected on 47mm Tissue Quartz filters 2500QAT-UP (Pall number 7202). The filters were pre-combusted at a temperature of 900°C for 3 hours in an oven and allowed to cool to room temperature before being removed. The filters were placed in a sealed bag prior to testing to ensure no contamination of the unloaded filter. Engine exhaust gas was diluted approximately 12:1 with clean and dry bottled nitrogen gas. The dilution ratio (DR) was determined by measuring the CO₂ concentrations in the exhaust gas, the bottled N₂, and in the diluted flow,

$$DR = \frac{[CO_2]_{\text{exh,wet}} - [CO_2]_{\text{diluent,wet}}}{[CO_2]_{\text{total,wet}} - [CO_2]_{\text{diluent,wet}}} \quad (4.8)$$

The sample line has multiple ports where a portion of the diluted sample is drawn into each of the particulate matter measurement instruments. There is approximately two meters of mixing length, after the diluent is mixed with raw exhaust before a sample is drawn from the sample line. The entire system is heated and fully insulated to minimize thermophoretic particle losses to the walls. The residence time in the sample line is 3 s as recommended by
4.5. Apparatus and Procedures

the European Commission (Directorate General Transport and Environment) [18].

Diluted exhaust gas was sampled by drawing a flow of approximately 15 slpm through the quartz filters held by a stainless steel filter holder for between 10 and 30 minutes depending upon the engine operating condition. The aim was to obtain a minimum of 200 μg of elemental carbon on the filter, necessary to obtain accurate results from the AMS analysis.

Filters were handled with clean stainless steel forceps and placed in clean 47 mm disk filter holders immediately after the sample was collected. Each sample was then placed in a separate sealed plastic bag to prevent volatile evaporative losses and filter contamination. Twenty filter samples were collected for analysis; a summary is given in Table 4.4.

<table>
<thead>
<tr>
<th>Operating Condition</th>
<th>Pilot Fuel</th>
<th>Number of Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Φ=0.4, no EGR, low pilot</td>
<td>B50</td>
<td>2</td>
</tr>
<tr>
<td>Φ=0.4, no EGR, high pilot</td>
<td>B50</td>
<td>2</td>
</tr>
<tr>
<td>Φ=0.4, 25% EGR, low pilot</td>
<td>B50</td>
<td>2</td>
</tr>
<tr>
<td>Φ=0.4, 25% EGR, high pilot</td>
<td>B50</td>
<td>2</td>
</tr>
<tr>
<td>Φ=0.6, no EGR, low pilot</td>
<td>B50</td>
<td>3</td>
</tr>
<tr>
<td>Φ=0.6, no EGR, high pilot</td>
<td>B50</td>
<td>2</td>
</tr>
<tr>
<td>Φ=0.6, 25% EGR, low pilot</td>
<td>B50</td>
<td>2</td>
</tr>
<tr>
<td>Φ=0.6, 25% EGR, high pilot</td>
<td>B50</td>
<td>3</td>
</tr>
<tr>
<td>Φ=0.6, 25% EGR, high pilot</td>
<td>diesel</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 4.4: Filter samples taken for ¹⁴C analysis

4.5.4 Filter Sample Preparation Method

The filters were analyzed for ¹⁴C content at the Center for Accelerator Mass Spectrometry (CAMS) at the Lawrence Livermore National Laboratory (LLNL).

Particulate matter is composed of a non-volatile fraction (NVF) and a volatile fraction (VF). The non-volatile fraction consists of solid particles of carbon and ash and is commonly referred to as "soot" or "black carbon". The VF consists of all condensible organic species such as unburned fuel, unburned lubricating oil and other products of incomplete combustion.

The filters were analyzed for only the black carbon fraction (soot) of the particulate matter. It is difficult to accurately measure the total particulate matter with this method because of possibility of semi-volatile species collected on the filter re-vaporizing and also the possibility of organics in the atmosphere adsorbing to the filter after collection.
Loaded filters were heated for 2 hours in an oven at a temperature of 330°C. This temperature was chosen because it removes most of the volatile fraction of particulate matter likely to be contained within the filter. It is likely that the filter contains lubricating oil and some lighter hydrocarbons (such as benzene and toluene) and heavier hydrocarbons like PAH's such as benzoapyrene (BP=310°C) and napthalene (BP=217°C). The temperature at which the volatile fraction is removed is up to the discretion of the researcher but generally 330°C is well accepted [19] [9].

After the VF has been removed, the filter was cut into strips and placed in quartz combustion tube with CuO to combust the carbon to CO₂. The CO₂ is then converted to a graphite sample for the AMS analysis.

4.6 Results and Discussion

4.6.1 AMS Results

Carbon-14 content of all of the possible particulate matter sources has been determined. Table 4.5 shows the percent modern carbon in diesel, 100% biodiesel (B100), Biodiesel/Diesel mixture, lubricating oil and natural gas. Diesel, biodiesel and lube oil were sent for analysis as liquid samples and natural gas was burned and the soot was collected. Diesel fuel contains practically no contemporary carbon, the lube oil contained a small amount of contemporary carbon most likely from additives, and biodiesel contained 100% contemporary carbon. The natural gas soot turned out to contain 4.5% modern carbon. Natural gas was burned and the soot produced was collected on a beaker that was placed over the flame. A quartz filter was wiped around the beaker to collect the soot. The beaker was likely contaminated with modern carbon (possibly due to the drying with paper towel). Due to this suspicion of contamination, the fraction modern of natural gas was assumed to be zero (this will be verified in the future).

<table>
<thead>
<tr>
<th>Fuel</th>
<th>% Modern Carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diesel</td>
<td>0.09</td>
</tr>
<tr>
<td>B100</td>
<td>101.9</td>
</tr>
<tr>
<td>B100/Diesel Mix</td>
<td>42.7</td>
</tr>
<tr>
<td>Lube oil</td>
<td>0.29</td>
</tr>
<tr>
<td>Natural Gas</td>
<td>4.5</td>
</tr>
</tbody>
</table>

Table 4.5: Percent Modern Carbon of each possible particulate source
4.6. Results and Discussion

Included in the set of filters sent for AMS analysis, was one filter that should have contained no contemporary carbon. The filter sample was taken with diesel as the pilot fuel (i.e. biodiesel was not used). This sample came back with 1.3% modern carbon. There are two possible sources of error: 1. natural gas at UBC contains some contemporary carbon or 2. the diesel pilot fuel was contaminated with some biodiesel. It is not likely that the natural gas contains any contemporary carbon. There is a high probability that the diesel fuel was contaminated with biodiesel slightly when this filter sample was collected. This filter was sampled during a set of tests that were performed after the biodiesel tests. The biodiesel may not have been completely flushed from the fuel lines and tank effectively, there may have easily been some contamination. If this is the cause for higher modern carbon in the diesel piloted soot sample (rather than natural gas actually containing contemporary carbon) then there is no need for concern; the results remain accurate and are consequently unaffected since the biodiesel testing was done prior to this testing. As stated previously, the natural gas contemporary carbon level will be verified in the future.

Table 4.6 shows the results of the AMS analysis of each filter sample. The mean % pilot contribution was obtained by taking the average of the sample repeat points after removing any outliers (points more than 2 standard deviations from the mean). Few filters were sent for analysis because the cost per filter is very high. The soot loading on the filters was not high enough to guarantee accurate results for 2 of the filters (highlighted) at low equivalence ratio without EGR: the 50.3% reading and the 40.1% reading. The 50.3% reading seems to be off and has been excluded from the average but the 40.1% reading is very close to the companion point reading at 39.8% so it has been included in the average.

<table>
<thead>
<tr>
<th>Operating Condition</th>
<th>% $Soot_{pilot}$ (–outliers)</th>
<th>1 (%)</th>
<th>2 (%)</th>
<th>3 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Phi=0.4$, no EGR, low pilot</td>
<td>35.3</td>
<td>35.3</td>
<td>50.3$^\xi$</td>
<td></td>
</tr>
<tr>
<td>$\Phi=0.4$, no EGR, high pilot</td>
<td>39.9</td>
<td>39.8</td>
<td>40.1$^\xi$</td>
<td></td>
</tr>
<tr>
<td>$\Phi=0.4$, 25%EGR, low pilot</td>
<td>17.1</td>
<td>16.0</td>
<td>18.2</td>
<td></td>
</tr>
<tr>
<td>$\Phi=0.4$, 25%EGR, high pilot</td>
<td>23.0</td>
<td>23.8</td>
<td>22.2</td>
<td></td>
</tr>
<tr>
<td>$\Phi=0.6$, no EGR, low pilot</td>
<td>4.9</td>
<td>5.6</td>
<td>4.3</td>
<td>10.1</td>
</tr>
<tr>
<td>$\Phi=0.6$, no EGR, high pilot</td>
<td>5.9</td>
<td>7.0</td>
<td>4.7</td>
<td></td>
</tr>
<tr>
<td>$\Phi=0.6$, 25%EGR, low pilot</td>
<td>3.5</td>
<td>2.9</td>
<td>3.4</td>
<td>4.1</td>
</tr>
<tr>
<td>$\Phi=0.6$, 25%EGR, high pilot</td>
<td>4.9</td>
<td>4.2</td>
<td>5.6</td>
<td>9.4</td>
</tr>
</tbody>
</table>

Table 4.6: Pilot Contribution to Soot Emissions

$^\xi$: Filter samples did not have sufficient mass to be guaranteed accurate
Figure 4.1 shows the pilot contribution to the soot emissions as a percent of total soot and as a mass. Over the tested operating conditions the pilot contribution to the soot emissions ranges from 4 to 40%; soot emissions due to natural gas and lubricating oil range from 60 to 96%. The highest pilot contribution on a fractional basis is at low load without EGR and high pilot fuel flow. The fraction of soot due to pilot fuel is rather high at 40% at low load without EGR considering that the pilot fuel fraction of the total fuel injected is only approximately 5%. This indicates that the pilot fuel will contribute significantly to engine idle particulate emissions.

