Fuel Influence on Gasoline Direct Injection Particulate Matter Emissions

by

Khaled Rais

A thesis submitted in conformity with the requirements for the degree of Master of Applied Science
Department of Mechanical and Industrial Engineering
University of Toronto

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Abstract

Particulate emissions from gasoline direct injected engines are a topic of growing research interest due to health concerns. Using engine tests of extended length and fueled with custom hydrocarbon blends, this study aimed to experimentally investigate temporal and test-to-test gasoline particulate emissions variability that has been observed in earlier work. Gasoline property changes during engine operation and engine control module adjustments were ruled out as the source of the temporal variation. Crankcase ventilation system deposits were also ruled out but they were found to increase average particle numbers. Testing of custom fuel blends demonstrated that transient cold and hot start particulate emissions are fuel independent, steady state emissions are highly influenced by fuel properties and the commonly used model to assess that influence, the PM Index, is incomplete, and that the use of fuel of consistent composition reduces test-to-test variability.
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Chapter 1
Introduction

In recent years, climate change, energy sustainability, and air pollution have become prominent global challenges. Gasoline powered vehicles contribute significantly to all of these issues accounting for 16% of primary energy consumption and 20% of greenhouse gas (GHG) emissions in the United States [1]. The sector is also unique in that it is driven both by increased consumer awareness, as the automobile is a mass-marketed product, and government regulation.

The primary regulations that affect the automotive industry are the US Corporate Average Fuel Economy (CAFE) standards. CAFE requires that automakers have a fleet average fuel economy of 54.5 mpg over the EPA drive cycle by 2025 which represents an increase of 20 mpg or 58% over the 34.5 mpg 2016 standard. To put this in perspective, in 30 years from 1980 to 2010 actual fleet average fuel economy increased by less than 40% [2].

This unprecedented regulatory challenge has promoted the development and adoption of many automotive technologies including lightweight materials, novel transmissions, and vehicle electrification, but the most widely applied technology has been gasoline direct injection (GDI). GDI technology, which involves injection of fuel directly into the cylinders of an engine as opposed to upstream in the intake ports, has the potential for significant fuel economy benefits. In less than a decade, it has gone from near zero marketshare to representing 38% of US and over 50% of EU new gasoline vehicles [3].

Unfortunately as a by-product of this accelerated adoption, emissions challenges associated with GDI have been discovered that are only now beginning to be addressed by regulations and research. Of these, Particulate Matter (PM) emissions have proven to be the most difficult. The novel mixture preparation in direct injected engines leads to PM emissions which has previously only been a concern in diesel vehicles. Since traditional gasoline vehicles do not produce PM in significant quantities, current GDI exhaust aftertreatment systems do not address it.
1 GDI Overview

1.1 Comparison to port fuel injection (PFI)

Port fuel injection has been the dominant fuel setup in gasoline powered vehicles since it displaced carburetion in the 1980s. In PFI vehicles, an injector in the intake port with its nozzle directed towards the back of the intake valves supplies the engine’s fuel during the intake stroke allowing atomization and vaporization to begin in the port and leaving sufficient time for a more or less homogenous mixture to form prior to combustion. In GDI vehicles, an injector is mounted in each cylinder head, either centrally or on an angle, to supply liquid fuel directly to combustion chamber where it must atomize and mix rapidly. A feature of this configuration is that air alone is drawn into the combustion chamber during the intake process. The two systems are illustrated in figure 1.1.

![GDI vs PFI Configuration](image)

**Figure 1-1 GDI vs PFI Configuration [4]**

1.2 GDI Advantages

The benefits of GDI stem from the finer control of fuel that injection directly into the combustion chamber allows. These benefits are numerous and include improved engine responsiveness, reduced unburned hydrocarbon emissions (UHC) at cold start, greater exhaust gas recirculation (EGR) tolerance, and the potential for more power, but the primary advantage of GDI and motivation for its adoption is increased fuel economy. There are three effects of GDI that are used to reduce fuel consumption: stratified operation potential, intake fuel film elimination, and charge cooling.
With in-cylinder mounted injectors, it becomes possible to operate in lean stratified mode; instead of controlling engine output by restricting intake air with a throttle valve as in typical gasoline vehicles, an unrestricted charge of air is brought into the combustion chamber and the quantity of injected fuel is varied as necessary for the desired power output. This means that under normal part-load driving conditions, the engine will operate overall lean which leads to higher efficiency through increased fuel utilization and reduced heat loss as excess air is available for combustion and insulation of the flame from cylinder walls. Efficiency is also improved by elimination of the pumping losses associated with throttling. In practice, GDI vehicles have not yet realized the fuel economy benefits of stratified operation due to emissions and control difficulties. Three way exhaust catalysts are ineffective at lean air-to-fuel ratios and by occurring later in the 4-stroke cycle, stratified injection reduces premixing thereby increasing UHC and PM emissions.