![Figure 4.1: Contribution of the Pilot Fuel to the Soot Emissions](image)

The total black carbon mass on a gross indicated basis was found using an Aethalometer. Table 4.7 shows the average corrected black carbon mass concentration of three points for each operating condition. The results obtained from the Aethalometer were corrected according to the procedure detailed in Appendix A. It was shown in Chapter 3 that the corrected Aethalometer data correlated well with elemental carbon analysis of quartz filters. Therefore there is a high confidence in this data. Table 4.7 also gives the mass of soot from
4.6. Results and Discussion

the pilot fuel (found by multiplying the pilot % of soot by the total soot mass) and the mass of soot from ‘other’ sources (natural gas and lube oil).

<table>
<thead>
<tr>
<th>Operating Condition</th>
<th>( m_{\text{totalBC}} ) (mg/GikWh)</th>
<th>( m_{\text{pilotBC}} ) (mg/GikWh)</th>
<th>( m_{\text{otherBC}} ) (mg/GikWh)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Phi=0.4 ), no EGR, low pilot</td>
<td>1.2(+0.12/-0.2)</td>
<td>0.43(+0.04/-0.07)</td>
<td>0.8(+0.08/-0.13)</td>
</tr>
<tr>
<td>( \Phi=0.4 ), no EGR, high pilot</td>
<td>2.4(+0.24/-0.4)</td>
<td>0.97(+0.1/-0.16)</td>
<td>1.5(+0.15/-0.24)</td>
</tr>
<tr>
<td>( \Phi=0.4 ), 25%EGR, low pilot</td>
<td>5.8(+0.58/-0.95)</td>
<td>0.99(+0.1/-0.16)</td>
<td>4.8(+0.48/-0.79)</td>
</tr>
<tr>
<td>( \Phi=0.4 ), 25%EGR, high pilot</td>
<td>11.0(+1.1/-1.8)</td>
<td>2.52(+0.25/-0.41)</td>
<td>8.5(+0.84/-1.39)</td>
</tr>
<tr>
<td>( \Phi=0.6 ), no EGR, low pilot</td>
<td>19.3(+1.93/-3.17)</td>
<td>0.96(+0.1/-0.16)</td>
<td>18.4(+1.84/-3.01)</td>
</tr>
<tr>
<td>( \Phi=0.6 ), no EGR, high pilot</td>
<td>25.3(+2.5/-4.15)</td>
<td>1.48(+0.15/-0.24)</td>
<td>23.8(+2.38/-3.91)</td>
</tr>
<tr>
<td>( \Phi=0.6 ), 25%EGR, low pilot</td>
<td>83.8(+8.4/-13.7)</td>
<td>2.90(+0.3/-0.5)</td>
<td>80.9(+8.1/-13.3)</td>
</tr>
<tr>
<td>( \Phi=0.6 ), 25%EGR, high pilot</td>
<td>121.6(+12.2/-19.9)</td>
<td>5.94(+0.6/-1.0)</td>
<td>115.6(+11.6/-19.0)</td>
</tr>
</tbody>
</table>

Table 4.7: Total BC, Pilot-Derived BC and Fossil-Derived BC

The errors given in Table 4.7 account for the uncertainty in the Aethalometer data correction method and are only applicable if all positive errors are taken at once (i.e. do not compare the maximum total black carbon with the minimum pilot derived black carbon or with the minimum fossil derived black carbon).

4.6.2 Effect of the Pilot Fuel Flow

Increasing the pilot fuel flow tends to increase the pilot contribution to the soot emissions. Increasing the pilot fuel flow rate from 0.15 kg/hr to 0.25 kg/hr increases the pilot contribution on a fractional basis by 15-20% without EGR and 25-35% with EGR.

The actual pilot fuel mass fraction (of the total fuel) is increasing from approximately 4.5% to 7% at low equivalence ratio and from approximately 3% to 5% at high equivalence ratio. Pilot fuel contribution to soot is dependent upon the relative mass fraction of pilot fuel in the total fuel injected to the engine. The highest pilot contribution to soot emissions compared to the actual amount of pilot fuel injected into the combustion chamber is at low load with low pilot fuel amount without EGR.

It is very interesting to see in Table 4.7 that the pilot fuel is not fully responsible for the increase in mass emissions with the increase in pilot fuel amount. The total soot mass emissions increase by approximately a factor of 2 at \( \Phi = 0.4 \) and by approximately a factor of 1.4 at \( \Phi = 0.6 \). The pilot derived soot emissions increase similarly by approximately a factor of 2.3-2.5 at \( \Phi = 0.4 \) and by approximately a factor of 1.1-1.6 at \( \Phi = 0.6 \). Soot emissions
from 'other' sources (i.e. natural gas and lube oil) increase by approximately a factor of 1.8 at \( \Phi = 0.4 \) and by approximately a factor of 1.4 at \( \Phi = 0.6 \). Evidently, an increase in pilot fuel flow is causing more soot from natural gas to form. The pilot is promoting soot formation within the cylinder during combustion. This is a very significant result. It was expected that a change in pilot fuel amount would only change the total soot emissions by a small amount (since the pilot fuel flow is only changing by 0.1 kg/hr). However, this is not the case. Pilot fuel derived soot is increasing significantly but it does not account for the major increase in soot mass because it is a very low fraction of the total soot at most operating conditions (other than engine idle operation). This drastic effect of pilot fuel on soot emissions could be due to the injection pressure. Injection pressure for the HPDI technology is around 3000 psi where typical diesel injection pressures are around 20000 psi [20].

![Legend for x-axis: \( \Phi, \%\text{EGR}, \text{pilot flow} \)]

**Figure 4.2: Pilot Fraction of BC Mass Emissions**

Figure 4.2 shows the mass of pilot derived soot mass emissions along with the total soot mass emissions. It is very interesting to note that while the pilot fractional contribution to soot is changing greatly over the tested operating conditions, the actual soot mass due to
the pilot is not changing much (from 1 to 6 mg/GkWh).

4.6.3 Effect of Equivalence Ratio

Increasing the equivalence ratio from 0.4 to 0.6 tends to decrease the fractional pilot contribution to the soot emissions by 80 to 85%. In terms of actual mass emissions, the increase in equivalence ratio tends to increase the soot mass due to the pilot by 120-200%. While the relative fraction of soot due to the pilot is decreasing, the overall soot mass increases substantially with an increase in equivalence ratio as can be seen from Figure 4.2.

It should also be noted that since the flow rate of the pilot fuel is fixed regardless of equivalence ratio, an increase in $\Phi$ actually means that the contribution of the pilot fuel to the total amount of fuel has decreased (i.e. the pilot fraction of the total fuel on an energy or mass basis decreases with increasing $\Phi$).

4.6.4 Effect of EGR

EGR tends to decrease the fraction of soot due to the pilot by between 15 and 50%. The largest effects are observed at low equivalence ratio. Contrary once again to the fractional soot allocation, EGR tends to increase the soot mass due to the pilot substantially. Soot mass due to the pilot increases by approximately 150% at low equivalence ratio and 200-300% at high equivalence ratio with EGR.

With EGR there is much more time for condensed organics to burn partially. Recirculated particles that have a layer of condensed organics will have the chance to burn as they re-enter the combustion chamber. This condensible material may sinter to the existing soot particle forming a larger soot particle. In the previous chapter, it has been found that EGR tends to increase the black carbon fraction of the particulate matter and the particles tend to be larger with EGR than without.

4.6.5 Comparison to Previous Results at UBC

In August of 2003 similar testing was attempted. Twelve filters were analyzed for $^{14}$C content at the Isotrace Laboratory at the University of Toronto. The results were inconclusive. The details are given in Appendix H. Sample filters were not heated to remove the VOC prior to AMS analysis, i.e. they were analyzed for pilot contribution to the total particulate matter. No clear correlation between engine operation and pilot contribution was found.
4.7. Conclusions

The pilot contribution ranged from 6-19% and the maximum pilot contribution was found at low equivalence ratio, 30% EGR and low pilot fuel flow. The lowest pilot contribution was found at high equivalence ratio, 30% EGR and high pilot fuel flow. There was no strong correlation between pilot fuel flow and pilot contribution to PM emissions. However it did appear that an increase in pilot fuel flow with EGR caused a decrease in PM due to the pilot fuel and an opposite trend without EGR was observed.

4.7 Conclusions

1. Over the tested operating conditions the pilot contribution to the soot emissions ranges from 4 to 40%; hence soot emissions due to natural gas and lubricating oil range from 60 to 96%. The highest pilot contribution on a fractional basis is at low load without EGR. The pilot contribution to soot is minimal at high load with EGR, which is the operating condition that contributes most to PM emissions in multi-mode engine certification tests.

2. Increasing the pilot fuel flow tends to increase the pilot contribution to the soot emissions. Increasing the pilot fuel flow rate from 0.15 kg/hr to 0.25 kg/hr increases the pilot contribution on a fractional basis by 15-20% without EGR and 35-40% with EGR.

3. The pilot fuel is promoting black carbon formation from other sources within the combustion chamber (most likely natural gas). An increase in pilot fuel flow of 75% causes an increase in soot emissions not derived from the pilot fuel of somewhere between 30 and 86% depending upon the engine operating condition. The pilot causes a significant increase in soot emissions.

4. Increasing the equivalence ratio from 0.4 to 0.6 tends to decrease the fractional pilot contribution to the soot emissions by 80 to 85%. In terms of actual mass emissions, the increase in equivalence ratio tends to increase the soot mass due to the pilot by 120-200%. While the relative fraction of soot due to the pilot is decreasing, the overall soot mass increases substantially with an increase in equivalence ratio.

5. EGR tends to decrease the fraction of pilot-derived soot by between 15 and 50%. The largest effects are observed at low equivalence ratio. Pilot-derived soot mass increases by approximately 150% at low equivalence ratio and by 200-300% at high equivalence ratio with EGR.
4.8 Recommendations

1. Since such a small fraction of the total soot is due to the pilot fuel under most operating conditions, strategies to reduce particulate matter due to natural gas and lubricating oil should be investigated. However, since it was shown that the diesel pilot fuel has an impact upon the soot formation of not only pilot derived soot but on natural gas derived soot, strategies to reduce the necessary quantity of diesel pilot fuel are required.

2. From this analysis we do not have any insight into the contribution of the diesel pilot fuel to the soluble organic fraction of the particulate matter. It is recommended that the same analysis be done without heating the filter samples so the total particulate matter can be analyzed.

References


5. Summary

Research data has been presented here that determines the pilot fuel derived soot emissions from a heavy-duty high pressure direct-injection (HPDI) of natural gas engine. In addition to the pilot fuel study, particle size and mass as well as gaseous emissions have been characterized under a wide range of engine operating conditions.

In Chapter 2 the independence of the particulate sampling conditions in the particulate sampling system was established. Dilution ratios in the typical range of 10 to 20 did not affect the particle mass or size measurements significantly. Very low dilution ratios did affect the particulate measurements substantially so it is recommended not to run the particulate system with dilution ratios below 10. Dilution conditions theoretically can have a significant impact upon particle nucleation. Cooler temperatures and lower dilution ratios are conditions that generally support particle nucleation due to the condensation of vapor phase organic compounds. It was expected therefore that the dilution ratio may affect particles in the ultrafine range (< 100 nm) but tests results show no impact of dilution ratio on the smaller particles in the dilution ratio range of 10 to 20. This is a very positive result; any reasonable dilution ratio chosen will not affect particulate matter results.

Chapter 3 presented a combination of experiments encompassing the effects of engine operating parameters on particulate and gaseous emissions. Particle mass concentrations as well as particle size distributions were measured. The black carbon fraction of particulate matter was also established. Gaseous pollutant emissions (NO\textsubscript{x}, CO, tHC) were characterized based upon engine operation. It was found that this particular engine had a much lower black carbon fraction of particulate matter than a conventional diesel engine. The black carbon fraction ranged from approximately 5% at low load without EGR to approximately 65% at high load with 25% EGR.

The effects of equivalence ratio and exhaust gas recirculation have been studied extensively in the past on this research engine and by many other researchers using different facilities. It is well known that the purpose of adding EGR is to lower nitrogen oxide emissions; this is done at the cost of increasing particulate matter emissions. It is also well known that the richer the combustion the more incomplete the combustion is; products of incomplete combustion include carbon monoxide and particulate matter. What is not as well known is the relative increase in gaseous and particulate emissions with increases in equivalence ratio
and EGR and the corresponding particle size distributions; this is what was investigated here.

EGR and equivalence ratio greatly affect particulate matter emissions. Total PM approximately doubles without EGR and increases five-fold with EGR going from low to high equivalence ratio. As equivalence ratio increases there are also more particles of all sizes but this is not a uniform increase. Particles around 100 nm experience an increase in number of about 2 orders of magnitude and particles around 20 nm only double in number approximately. The peak particle size is greater with higher equivalence ratio. EGR increases PM dramatically at high equivalence ratio and moderately at low equivalence ratio. There is a larger average particle size with EGR and many more particles in the range of 100-400 nm for $\Phi = 0.6$ and more particles in the range of 20-200 nm at $\Phi = 0.4$. The number of particles less than 40 nm decreases with 25% EGR at high equivalence ratio. Particles in the nuclei mode are likely joining the recirculated exhaust particles.

Higher equivalence ratio gives slightly lower NO$_x$ and tHC’s but significantly increases CO emissions on a g/GikW basis. Adding 25% EGR tends to reduce NO$_x$ by approximately a factor of between 3 and 3.5. CO and PM do not correlate well without EGR but with EGR the correlation is reasonable.

Size and number concentration of particles is not significantly affected by pilot amount without EGR. However, with EGR, more pilot fuel causes an increase in the number of particles in the 100-300 nm range. Smaller particles appear to be unaffected by EGR addition. Pilot fuel amount does not affect CO or NO$_x$ significantly but may slightly affect tHC emissions at low equivalence ratio where higher pilot amount appears to decrease tHC emissions.

The effect of the pilot fuel on particulate soot emissions has been established in this work. With this information available, it will now be possible to reduce particulate emissions by operating the engine under favorable conditions for low emissions and perhaps by making small design changes to the injector. It was believed that the diesel pilot fuel was the source of much of the particulate emission in the past but this work has proven this theory partially untrue. Soot emissions from the engine on a fractional basis varied from 4 to 40%; the greatest contribution being at low equivalence ratio without EGR. The fraction of pilot derived soot was found to be minimal under high load with EGR, which is the operating condition that contributes most to PM emissions in multi-mode engine certification tests. On a fractional basis the pilot fuel contributes minimally to soot emissions under most operating conditions except that of engine idle. This result is contrary to previous beliefs that the pilot fuel was the main source of particulate matter emissions.

However, it was found that the diesel pilot fuel is causing soot from non-diesel sources to
This was an unexpected and very significant finding. As the amount of pilot fuel is increased, the soot derived from the pilot increases but this increase can not account for the total increase in soot mass. As the pilot fuel flow is increased the amount of soot derived from fossil sources (natural gas and lubricating oil) increases significantly. An increase in pilot fuel flow of 75% causes an increase in soot emissions not derived from the pilot fuel of somewhere between 30 and 86% depending upon the engine operating condition. Since the pilot fuel fraction of the total soot is very low, this increase in soot from fossil sources is huge in comparison with the increase in soot mass due to the pilot. While the diesel pilot is contributing minimally to soot on a fractional basis over most engine operating conditions, it is causing the soot formation in natural gas and possibly lube oil. Hence it is extremely important to keep tight control on the diesel pilot fuel for research (so that results from one test to another will be comparable) and for the development of the HPDI product.
6. Recommendations

1. We do not have any measure of the contribution of the pilot fuel to the soluble organic fraction of particulate matter. The effect of pilot fuel amount on soot emissions has been determined using AMS. It is recommended that the total particulate matter emissions be analyzed by using the same technique.

2. Particle size distributions showed significant particle numbers in the ultrafine particle size range. The smallest particle that was measured with accuracy using the DMA - CPC combination presented in this thesis was around 20 nm. It is recommended that particle size distributions be further characterized in the ultrafine particle range. A new SMPS has just been purchased that will be able to read particle sizes in the range of 3 to 300 nm.

3. Future plans for research on the SCRE include adding optical access. Optical access into the cylinder would provide insight into the mechanisms by which pollutants are forming within the combustion chamber.

4. It is recommended that the lubricating oil contribution to particulate matter at various engine speeds be characterized. This can be accomplished by using trace metal analysis. The lubricating oil can be trace metal content can be characterized and then filter samples of exhaust soot can be analyzed for the same trace metals. This method will likely only provide relative increases/decreases in oil consumption between operating points but will not give actual oil-derived particulate matter due to the issues mentioned in section 4.3.1.

5. Analyze SOF for “fuel-like” and “oil-like” compounds. This will help determine if most of the volatile matter is coming from the lube oil or the diesel fuel.

6. Analyze some filters for elemental carbon fraction of particulate mass. This will serve as a cross check to the Aethalometer data.

7. Some effort has been put in into determining the feasibility of using $^{13}$C isotope as a tracer to determine particulate matter sources. This has not been an exhaustive study; while it seems difficult and costly to employ this method, it is recommended that this be further investigated.
A. Aethalometer Correction

A.1 Key Question/Problem

What can we do to correct for the apparent decrease in black carbon with time due to non-linearity in the Aethalometer? We have a decrease in mass concentration of up to five times the starting mass concentration over a 10-minute period in some cases and this is definitely a problem. We can either correct this data somehow or throw it out because it is useless in its current state.

A.2 Summary

The fact that the measured black carbon mass concentration obtained using an Aethalometer may differ significantly from the actual black carbon mass concentration has been studied extensively in the past. Typically, two calibration factors are introduced to convert the measured values to the actual values so that the actual mass concentration is given by,

\[ M_{BC,\text{Actual}} = \frac{M_{BC,\text{Measured}}}{C \, R(\text{ATN})} \]  

(A.1)

The first calibration factor 'C' describes an effect caused by "multiple scattering of the light beam at the filter fibers in the unloaded filter [1]". 'C' depends mainly upon the filter paper type and the apparatus used and should be nearly constant during an experiment. In previous experiments 'C' has been in the range of 1.9 - 2.5. Weingartner et al. find 'C' to be 2.09 for diesel soot. This scattering effect is minimized if the filter is coated in an oil with similar refractive index to the filter fibres.