Unlike PFI engines, GDI engines do not form fuel films within their intake ports thus there is a direct connection between injected and combusted fuel over each individual cycle. This enables GDI to quickly and efficiently respond to transient power demands. There are three scenarios where this advantage manifests itself: deceleration fuel cut-off, acceleration enrichment, and torque reserve motivated timing retard. Fuel injection would ideally cut-off during deceleration but that is not possible with PFI vehicles because it leads to complete exhaustion of intake films which can cause lean misfire during subsequent acceleration. With GDI, fuel entering the combustion chamber can be cut-off and restarted rapidly enough to avoid this issue. The quantity of fuel is also more precisely controlled as it is metered by the injector itself which allows stoichiometric air-to-fuel ratios to be maintained at all operating conditions. PFI systems are forced to compensate for their imprecise metering from fuel films by enrichment to ensure that adequate fuel is available for sudden increases in load due to acceleration or use of air-conditioning. The final scenario, spark timing retard, has similar motivations. Gasoline vehicles normally operate at spark timings retarded from the point of peak efficiency (max brake torque) to leave a quickly accessible “torque reserve” to meet any sudden demands. With GDI, an engine can operate at its optimal timing continuously and vary injected fuel as necessary for the desired torque.
To date, charge cooling has been the effect of GDI most exploited by automakers to reduce fuel consumption. With in-cylinder injection, vaporization also takes place in-cylinder where the latent heat of fuel can be utilized to reduce intake air and residual gas temperatures. Lower intake temperatures improve volumetric efficiency and lower peak temperatures enable higher compression ratios and higher brake mean effective pressure (BMEP) engine designs through overcoming knock limits. The latter effect enables a process called engine downsizing where a large engine is replaced with a lower displacement and often turbocharged engine with fewer cylinders that is more efficient at typical part-load driving conditions. This is an increasingly popular trend in the automotive industry with the midsize family sedan segment being an excellent example; where a V6 was once the standard high power engine choice, Hyundai/Kia, Chevrolet, and Ford have all moved to 2L turbo engines as their upgrade option for the 2016 model year. Unfortunately, the 2016 sedans have too many other changes including vehicle weight for a meaningful fuel economy comparison to earlier V6 models but many estimates of the improvement from turbo downsizing are available in the literature. Considering turbo-downsizing alone without the added benefit of GDI, Petitjean et al. found recent production engines with improvements of 8-10% and estimated that experimental engines could yield 15-18% improvement [5]. GDI engines would be expected to reach levels closer to the experimental engines. This is achieved by more efficiently heating up the additional mass in the exhaust that a turbocharger would introduce, by decoupling valve timing from the amount of fuel that enters the combustion chamber (which allows more control of residual gas fraction and volumetric efficiency), and by enabling higher charge motion intake system designs because the constraint of having to promote fuel and air mixing has been eliminated.

1.3 GDI Challenges

The increasing availability of precise electronic controls has largely eliminated what was once the greatest hurdle to GDI adoption, regulating fuel injection timing and quantity, but challenges with post-injection processes remain. Some of the current issues include more severe knock in turbocharged engines, dilution of engine oil, and increases in certain types of emissions, especially PM.

Much of the fuel economy improvement of turbocharged GDI engines comes from increased compression ratios and BMEPs that have the side-effect of promoting knock. In fact, a
new more severe form of knock specific to turbo GDI vehicles known as low speed pre-ignition (LSPI) has recently become a major concern within the automotive industry. Traditional knock is a type of abnormal combustion that occurs when there is local oxidation of a pocket of fuel ahead of the main flame front when the conditions, increased pressure and stoichiometric mixing, are conducive to compression ignition or, according to the less popular theory, when rapid propagation of the flame front reaches sonic velocity leading to detonation [6]. Regardless of the fundamentals, knock in MPFI vehicles has typically occurred post-ignition and been addressable based on the source of initiation. Knock that begins at a recurring point of crank angle rotation is often caused by advanced spark timing and will be avoided if timing is retarded. Occasional knock early in a cycle might indicate that the residual gas fraction is too high due to insufficient scavenging [7]. If knock occurs near the inlet valves, it may indicate in-cylinder flows poorly optimized for the pistons approach to top dead center (TDC). Surface ignition, which is normally classified as a form of knock, is promoted by presence of hot spots or combustion chamber deposits and can also be addressed through combustion chamber geometry or by anti-deposit oil formulations.