The second calibration factor 'R', not so widely studied as 'C', accounts for an effect in which the accumulation of particles onto the filter paper causes an increased tendency to absorb light that would have otherwise been scattered. This leads to a reduction in the optical path and generally lower measured attenuation coefficients. Weingartner et al. call this the "shadowing effect" [1].
A.3 Method

Weingartner et al. [1] suggest using a simple method to account for this shadowing effect. Basically, the method is to convert all of the attenuation coefficients to the value when the attenuation is only 10%. Attenuation is defined as, \( ATN = \ln(I_0/I) \) where \( I_0 \) is the incidence light intensity and \( I \) is the remaining light intensity after passing through the sample. Attenuation coefficient is defined as,

\[
b_{ATN} = \frac{A \Delta ATN}{Q \Delta t}
\]

where \( A \) is the cross sectional area of the sample spot on the filter paper \( 0.5cm^2 \), \( Q \) is the flow rate, \( \Delta t \) is the time step and \( \Delta ATN \) is the change in attenuation over the sample time step.

To convert all black carbon measured to what would have been measured at 10% attenuation (when the filter paper is practically clean) a correction factor ‘f’ is applied using the following equation,

\[
R(ATN) = 1 - \frac{f - 1}{f} \left[ \frac{\ln(ATN) - \ln(10\%)}{\ln(50\%) - \ln(10\%)} \right]
\]

then,

\[
b_{10\%} = \frac{b_{ATN}}{R(ATN)}
\]

and then converting this attenuation coefficient at 10% over to the absorption coefficient, the second correction factor ‘C’ is applied, \( b_{ABS} = b_{10\%}/C \). Finally, the mass concentration of black carbon is given by, \( M_{BC} = b_{ABS}/\sigma_{ATN} \) where \( \sigma_{ATN} \) is 16.6 \( m^2/g \) by default in the AE21.

A.4 Determination of ‘f’

The factor ‘f’ changes with aerosol type so it is impossible to use it as a constant over our very different operating conditions. ‘f’ has been determined for each of the 8 tested operating conditions and averaged to get a mean ‘f’ applicable for each operating condition. The mass concentration of black carbon is given by,

\[
M_{BC} = M_{BC,10\%} \left[ \left( \frac{1}{f} - 1 \right) \left( \frac{\ln(ATN) - \ln(10\%)}{\ln(50\%) - \ln(10\%)} \right) \right] + 1
\]
We can plot the mass concentration of black carbon against $\ln(AN)$ and by doing this we can find the value for 'f'. By rearranging the previous equation into 2 equations, one for slope and one for intercept,

$$\text{slope} = -0.62M_{BC10\%} \left( \frac{f - 1}{f} \right)$$  \hspace{1cm} (A.6)

and

$$\text{Intercept} = M_{BC10\%} \left( 2.44 - \frac{1.44}{f} \right)$$  \hspace{1cm} (A.7)

and solving for a given operating condition we can find 'f'.

Figure A.1 shows a typical plot (uncorrected data) of black carbon mass concentration versus attenuation on a log scale. Taking the slope and intercept from each of these lines we can find 'f'. For each operating condition, 9 values for 'f' were found. These values are presented in Table A.4. It can be seen that higher particulate matter loading conditions lead to higher values of 'f'. At the dirtiest conditions 'f' is around 2 and for the cleanest conditions (not shown in Table A.4) 'f' turned out to be equal to 1. Showing that the cleanest conditions do not require correction. Another reason why this is the case is for the lower loading conditions there are more 'oily' type particles, rather than soot, that tend to increase light scattering and hence reduce the effect of increased absorption of scattered light (the shadowing effect).
A.4. Determination of ‘f’

Figure A.1: Black carbon mass concentration vs. ln[ATN]
A.4. Determination of ‘f’

<table>
<thead>
<tr>
<th>f1</th>
<th>f2</th>
<th>f3</th>
<th>f4</th>
<th>f5</th>
<th>f6</th>
<th>f7</th>
<th>f8</th>
<th>f9</th>
<th>mean</th>
<th>std. Dev.</th>
<th>std. Err.</th>
<th>mean - outliers</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6, 0%, high</td>
<td>1.51</td>
<td>1.57</td>
<td>1.52</td>
<td>1.16</td>
<td>1.32</td>
<td>1.46</td>
<td>1.62</td>
<td>1.45</td>
<td>1.65</td>
<td>1.47</td>
<td>0.15</td>
<td>0.05</td>
</tr>
<tr>
<td>0.6, 0%, low</td>
<td>1.31</td>
<td>1.49</td>
<td>1.48</td>
<td>1.47</td>
<td>1.44</td>
<td>1.45</td>
<td>1.56</td>
<td>1.57</td>
<td>1.61</td>
<td>1.49</td>
<td>0.09</td>
<td>0.03</td>
</tr>
<tr>
<td>0.4, 25%, high</td>
<td>1.08</td>
<td>1.62</td>
<td>1.63</td>
<td>1.10</td>
<td>1.03</td>
<td>1.06</td>
<td>1.16</td>
<td>1.29</td>
<td>1.29</td>
<td>1.25</td>
<td>0.23</td>
<td>0.08</td>
</tr>
<tr>
<td>0.4, 25%, low</td>
<td>1.43</td>
<td>1.20</td>
<td>1.10</td>
<td>1.04</td>
<td>1.15</td>
<td>1.04</td>
<td>1.07</td>
<td>1.18</td>
<td>1.17</td>
<td>1.15</td>
<td>0.12</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Table A.1: ‘f’ factors obtained from plot of BC mass vs. ln(ATN)

Besides a few outliers we have reasonably constant ‘f’ factors for each operating condition. Figure A.2 shows a plot of black carbon mass concentration versus attenuation on a log-log scale. It can be seen that the curves all have nearly the same shape and having the same shape means that they should have the same value of ‘f’.

Weingartner et al. also have found typical ‘C’ factors for different types of soot. They found C = 2.09± 0.41 for diesel soot particles. They also found that this factor was independent of light incidence wavelength and did not vary with time or attenuation as long as the soot was not too ‘oily’. If relatively high concentrations of semi-volatile species are present then ‘C’ was determined to be around 3.6 and also varied with time and attenuation. Since it is only the very high particulate loadings that are particularly affected by this ‘C’ factor and in our case the high particulate loadings have a high percentage of black carbon, rather than semi-volatiles, we will choose C = 2.09.
A.5 Corrected Aethalometer Data

The corrected black carbon mass concentration as a function of attenuation is shown in Figures A.3 and A.4. The graphs on the left are the uncorrected and the graphs on the right are the corrected versions. It can be seen that applying the correction procedure does flatten out the data consistently. The average concentration tends to be close to half of the peak concentration. Comparing this data to the total particulate matter mass concentration (from the TEOM) we find the maximum black carbon percentage of total particulate to be approximately 80% and this is reasonable.
Figure A.3: Left - Uncorrected AE data, Right - Corrected AE data
Figure A.4: Left - Uncorrected AE data, Right - Corrected AE data

Figure A.5 shows the black carbon mass concentration comparing corrected diesel and
biodiesel results with the uncorrected values (BC averaged over each test period). At high particulate loadings, in this case 0.6 equivalence ratio and 25% EGR, the Aethalometer tends to underestimate the black carbon. This difference is in fact very large, for example the BC from biodiesel at maximum loading is approximately 25 uncorrected and 35 corrected $mg/m^3$. This is at 40% underestimation of the actual black carbon. With lower black carbon loadings the Aethalometer average mass concentration would overestimate the actual black carbon mass concentration.

![Figure A.5: BC mass concentration results - corrected vs. uncorrected](image)

**A.6 Conclusions**

The raw Aethalometer data taken during the June 2004 testing on the engine must be corrected to gain meaningful results. The problem is that the Aethalometer readings decrease with time and loading on the filter paper and so a meaningful average is not possible.
A method for correction of Aethalometer data was presented by Weingartner et al. [1] and it has been used here to show its effectiveness as applied to the engine particulate data. Correction factors for each operating point have been found and applied to the data. The result is a flat distribution of BC mass concentration over the testing time. The maximum BC percentage of total particulate matter turned out to be approximately 70%, very reasonable.

A.7 Recommendations

It is recommended that this correction method be used when treating all Aethalometer data obtained from engine exhaust sampling at UBC.

References

B. Effects of Humidity and Temperature on TEOM Operation

B.1 Summary

The TEOM was tested for its sensitivity to inlet temperature and humidity of the sample gas stream. The TEOM inlet temperature was varied from 48°C to 58°C and this resulted in a 50% increase in mass concentration measured. To test humidity effects, a desiccant dryer was placed at the inlet to the TEOM. The dryer reduced particulate mass concentration to approximately half of the undried sample. It is believed that the decrease in mass concentration is due to semivolatile vapours being absorbed by the dryer and particles being lost due to diffusion in the dryer and not due to water vapour. Therefore it is not recommended that a dryer be used at the TEOM inlet.

B.2 Effect of TEOM inlet temperature

TEOM inlet temperature greatly affects the measured particulate matter mass concentration at inlet temperatures above approximately 54°C. The TEOM inlet temperature is measured approximately 20cm away from the actual inlet to the TEOM so it is believed that the temperature drops slightly from this measured value before it reaches the inlet.
B.2. Effect of TEOM inlet temperature

Figure B.1: Effect of TEOM inlet temperature on the measured PM mass concentration

The TEOM does not have a cooler inside but only a heated sample line so it is puzzling that the higher temperatures even work properly since a tight temperature control is required for mass measurement.

Figure B.1 shows the relationship between TEOM inlet temperature and measured particulate mass concentration. The operating condition remained constant and hence it is assumed that the actual particulate matter mass concentration also remained constant. The graph is showing the discrepancy in particulate mass measurement when the TEOM inlet temperature is varied from 48°C to 58°C. The x-axis of the graph shows the actual head temperature inside the TEOM. This temperature is supposed to be controlled to be 50°C at all times. It can be seen that a 10°C difference in inlet temperature makes about a 0.5°C difference in TEOM head temperature. This results in an increase in PM mass concentration of about
B.3 Effect of humidity

50%. Hence there is a very significant effect of TEOM inlet temperature on measured particulate matter mass concentration. The TEOM mass matches the filter mass measurements best when the inlet temperature is kept between 55 and 58°C.

B.3 Effect of humidity

Tests were done with a long desiccant dryer at the inlet to the TEOM. This dryer was designed to have a very low velocity and hence a long residence time so that 95% of the water vapour will diffuse out of the sample stream. The problem is that the dryer may have been in fact removing semivolatile vapours that would have condensed to form particles and also may have been removing some of the small particles. Calculations show that 72% of methylnaphthalene and 42% of hexadecane could be removed in this dryer. Calculations also show that the transport efficiency of very small particles (< 10 nm) is about 90%. This seems very good but considering that we have many very small particles (known from the DMA results) a 10% loss in these particles could possibly prove to be a significant mass.

<table>
<thead>
<tr>
<th>Condition</th>
<th>$\phi$</th>
<th>$MC\ (mg/m^3_{exhaust})$</th>
<th>$m_{dryer}/m_{nodryer}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dryer</td>
<td>0.4</td>
<td>1.16</td>
<td>2.9</td>
</tr>
<tr>
<td>no Dryer</td>
<td>0.4</td>
<td>3.38</td>
<td></td>
</tr>
<tr>
<td>Dryer</td>
<td>0.5</td>
<td>4.15</td>
<td>2.3</td>
</tr>
<tr>
<td>no Dryer</td>
<td>0.5</td>
<td>9.55</td>
<td></td>
</tr>
</tbody>
</table>

Table B.1: Results from tests with and without a dryer at TEOM inlet

Table 1 shows the results from the tests with and without the dryer at the inlet to the TEOM. Tests were done at 2 different equivalence ratios, 0.4 and 0.5. Without the dryer the mass concentration measured by the TEOM is between 2 and 3 times more than the mass with the dryer. With 5% maximum water vapour in the sample stream it is unlikely that this mass difference is solely due to water vapour condensing. Particles are likely being lost into the dryer and similarly semivolatile vapours are likely being absorbed by the desiccant. It is not recommended that a dryer be used at the inlet to the TEOM when running with high enough dilution ratios (> 10) (diluting with dry bottled gas).
B.4 Conclusions

1. The TEOM inlet temperature affects the mass measurements greatly. This temperature must be kept high (between 55 and 58°C) to get reasonable correlation between the TEOM and gravimetric analysis.

2. Whether humidity affects the TEOM readings is inconclusive at this point. The relative humidity in our line is no more than 5% at any given time and it is believed that this little humidity will not affect the TEOM operation.

B.5 Recommendations

1. Keep the TEOM inlet temperature between 55 and 58°C and insulate the line well.

2. Do not use a dryer in the sample line before the TEOM; it is unnecessary and may be removing particles and semivolatile vapors.
C. Dilution System Design Overview

C.1 Overview

Figure C.1: Dilution system layout
C.2 Transfer Tube

Section 'A' of tubing in Figure C.1 is a tube with the purpose of creating a large pressure drop and inducing a certain amount of flow through the tube while minimizing thermophoretic particle losses. The tube has been sized so that less than 10% of the exhaust flow leaving the engine travels through to the particulate matter sampling system. The remaining exhaust flow is needed for exhaust gas recirculation and gaseous emissions sampling at the emissions bench. The transfer tube is fully insulated to minimize particle losses.

A back pressure regulator regulates the pressure at the outlet of the 1/4" tube between 7 kPa gage and 25 kPa gage. Assuming that the back pressure regulator is regulating 7 kPa and that the engine exhaust pressure is between 17 kPa and 197 kPa the pressure drop in the 1/4" tube assembly will be at a minimum 10 kPa and at a maximum 190 kPa. Losses due to sudden contraction at the 1/4" inlet and a sudden expansion at the 1/4" outlet are included in the calculation so that the total pressure drop is 10 kPa at a minimum and 190 kPa at a maximum. The induced flow through the 1/4" tube is calculated based upon those pressure drops. The minimum flow was calculated to be approximately 27 slpm and the maximum flow was calculated to be approximately 165 slpm. If the back pressure regulator is set at 25 kPa the maximum flow rate will be slightly less that 165 slpm at the high engine exhaust pressures (197 kPa). The engine exhaust pressure must be at least 5 kPa above the back pressure regulator setting to induce a reasonable amount of flow through to the dilution system. If the back pressure regulator is set at 25 kPa the engine exhaust pressure must be at least 30 kPa.

Based upon the pressure drop from the engine outlet to the regulated back pressure the flow velocity can be calculated using the following formula:

\[ u = \sqrt{\frac{2 \Delta P \cdot d}{f \cdot \rho \cdot L}} \]

(C.1)

Where,

- \( d \) is the pipe diameter (m)
- \( L \) is the pipe length (m)
- \( \rho \) is the fluid density (kg/m\(^3\))
- \( f \) is the friction factor
- \( \Delta P \) is the pressure drop across the tube (Pa)

The friction factor was read from the Moody diagram after calculating the Reynolds number. After this velocity is known the mass flow rate can be calculated. To convert the mass flow...
rate in kg/s to slpm standard conditions of air at 15°C and 101.325 kPa were used.

C.3 Back Pressure Regulator (BPR)

Fluctuations in exhaust back pressure adversely affect particulate matter measurements in the dilution system. A back pressure regulator is included in this revised dilution system for the purpose of eliminating back pressure fluctuations in the sample line. This should provide accurate and stable measurements of particulate matter.

The back pressure regulator is located at the end of a 3/4" exhaust line. A 3/4" line was chosen so that the pressure drop is not large at the highest flow conditions. The reason for wanting no pressure drop in the 3/4" line is so that the set back pressure is the same at the tee intersection as it is at the regulator. The flow through the back pressure regulator was calculated to be between 27 and 165slpm.

C.4 Heat Exchanger (HE)

The back pressure regulator can not tolerate temperatures higher than about 200°C so a tube-in-tube heat exchanger was added to the 3/4" line just before the regulator to cool the exhaust. Water flows counter to the exhaust around the outside of the 3/4" tube through a 1" copper pipe. The clearance between the tube and pipe is approximately 1/8". The heat exchanger is 3 feet long. Basic heat transfer calculations indicate that the exhaust temperature should drop to around 200°C after 3 feet of heat exchange. The heat transfer rate is limited by the exhaust flow in the tube. Therefore it does not really matter how much water is flowing through the heat exchanger, just a trickle or a large flow will achieve approximately the same result. The exhaust temperature and the water temperature at the outlet of the heat exchanger will be monitored.

Basic heat transfer calculations were done that assumed forced convection through a smooth pipe. An iterative approach was taken in calculating the temperatures. First the water outlet temperature was guessed and then a program was run to calculate the inlet water temperature. If this water temperature was not 10°C the calculation was iterated until it was.

For the simulation, basically the heat exchanger was broken down into small steps (cells) and a constant wall temperature was assumed for each of the small sections. The inlet conditions were the exhaust inlet flow rate and temperature as well as the water flow rate and an assumed outlet water temperature (since it is a counter flow heat exchanger). For
each cell, heat transfer by forced convection of the exhaust was calculated and then the wall temperature was known. It was assumed that the wall was so thin and a perfect conductor so that the inner wall temperature was the same as the outer wall temperature. Knowing this wall temperature, the rate of heat transfer from the wall to the water was calculated. Now the new water and exhaust temperatures are known for the next cell and so on.

This heat exchanger has proven to provide more cooling than needed and caused water to condense out of the exhaust gas and now it is no longer used. The back pressure regulator has easily been able to handle the high exhaust gas temperature.

C.5 Orifice Plate

To lower the pressure from the regulated pressure down to near atmospheric, some orifice plates have been designed to be inserted inside a 1/2” tube union tee fitting. The exhaust comes into the fitting and passes through the first orifice plate and then air is mixed with the exhaust. The mixture then passes through a second orifice plate where the pressure drops down to approximately atmospheric pressure. The first orifice plate has been designed to have a larger pressure drop than the second orifice plate. This is to ensure that there is no back flow from the dilution air into the exhaust line.
The orifice plate hole size was calculated by specifying the pressure drop required if the back pressure regulator were set to 10 kPa gage. The pressure drop across the two orifice plates must then sum to approximately 9-10 kPa. So a pressure drop of 7 kPa was chosen across the first orifice plate and a pressure drop of 2 kPa was chosen across the second. This was done for the lowest dilution ratio and then using those orifice sizes the pressure drop for the largest dilution ratio was calculated based upon the increased dilution air flow. The pressure drop was found to be about 6 kPa in the second orifice and about 3kPa in the first.