Unfortunately, the array of knock sources and responses catalogued over generations of PFI vehicles has failed to translate to LSPI in turbo GDI engines. The inability to use ignition timing is particularly alarming for automakers because most engines rely on a system that incorporates timing adjustments based on feedback from the knock sensor, a vibration based piezoelectric device. Unlike traditional knock, LSPI is a larger and more rapid increase in in-cylinder pressure due exclusively to pre-ignition that occurs under the low speed and high load conditions frequently encountered in downsized turbo engines. Recent findings suggest that it originates from two possible sources: excess hydrocarbons due to oil and/or fuel droplets exiting piston crevices [8], or deposits peeling off combustion chamber walls [9]. Having liquid fuel spray directly into the combustion chamber as in GDI contributes to both of these sources by reducing premixing leading to more UHC, and introducing fuel wall-wetting leading to more deposits and dilution of engine oil. Despite the difficulties of LSPI and direct injection, there has been recent progress through novel injection strategies [4] and a large industry supported program for new engine oil formulations. The next set of international oil specifications is expected to include an LSPI test conducted on a Ford turbo direct injection engine and additive
companies have already discovered a strong correlation between oil calcium content and LSPI frequency [10].

Much like it does for knock, the wall-wetting and reduced mixture preparation associated with in-cylinder injection has negative effects on UHC, NOx, and most markedly, PM emissions. There are four textbook sources of hydrocarbon emissions: cylinder gases that are forced into combustion chamber crevices during the high pressure compression and combustion strokes and subsequently exit during the expansion and exhaust strokes, hydrocarbons gases near cylinder walls that are not consumed due to flame quenching, oil films which absorb some fuel vapors prior to combustion and desorb them later in the cycle, and incomplete combustion [11]. Considering these sources, the effects of direct injection on UHCs are understandable. During cold start, GDI avoids the initial time at rich conditions and intake fuel films of PFI and warms up faster which promotes oxidation. After the initial start-up, the possibility of local rich or lean zones along the injection spray leads to incomplete combustion and the increased wall-wetting and oil dilution creates films that can’t be reached by the combustion flame front [4]. Overall taking into account normal driving cycles, GDI engines increase UHC emissions. NOx is not significantly different in GDI and PFI vehicles [4]. NOx is highly temperature dependent and requires available elemental oxygen so the higher temperatures associated with high BMEP turbo GDI engines would be expected to enhance NOx production but a strong effect has not been observed [4].

Particulate matter emissions have emerged as the most challenging aspect of direct injection. Several studies have shown that the novel injection configuration introduces new sources of PM that lead to an order of magnitude increase when compared to PFI technology [12]–[14]. Currently, organic and elemental carbon (soot) are what is normally being referred to when PM is discussed because these two forms of carbon make up the overwhelming majority of GDI PM. Historically, spark-ignited engines have emitted three classes of particulate matter: lead, organic matter, and sulfates. The source of lead was largely eliminated by the switch to unleaded fuel leaving sulfates, mainly from the motor oil, and soot [15]. PFI engine-out soot emissions were so low that sulfate production made up nearly half of its PM by mass and sulfate catalyst poisoning was actually the primary concern with respect to particulate matter emissions [6]. In contrast, the much more numerous and massive GDI emissions are almost entirely carbon-based so health effects due to inhalation are now paramount and the sulfate that is present is
mostly adsorbed on the organic particulate [13]. GDI particulate is thought to originate in a manner similar to diesel particulate, a long-known and studied pollutant, due to the similar fuel systems. In either case, unburned hydrocarbons are required for initial formation as they are both primarily carbon-based. Carbonaceous PM has been shown to be generated in fuel rich or very lean regions of injections sprays, crevice volumes, injector sac volumes (the portion of fuel left between the injector valve seat and nozzle), and oil and fuel pools on combustion chamber surfaces [11]. Much of this theory has been confirmed by optical studies of GDI engines that have shown that over a range of on-road representative injection timings, fuel pools with soot producing diffusion flames persist through the exhaust stroke [12]. Studies have also begun to characterize the relative magnitude of the issue with unexpected results. Since new diesel engines are equipped with diesel particulate filters (DPFs) in order to meet regulations, GDI vehicles are actually the largest producers of PM still being sold. Currently, the largest on road emitters would be older non-DPF diesels, followed by new GDI, new DPF diesels, and then PFIs in decreasing order with DPF diesels and PFIs producing near ambient levels of PM [13].