The pressure loss across an orifice is given by:

\[ P_{\text{loss}} = (1 - \beta^{1.9}) \Delta P \]  
\[ \text{(C.2)} \]

Where,

\[ \beta = \frac{d}{D} \]  
\[ \text{(C.3)} \]

where \( d \) is the orifice diameter and \( D \) is the upstream diameter.

**Figure C.2:** Detailed view of the 1/2" mixing tee with orifice plate inserts
C.6 Control of the Dilution Ratio

\[ \Delta P = \frac{1}{2} \rho \left( \frac{4 \dot{m}}{\pi E \epsilon d^2} \right)^2 \]  

(C.4)

Where,

- \( \dot{m} \) is the mass flow rate in kg/s,
- \( \rho \) is the fluid density kg/m\(^3\),
- \( \epsilon \) is the compressibility factor (\( \epsilon = 1 \) for incompressible fluids) and

\[ E = \frac{1}{\sqrt{1 - \beta^4}} \]  

(C.5)

Using this method the first orifice size was calculated to be 0.8 mm and the second orifice size was calculated to be 3.5 mm. Since it is difficult to predict the pressure drop exactly across such small orifices, 6 different orifice plates were manufactured, 3 for the first orifice and 3 for the second.

Currently, the second orifice is not being used. It was found that the orifice was blocked quickly with particulate if the orifice was not heated. A heating tape was wrapped around the fitting and this heater must be on at any time during particulate sampling, the consequence of not turning the heater on will be a clogged orifice in less than 30 minutes and the fitting will have to be taken apart for cleaning. This is very important!

C.6 Control of the Dilution Ratio

The dilution ratio can either be controlled by setting the dilution air mass flow rate at a fixed back pressure or by fixing the dilution air flow rate and varying the back pressure. For the calculation of the required orifice sizes, it was assumed that the first method of dilution ratio control would be used: varied air flow rate at a fixed back pressure.

If the back pressure is used to control the dilution ratio and the air flow rate is fixed at approximately 33 slpm, the orifice sizes calculated are slightly different. The first orifice size was calculated to be 0.55 mm and the second 3.2 mm. If this method of control were used, to get the minimum dilution ratio (about 15) the back pressure should be set at the maximum, 25 kPa. To get the maximum dilution ratio (about 35) the back pressure should be set at the minimum, 7 kPa. The benefit to controlling the dilution ratio by controlling the back pressure is that less dilution air will be used and the rate of dilution air depletion is fixed.
At the high dilution ratios (35) the dilution air flow rate will be half as much as would be needed if the dilution ratio were controlled by increasing the dilution air flow rate.

Both methods of dilution ratio control are feasible. Orifice plates have been manufactured to fit both control methods. Dilution ratio is best controlled by varying the back pressure and fixing the diluent flow rate.

C.7 Particle Losses

Diffusional losses have been minimized by keeping the particulate sampling line as short as possible. Diffusional losses have been calculated using the method provided by EU DGTREN [1]. For turbulent flow in a pipe the transport efficiency is given by,

\[ \eta = \exp \left( \frac{-4L_s V_{diff}}{D_s U_s} \right) \]  \hspace{1cm} (C.6)

where \( V_{diff} \) is the diffusional deposition velocity and is given by,

\[ V_{diff} = \frac{ShD_k}{D_s} \]  \hspace{1cm} (C.7)

and the Sherwood number (Sh) is given by,

\[ Sh = 0.0118Re^{7/8}Sc^{1/3} \]  \hspace{1cm} (C.8)

Where Sc is the Schmidt number \( Sc = \frac{\nu}{D_k} \), Re is the Reynolds number \( Re = \frac{\rho ud}{\mu} \), \( \rho \) is the density of the gas, u is the velocity in the pipe, d is the pipe diameter, \( \mu \) is the viscosity of the gas and \( \nu \) is the kinematic viscosity.
Figure C.3: Transport efficiency due to diffusional losses in the sampling system

Figure C.3 shows the calculated transport efficiency for our sampling line. 90% of the particles above 10 nm will be transported through the pipe. Very few particles will be deposited on the walls of the sampling line due to diffusion.

Impaction losses were also considered in the design of the sampling system. The method provided by EU DG TREN [1] was used for calculating impaction losses in a straight tube. The transport efficiency is expressed as,

\[ \eta_{\text{turb,inert}} = \exp \left( -\frac{\pi d L V_i}{Q} \right) \]  \hspace{1cm} (C.9)

where \( L \) is the length of the tube, \( d \) is the diameter of the tube, \( Q \) is the volumetric flow rate, and \( V_i \) is the turbulent inertial deposition velocity, given by \( V_i = \frac{V_{+}u}{5.03 Re^{1/8}} \), where \( u \) is mean flow velocity, and \( V_{+} \) is the dimensionless turbulent deposition velocity and can be obtained
from,

\[ \tau_+ = 0.0395 \text{Stk} \text{Re}^{3/4} \]

\[ V_+ = 0.0006 \tau^2 \quad \text{for} \quad \tau_+ < 12.9 \]

\[ V_+ = 0.1 \quad \text{for} \quad \tau_+ > 12.9 \]

and finally the Stokes number can be obtained from: \( stk = \frac{\rho_p C \mu D^2}{18 \mu} \) where \( \rho_p \) is the particle density, \( C \) is the slip correction factor, \( d \) is the pipe diameter and \( \mu \) is the viscosity of the gas.

Figure C.4 shows the transport efficiency considering impaction losses as a function of particle diameter. It can be seen that impaction losses are negligible in our sampling system for the typical size of particles that we encounter during sampling of engine exhaust. This can be attributed to our very low velocity in the sample tube.
Figure C.4: Transport efficiency due to impaction losses in the sampling system

References

D. Effects of Humidity and Conditioning Time on Filter Mass

D.1 Humidity Effects

Dirty filters (filters that have previously been used to collect particulate matter) and clean filters were weighed after being held at 35% relative humidity and after being held at 0% humidity in a desiccator. A comparison of the clean filters “dry” and “wet” is shown in Table D.1. It can be seen that water collection on the filter is practically not an issue with clean filters.

<table>
<thead>
<tr>
<th>Filter ID</th>
<th>Dry mass (mg)</th>
<th>Wet Mass (mg)</th>
<th>Difference (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>REF1</td>
<td>88.506</td>
<td>88.502</td>
<td>0.004</td>
</tr>
<tr>
<td>REF2</td>
<td>86.916</td>
<td>86.916</td>
<td>0.000</td>
</tr>
<tr>
<td>REF3</td>
<td>87.065</td>
<td>87.063</td>
<td>0.002</td>
</tr>
</tbody>
</table>

Table D.1: Clean filters weighed at 35% relative humidity and at 0% relative humidity

Table D.2 shows the result of weighing three dirty filters three times at 0% relative humidity and twice at 35% relative humidity. The maximum day-to-day variation in weighing the dry filters was 10 mg and the maximum day-to-day variation in weighing the wet filters was 5 μg. The maximum difference between wet and dry filter mass was 14 μg.

<table>
<thead>
<tr>
<th>Filter ID</th>
<th>$m_{dry}$ (mg)</th>
<th>$m_{dry}$ (mg)</th>
<th>$m_{dry}$ (mg)</th>
<th>$\Delta m_{dry}$ (mg)</th>
<th>$m_{wet}$ (mg)</th>
<th>$m_{wet}$ (mg)</th>
<th>$\Delta m_{wet}$ (mg)</th>
<th>$\Delta m_{max(WetDry)}$ (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spare5</td>
<td>89.045</td>
<td>89.055</td>
<td>89.051</td>
<td>0.010</td>
<td>89.054</td>
<td>89.059</td>
<td>0.005</td>
<td>0.014</td>
</tr>
<tr>
<td>REP1-0.4</td>
<td>88.749</td>
<td>88.753</td>
<td>88.752</td>
<td>0.004</td>
<td>88.761</td>
<td>88.763</td>
<td>0.002</td>
<td>0.014</td>
</tr>
<tr>
<td>REP2-0.6</td>
<td>89.827</td>
<td>89.829</td>
<td>89.829</td>
<td>0.002</td>
<td>89.835</td>
<td>89.837</td>
<td>0.002</td>
<td>0.010</td>
</tr>
</tbody>
</table>

Table D.2: Dirty filters weighed at 35% relative humidity and at 0% relative humidity

Filters are slightly sensitive to humidity. Clean filters are less sensitive to humidity than dirty filters. For all of our gravimetric measurements for engine PM analysis, the difference
between filter mass before and after will always be at least 200 μg. An error of at most 14 mg in the pre and post weigh stages would result in an error of at most 7%. This is a significant error so care should be taken to always weigh the filters after being conditioned for at least 24 hours at 35% relative humidity ± 3%.

The TEOM filter media is the same as the filters used in gravimetric analysis and therefore it is expected that the TEOM filters will behave in the same way. The changes in relative humidity in the sample line to the TEOM should be minimized. Running at a high dilution ratio will help to damp out any uncertainty due to humidity. Humidity is not expected to be high in the sample line. The relative humidity will be less than 5% under normal load conditions at high dilution ratios.

### D.2 Conditioning Time Effects

To establish the effect of conditioning time on measured filter mass, 7 filters were weighed after 24 hours, 45 hours and 96 hours. Three of the filters were clean (i.e. no particulate sample on them) and four of the filters had particulate sample on them. Tables D.3 and D.4 show the filter masses for the clean filters and the dirty filters respectively.

#### Table D.3: Filter mass (mg) as a function of conditioning time (clean Pallflex TX40 filters)

<table>
<thead>
<tr>
<th></th>
<th>24 hours</th>
<th>45 hours</th>
<th>96 hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>clean sample 1</td>
<td>88.902</td>
<td>88.904</td>
<td>88.901</td>
</tr>
<tr>
<td>clean sample 2</td>
<td>88.976</td>
<td>88.978</td>
<td>88.986</td>
</tr>
<tr>
<td>clean sample 3</td>
<td>88.355</td>
<td>88.353</td>
<td>88.351</td>
</tr>
</tbody>
</table>

#### Table D.4: Filter mass (mg) as a function of conditioning time (dirty Pallflex TX40 filters)

<table>
<thead>
<tr>
<th></th>
<th>24 hours</th>
<th>45 hours</th>
<th>96 hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>dirty sample 1</td>
<td>85.729</td>
<td>85.731</td>
<td>85.727</td>
</tr>
<tr>
<td>dirty sample 2</td>
<td>90.092</td>
<td>90.088</td>
<td>90.089</td>
</tr>
<tr>
<td>dirty sample 3</td>
<td>89.291</td>
<td>89.297</td>
<td>89.297</td>
</tr>
<tr>
<td>dirty sample 4</td>
<td>88.990</td>
<td>88.995</td>
<td>88.984</td>
</tr>
</tbody>
</table>

There is practically no effect of conditioning time on dirty or clean filters in the conditioning time range tested. Conditioning times between 24 hours and 96 hours will result in good filter mass measurements.
D.3 Conclusions

Relative humidity has a small effect on filter mass measured. The largest observed variation in filter mass between 35\% relative humidity and 0\% relative humidity was 14 \mu g. This can account for an overall error in measurement of approximately 7\%. Relative humidity should be controlled to be 35\% \pm 3\% at all times.

There is no significant effect of filter conditioning time on filter mass in the conditioning time range of 24 hours to 96 hours. It is therefore recommended that all filters be weighed within this conditioning time range.
E. Gravimetric Filter Analysis Procedure

1. Place filters in a filter holder (Gelman Sciences 47mm holder)

2. Label holder

3. Leave filters in conditioning room with lid loosely on top of filter holder to let air in but not to allow particles to drop onto it (UBC Occupational Health and Hygiene).

4. Condition for between 24 and 48 hours.

5. Keep 2 reference filters in conditioning room (for no more than 2 months) and weigh prior to weighing any sample filters. If the mass differs by more than 10μg, then do not weigh the sample filters. Relative humidity should be 35%± 3% and the temperature should be 20± 2°C.

6. Pre-weigh all sample filters. Tare the balance, weigh each filter 3 times and tare after each weighing. If any filter mass differs by more than 10μg, reweigh the filter.

7. Collect filter sample by having two filters in series. The first filter will collect all particulate matter and the second will collect condensible organic vapors.

8. Once sample is collected bring directly to the conditioning room and condition again for 24-48 hours.

9. Post-weigh all sample filters. Make sure that the conditioning conditions are within the set range and that the reference filters are within 10μg of the normal mass.

10. Obtain the filter mass by subtracting the original filter mass from the sample filter mass.

11. Obtain the total sample mass by subtracting the second filter sample mass (in the series filter sample) from the first filter sample mass. This will give only sample mass and not organic vapors which would generally not condense unless there would be media to condense upon. These vapors will not normally condense in the air and should not be considered particles.
Tips:

1. Do not lean on the marble table that the balance is mounted upon, in fact do not even touch the table.

2. Make sure that the balance is level (level indicator on right rear corner of scale).

3. Calibrate balance with the internal calibration often.
F. TEOM Operating Guidelines

F.1 Starting up

1. Plug in the TEOM computer and turn it on

2. Hook up the purge air line (the quick connect on the bottled air line) and open the valve and bottled air. Make sure that the sample inlet line (black tubing) is not capped when you do this or the TEOM will be pressurized and could be damaged.

3. Connect the TEOM Swagelok sample inlet line to the main sampling line (black tubing).

4. If the shut-off valve for the sampling line is closed, open it (if you don’t the TEOM will get pressurized and it may be damaged). Make sure that the Kenmac back pressure regulator is fully open (fully to the left).

5. Plug in the TEOM pump

6. Start the DOS TEOM software on the computer

7. When the software is running and you are on the main display page (it should say warm-up in the top left corner) then turn on the TEOM (on/off switch).

8. Turn on the electric line heater to a setting of about 25 (adjust to achieve a sample temperature of approximately 45-50°C).

9. Wait until the TEOM warm-up period is finished and then run the TEOM on purge air and display on the screen. To do this press F1, enter a file name and then press Alt P to switch from sampling from the sample line to purge air. The TEOM should display nearly zero PM concentration.

F.2 Shutting Down

1. Open the back pressure regulator fully
2. Stop any file collection that you are doing by pressing F2 and then F3 to return to initialization mode

3. Turn off the TEOM (on/off switch)

4. Unplug the TEOM pump

5. Press F10 on the TEOM computer to exit the software

6. Continue shutting down the computer

F.3 Changing the TEOM Filter

1. Place TEOM in initialization mode (If in collection mode press F2 and then F3 and say yes to initialization mode)

2. Leave the pump running and the TEOM power on

3. Open the door and remove the old filter with the tool

4. Remove the next filter from the box and install it on the tapered element, pressing firmly but not hard

5. Close the TEOM door and wait for the countdown to finish. When the countdown is done, the flashing light should stop and the status of the instrument should be "INIT" again

6. If the status does not return to INIT, the filter is probably not attached properly. Remove it and try again.

F.4 Useful commands

1. <alt> 2 (reduce scale by a factor of 2), <alt> 5 (reduce scale by a factor of 5), etc.

2. 2 (expand scale by a factor of 2), 5 (expand scale by a factor of 5), etc.

3. <alt> P (toggle between sample and purge mode)

4. F10 (quit using the software completely)

5. F1 (new file)

6. F2 (stop data collection)

7. F3 (return to initialization mode)
F.5  TEOM maintenance

1. Leak check the system every 6 months. Check TEOM in vacuum with small syringe to suck a slight vacuum and also check TEOM under pressure using the small hand-held pump (F. Bosch).

2. Clean TEOM head every year. Open black box inside TEOM, clean around the hole with a Q-tip and some alcohol (not much).

3. Change inline filter every 2 years. Filter goes in with arrow pointing in opposite direction to the flow.

4. Check the flow into and out of the TEOM every 6 months. The mass flow controller is calibrated to air at 0°C and 101.325 kPa.
G. Mass Flow Controller Calibration

G.1 Mass flow controller used for quartz filter flow control (MFC 56663 - serial number)

Figure G.1: MFC calibration curve - quartz filter flow control
It can be seen from Figure G.1 that the correlation is linear but there is an offset of about 0.03 g/s. This will cause a significant error in flow reading if the flow rate is low through the mass flow controller.

G.2 Mass flow controller used for quartz filter flow control (MFC 56662 - serial number)

It can be seen from Figure G.2 that the mass flow controller used to control the flow through the teflon filters for gravimetric analysis is almost perfectly calibrated. There is a little offset but the correlation is very nearly 1:1.

![Figure G.2: MFC calibration curve - Filter flow for mass sampling](image-url)
G.3 Mass flow controller used for diluent control
(MFC 59122 - serial number)

Figure G.3 shows the calibration curve for the mass flow controller that was controlling the mass flow rate of diluent. It can be seen that the calibration is totally off and since checking the calibration the flow controller is no longer in use. The mass flow controller is reading higher than what the flow actually is and this not a linear relationship. As the flow gets higher the reading vs. actual flow diverges. This mass flow controller was replaced with a rotameter because the exact diluent flow rate was not that important since the dilution ratio is determined by measuring $CO_2$ concentrations.

![Mass flow controller calibration curve](image)

**Figure G.3**: MFC calibration curve - Diluent flow control
G.4 Conclusions

Table G.1 shows a summary of the status of each of the mass flow controllers.

<table>
<thead>
<tr>
<th>MFC</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>56662 - gravimetric analysis</td>
<td>Excellent calibration - in use</td>
</tr>
<tr>
<td>56663 - quartz filter flow</td>
<td>Linear correlation, slight offset</td>
</tr>
<tr>
<td>59122 - diluent flow</td>
<td>Out of calibration - not in use</td>
</tr>
</tbody>
</table>

Table G.1: Status of mass flow controllers
H. Pilot Contribution to Particulate Matter: Results From C-14 Analysis Performed at U of T’s Isotrace Laboratory

H.1 Abstract

The purpose of the testing done was to quantify the contribution of the diesel pilot fuel under a wide range of engine operating conditions using the single cylinder research engine at UBC. This testing was performed in August of 2003. In total twelve quartz filter samples were collected and sent to the Isotrace Laboratory at the University of Toronto. The results obtained did not provide any concrete conclusions about the contribution of the pilot fuel to the particulate matter. It is believed that the results were erroneous and this could be due to a number of factors.

H.2 Test Procedure

Quartz filter samples of exhaust PM were collected during engine testing with a 100% biodiesel pilot and natural gas main fuel at two different equivalence ratios and two different pilot fuel mass fractions (pilot fuel mass flow/ total fuel mass flow). In total twelve filter samples were taken. The engine operating speed was held constant at 1200 rpm throughout testing. The GIMEP was held constant at each equivalence ratio (1050 kPa at $\Phi = 0.5$ and 1400 kPa at $\Phi = 0.7$). The cylinder charge mass was therefore increased as the EGR fraction was increased.