1.4 Significance of PM

That GDI’s most pronounced emissions effect is to encourage PM is particularly alarming since there is growing evidence that PM is severely detrimental to human health and there are ongoing developments to curb it by regulators. In addition, the black carbon component of PM emissions strongly absorbs solar radiation and can therefore partly negate the greenhouse gas emission benefit arising from a GDI engine’s lower fuel consumption [16].

1.4.1 Health Effects

Several epidemiological studies have established that particulate exposure is associated with pulmonary inflammation and increased risk of heart attacks as well as chronic ailments such as bronchitis and lung cancer [17]. In fact, an EU sponsored network, Air Pollution and Health: a European Information System (Apheis) estimated that in 23 studied cities, a reduction in average PM2.5 (particles less than 2.5 µm in diameter) concentration to 15µg / m3 would prevent 16 926 premature deaths annually [18]. The size specification is significant because recent work has shown that the lung penetration depth, and therefore potential damage of PM, is inversely proportional to particle diameter [19]. It is these small particles that motivated the World Health Organization (WHO) to classify diesel exhaust and particulate specifically as carcinogenic [20].
As yet, there are no original equipment manufacturer (OEM) included exhaust aftertreatment systems on gasoline vehicles that address PM because CO, UHC, and NOₓ were previously the primary gasoline emissions and they are sufficiently oxidized and reduced respectively by the common three-way catalytic converter.

1.4.2 Regulations

Regulators worldwide are beginning to respond to the emerging GDI PM health threat with the European Union being the most active so far. Their PM mass limit of 0.005 g/km was introduced in 2009 as part of the EURO 5 generation of emissions standards. The EURO 6 standard was intended to introduce the existing diesel particle number (PN) limit of $6 \times 10^{11}$ # /km to gasoline requirements in 2014 but, in a decision that highlights the difficulty of particle number reduction, 3 years of reprieve were granted to automakers giving them until 2017 to find solutions [21]. Even taking into account this concession, EURO regulations have rapidly gotten more stringent especially for PM as Figure 1.2 shows.

![EURO Emissions Standards Progression](image)

**Figure 1-2** % Change in g/km EURO emissions limits from 1993 to 2014
Chapter 2
GDI PM Emissions

In order to understand and ultimately reduce particulate matter emissions from GDI vehicles, researchers are studying the fundamentals of PM formation and attempting to connect them to quantitative results regarding the influence of operating parameters, mixture preparation, fuel composition, and sampling techniques. An introduction to recent work on each of these topics is provided here.

2 Literature Review

2.1 PM Formation Fundamentals

There are 6 major processes relevant to net soot production: pyrolysis, nucleation, surface growth, coagulation, aggregation, and oxidation. Beginning with a combustion region where the C/O ratio is at least 0.5, the precursors of soot must first be formed through decomposition and rearrangement of the original fuel hydrocarbons into less saturated lower molecular weight species through a process called pyrolysis. These reactions are very temperature dependent and often occur through a free radical mechanism so small quantities of OH, O2, and O are thought to increase pyrolysis despite also being significant in oxidation. The products of these reactions are normally aliphatic or polycyclic aromatic hydrocarbons (PAH), polyacetylene, and chiefly acetylene. The next step is the initial birth of a soot particle that avoids being consumed before it has a chance to grow and is known as nucleation. This ability to react and to grow while avoiding oxidation is thought to require a polar conjugated structure, which is why aromatics that can form such molecules directly are known to be a very effective soot precursor. The rate of oxidation reactions increase faster than nucleation with increased temperature so sooting in premixed flames is negatively correlated with temperature but positively correlated in diffusion flames which have fewer oxidative species. The next stage in soot formation is growth. While there is no clear distinction between nucleation and growth in terms of mechanisms, in general, small particles grow faster than large particles as they have more radical sites and thus growth can occur in cooler regions with fewer hydrocarbons than with nucleation. Coagulation is a process by which small particles collide and coalesce to form larger particles. This results in a greater mean size but lower total number of particles. It has been reported that primary particles
that are roughly 20-70 nm in size combine to form 100 nm to 2 μm agglomerates [22]. All 6 of these