The filters were sent away to the Isotrace laboratory at the University of Toronto for analysis. At the Isotrace laboratory a filter was placed in a sealed glass container with clean CuO. This container is placed in an oven which is ramped up to around 750 - 800 degrees and left for 24 hours. The organic sample fractionates into a gas component and a charred solid component. The gas reacts with the oxygen released from the CuO, this rapidly heats the inside of the container to high temperatures where the charred solid components combust. After the combustion, all of the CO$_2$ is converted to pure graphite for analysis in an
accelerator mass spectrometer (AMS). The results from the filter analysis are returned as percent modern carbon (pMC) in each sample (based upon a current carbon concentration of 103 amol carbon-14/ mg carbon).

H.3 Results and Discussion

The carbon 14 results were surprising. A strong correlation between the pilot mass fraction of the total fuel content was expected but was not clearly found. Figure H.1 shows the relationship between the high pilot fraction (10% for $\Phi = 0.5$ and 6% for $\Phi = 0.7$), low pilot fraction (5% for $\Phi = 0.5$ and 3% for $\Phi = 0.7$) and EGR fraction.

![Figure H.1](image)

**Figure H.1:** Percent Modern Carbon at Various Equivalence Ratios and EGR fractions for 2 different pilot mass fractions

The pilot contribution to the total particulate matter was found to be between 6 and 19 %.
H.3. Results and Discussion

The largest contribution of the pilot fuel to particulate matter was found at $\Phi = 0.5$, 30% EGR with a low pilot fuel flow rate. The same operating point but with higher EGR results in a lower pilot contribution. Similarly, the same operating point but with lower EGR results in a lower pilot contribution. It is difficult to believe that these results are accurate as they do not intuitively make any sense.

One interesting observation is that with EGR a higher pilot fraction tends to lead to a lower contribution of the pilot fuel to the overall PM. The opposite appears to be true running without EGR, a higher pilot fraction tends to lead to a higher contribution of the pilot fuel to the overall PM. One would expect the contribution of the pilot fuel to the overall PM to increase as the relative amount of pilot fuel is increased.

It also seems as though the difference between the two pilot fractions is more visible without EGR than with EGR. There is between a 50% and a 100% difference between the PM at the two different pilot fractions without EGR and only less than about a 25% difference between the PM at the two different pilot fractions with EGR.

There was a problem with repeatability amongst the carbon 14 data at constant operating conditions. Table H.1 shows the percent modern carbon results for the three repeat operating points. Obviously, the percent modern carbon in these samples is not the same and therefore the results are not very repeatable. Filter BD8 has twice the modern carbon as filter BD1.

<table>
<thead>
<tr>
<th>Filter ID</th>
<th>% Modern Carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>BD1</td>
<td>12.34</td>
</tr>
<tr>
<td>BD2</td>
<td>21.52</td>
</tr>
<tr>
<td>BD8</td>
<td>24.91</td>
</tr>
</tbody>
</table>

Table H.1: Repeat operating point results

The complete set of data is given in Table H.2.
H.4 Sources of Error

1. AMS sample preparation - there may have been inconsistencies at the Isotrace Laboratory in converting the filter samples to graphite for AMS analysis.

2. Sample collection - there may have been some exposure of sample filters to the atmosphere where some condensible organic vapors or carbon dioxide may have been absorbed into the filter prior to the AMS sample preparation.

3. Treatment method - Filters were analysed for total PM content. An alternative method would be to heat the filter after collecting the sample to remove the soluble organic fraction (SOF) of the particulate matter. The SOF collection may be dependent upon the amount of carbon contained in the filter.

4. Engine operation - The engine operation was variable due to the 100% biodiesel pilot fuel.

<table>
<thead>
<tr>
<th>Test #</th>
<th>TEOM file name</th>
<th>DAQ file name</th>
<th>Filter ID</th>
<th>GIMEP (kPa)</th>
<th>Speed (rpm)</th>
<th>%EGR</th>
<th>Pilot% (mass)</th>
<th>14C/12C (pMC)</th>
<th>Error (+/- pMC)</th>
<th>Sample mass (mg)</th>
<th>IsoTrace Lab Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>T-BD-1-a</td>
<td>D-BD-1-a</td>
<td>BD1</td>
<td>0.51</td>
<td>1057</td>
<td>1198</td>
<td>49</td>
<td>9.2</td>
<td>12.34</td>
<td>0.53</td>
<td>0.39</td>
</tr>
<tr>
<td>2</td>
<td>T-BD-2-a</td>
<td>D-BD-2-a</td>
<td>BD2</td>
<td>0.52</td>
<td>1022</td>
<td>1195</td>
<td>49</td>
<td>4.7</td>
<td>15.75</td>
<td>0.51</td>
<td>0.43</td>
</tr>
<tr>
<td>3</td>
<td>T-BD-3-a</td>
<td>D-BD-3-a</td>
<td>BD3</td>
<td>0.50</td>
<td>1057</td>
<td>1199</td>
<td>31</td>
<td>9.6</td>
<td>16.98</td>
<td>0.49</td>
<td>0.32</td>
</tr>
<tr>
<td>4</td>
<td>T-BD-4-a</td>
<td>D-BD-4-a</td>
<td>BD4</td>
<td>0.49</td>
<td>1030</td>
<td>1196</td>
<td>30</td>
<td>5.1</td>
<td>18.89</td>
<td>0.41</td>
<td>0.5</td>
</tr>
<tr>
<td>5</td>
<td>T-BD-5-a</td>
<td>D-BD-5-a</td>
<td>BD5</td>
<td>0.49</td>
<td>1041</td>
<td>1202</td>
<td>0</td>
<td>9.1</td>
<td>18.32</td>
<td>0.25</td>
<td>1.03</td>
</tr>
<tr>
<td>6</td>
<td>T-BD-6-a</td>
<td>D-BD-6-a</td>
<td>BD6</td>
<td>0.50</td>
<td>1042</td>
<td>1205</td>
<td>0</td>
<td>4.9</td>
<td>9.12</td>
<td>0.17</td>
<td>2.62</td>
</tr>
<tr>
<td>7</td>
<td>T-BD-7-a</td>
<td>D-BD-7-a</td>
<td>BD7</td>
<td>0.50</td>
<td>1020</td>
<td>1193</td>
<td>52</td>
<td>9.4</td>
<td>21.52</td>
<td>0.37</td>
<td>0.39</td>
</tr>
<tr>
<td>8</td>
<td>T-BD-8-a</td>
<td>D-BD-8-a</td>
<td>BD8</td>
<td>0.51</td>
<td>1180</td>
<td>1195</td>
<td>48</td>
<td>8.7</td>
<td>24.91</td>
<td>0.49</td>
<td>0.43</td>
</tr>
<tr>
<td>9</td>
<td>T-BD-9-a</td>
<td>D-BD-9-a</td>
<td>BD9</td>
<td>0.71</td>
<td>1334</td>
<td>1202</td>
<td>0</td>
<td>6.4</td>
<td>13.98</td>
<td>0.3</td>
<td>0.44</td>
</tr>
<tr>
<td>10</td>
<td>T-BD-10-a</td>
<td>D-BD-10-a</td>
<td>BD10</td>
<td>0.72</td>
<td>1315</td>
<td>1202</td>
<td>0</td>
<td>3.3</td>
<td>9.29</td>
<td>0.33</td>
<td>0.61</td>
</tr>
<tr>
<td>11</td>
<td>T-BD-11-a</td>
<td>D-BD-11-a</td>
<td>BD11</td>
<td>0.69</td>
<td>1397</td>
<td>1199</td>
<td>30</td>
<td>3</td>
<td>7.67</td>
<td>0.25</td>
<td>0.56</td>
</tr>
<tr>
<td>12</td>
<td>T-BD-12-a</td>
<td>D-BD-12-a</td>
<td>BD12</td>
<td>0.69</td>
<td>1318</td>
<td>1198</td>
<td>30</td>
<td>6.5</td>
<td>5.87</td>
<td>0.25</td>
<td>0.64</td>
</tr>
</tbody>
</table>

Figure H.2: Summary of Operating Points and Percent Modern Carbon Results
H.5 Conclusions

1. Without EGR, higher pilot fraction gives higher percent of modern carbon in the exhaust PM

2. With EGR, higher pilot fraction gives a lower percent of modern carbon in the exhaust PM

3. Not very repeatable results

4. No clear correlation of percent modern carbon with the amount of EGR
I. TEM Images

Images available:

287-289: $\Phi = 0.4$, 0% EGR, low pilot fuel
290-291: $\Phi = 0.6$, 0% EGR, low pilot fuel
309-311: $\Phi = 0.6$, 0% EGR, low pilot fuel, block 1
304-306: $\Phi = 0.6$, 0% EGR, low pilot fuel, biodiesel
293-295: $\Phi = 0.6$, 25% EGR, low pilot fuel
297-299: $\Phi = 0.6$, 25% EGR, high pilot fuel
300-303: $\Phi = 0.4$, 25% EGR, low pilot fuel
Figure I.1: 287, 288
Figure I.3: 291, 309
Figure I.4: 310, 311
Figure I.7: 294, 295
Figure I.8: 297, 298
Figure I.9: 299, 300
Figure 1.10: 301, 302
Figure I.11: 303