![Diagram](image)

**Figure 2-1 Illustration of soot formation in a homogeneous mixture [23]**

There has been considerable difficulty associated with isolating individual parameters affecting spark ignition direct injection soot because it involves a complicated, potentially partially diffusion in the case of stratified injection, turbulent, premixed flame. **Temperature** has been seen to have the most significant effect by increasing soot formation and oxidation reaction rates. In premixed flames, peak formation is seen between 1500 and 1700K above which oxidation results in net decrease. In diffusion flames, the soot-temperature correlation is not oxidation limited. **Pressure** greatly increases soot production in premixed flames with a dependence of $P^2$ having been observed. In diffusion flames, the relationship is roughly $P^1$ to $P^{1.4}$ depending on study conditions. Generally, increased **O/fuel ratio** reduces soot by increasing oxidation rate but if that oxygen is added through oxygenated fuel molecules there could be other
factors with counter-effects. It is noted that the critical equivalence ratio for soot prevention is only that which leads to CO as complete combustion to CO2 is not necessary.

2.1.1 GDI Particulate Morphology

The most prevalent size range for GDI particles is 70-100 nm which is referred to as the “accumulation mode” range. The smaller particles in the range of 5-20 nm are called “nucleation mode” particles. Typically, GDI PM is classified into these two “modes” because the names are easily relatable to the formation processes of nucleation and coagulation although having emissions of intermediate size is quite common. By mass, the particles are primarily organic carbon, approximately 65%, that has condensed onto an elemental core of 1-5 nm nuclei particles [24]. Through electron microscopy, it has been observed that GDI PM has a less ordered graphitic structure than diesel particulate [25]. It also contain more oil additive derived metals such as calcium and zinc which indicate that oil interactions are a more significant source of PM in GDI vehicles than in diesels [26].

2.2 Engine Operating Parameter Effects

Processes are summarized in Figure 2.1. The degree to which these processes occur determines the quantity and structure of resultant soot and is based on environmental conditions. With this in mind, more recent work has sought to determine the net effects on soot of changing environmental conditions without having to consider individual processes.

Studies have been conducted on the effects of many engine operating parameters on PM including start of injection (SOI), engine temperature, injection pressure, spark timing, valve timing, air-fuel ratio (AFR), speed and load, EGR, and engine mileage [27]–[29]. Multiple studies with both wall-guided and spray guided engines have shown that \textbf{SOI} is the controlled parameter with the most impact [27], [28]. He et al. found that retarding the SOI 60º from their engine control module’s stock starting point of 309º (before TDC) reduced particle number emissions by more than 80% at both hot and cold start conditions. Surprisingly, further retardation did not have any benefit although the piston position at SOI would still be further away until it reaches bottom dead center (BDC). A possible explanation for this response is that the reduction in mixing time begins to counteract the reduced piston impingement leading to an overall increase in PN. Engine temperature was also a significant factor, although it is not really
a controlled parameter in the same sense as the others. Increasing the engine coolant temperature to 88 °C from 30 °C reduced PN by 50% at low speed and load conditions at a full range of SOIs and by 33% at the minimum PN SOI at mid-speed and load conditions. Using the stock SOI time, there was no significant change in hot or cold PN at mid-speed and load [25].

**Injection pressure** is inversely correlated with PN and a 30% increase in pressure led to an 8-10% decrease in PN emissions [25]. Advanced **spark timing** can lead to a small net reduction in PN because it reduces mixing time but increases peak temperature which promotes oxidation. Advancing it for PM is not recommended though because the increased temperature has a more substantial negative impact on NOₓ. Delayed **exhaust valve** closing (and opening since the duration is fixed by cam geometry) delays blowdown leaving more time for soot oxidation and allowing more work to be extracted from combustion gases which improves fuel economy and therefore also reduces PN on per fuel basis. Intake cam phasing like spark timing, has a minor impact on PM but a large impact on NOₓ because it affects internal EGR so it is also a poor choice for PM based optimization. As expected, **AFR** has a strong impact on PM. At cold conditions, PN doubled when AFR was enriched to 13.1 from stoichiometric in experiments by He et al [25]. The greatest impact of **speed/load** is how it drives AFR. During transient operation, especially rapid acceleration, AFR will decrease and in TGDI vehicles there will be some enrichment during boost. At steady state, higher speeds and loads will decrease mixing time but increase temperatures thereby promoting oxidation so there are only moderate effects on particulate. External **EGR** has negligible effects on PM at low levels but high EGR can decrease in-cylinder temperature and reduce oxidation. **Engine mileage** even with catalyst ageing was shown to not alter PM production up 150 000 miles in two GDI vehicles in a study by Maricq et al [27].

Through targeted application of operating effects, PM reduction strategies are beginning to be developed and evaluated. Most proposals have focused on optimization of injection and exhaust cam phasing because as demonstrated by the parametric studies, they have strong effects without compromising other aspects of performance [30], [31]. The largest improvements have been witnessed when calibrations are drive cycle phase-specific. The cold start and transient phases produce the most PM and have thus garnered the most attention. The steps taken for these stages by Whitaker et al. are summarized here. For cold start, the very first injection benefited from high pressure that improved atomization which would otherwise be very poor in a cold
The start of injection was set at intermediate point that was not so early that the piston was near enough to TDC that there would be substantial wetting but not so late that there was too little charge motion to keep fuel from drifting onto the cylinder liner. After the initial injection, pressure was reduced to decrease penetration and a **multiple injection** strategy that minimized impingement and allowed late injection to help warm up the exhaust catalyst was employed. This was coupled with late ignition timing for further catalyst warming. The interaction of TWCs with PM is not yet well understood but there is a consensus that they drastically cut particle number [31]–[33]. The current theory is that the ideally hot, narrow channels of a catalyst promote coagulation while oxidizing and inhibiting the formation of nuclei particles. In [30], this led to a 65% reduction in total PN but an increase in the number of particles larger than 50 nm. In Whitakers et al.’s calibration scheme, the system switched to heating up the combustion chamber to prepare for transience once the catalyst reached light-off. Overall, the optimization strategy successfully took a EURO 5 design TGDI engine that originally did not comply with EURO 6 PN limits into compliance, reducing average PN over the New European Drive Cycle (NEDC) by 78% [30]. While this result is impressive there are some important caveats. The details of the base engine that was tuned were not provided and the initial PN number of 2.0 x10^{12} was the lowest of the 6 GDI engines that were plotted in their engine type comparison. Other listings of typical GDI PN also have this value as a lower bound [13]. Another factor to consider is there was no data provided on the effects of the tuning changes on other aspects of performance such as fuel economy, responsiveness, or other emissions. The authors also mentioned the integration of a particulate filter (GPF) as is done in diesels with DPFs as a possibility but it was not considered in the study because it adds cost and increases fuel consumption which negates the primary purpose of GDI. A comparison between the PM reduction effectiveness of their strategy and a GPF would have been valuable. Other work has shown up to 82% reductions over the U.S. test cycle, Federal Test Procedure 75 (FTP-75) [34]. Lastly, the low starting PN value indicates that the chosen engine has spray-guided mixture preparation so the tuning results might not be reproducible in other configurations.

### 2.3 Mixture Preparation Effects

GDI combustion chamber configurations are broadly classified by the primary type of charge motion that they employ [4]. There are three possible forms of charge motion: swirl, tumble, and squish. Swirl is the rotation of the cylinder gases around an axis parallel to the cylinder’s axis
and is the major flow in “air-guided” engines. It is generated by bowl shaped pistons that create air flows which direct the air-fuel mixture and is dependent on high engine speeds. Tumble is the rotation in the axis perpendicular to the cylinder axis and is the major flow in “wall-guided” engines, which are currently the most common. It is generated by pistons and heads shaped so that their solid surfaces direct the air-fuel mixture. Squish is the radial motion that occurs when the piston approaches TDC and is the major flow in “spray-guided” engines. The clearest visual manifestation of the configuration type is the injector mounting location. Air and wall-guided systems have side-mounted injectors while spray guided injectors are centrally mounted [4]. A visual comparison is provided in Figure 2.2 [35].

![Figure 2-2 GDI combustion chamber configuration comparison][35]

Studies have shown that configuration type has a considerable effect on PM emissions. In a 2006 comparison of a spray guided system and wall guided system fitted on the same single cylinder research engine, the spray-guided setup minimum PM was an order of magnitude lower than the wall-guided setup’s [36]. Tests were conducted at a range of injection timings on pure iso-octane and toluene fuels and at the same conditions, the spray guided system produced less PM by mass and number. An interesting additional effect of the system was that the average particle size was shifted smaller to a more PFI like distribution of primarily nucleation mode particles. The PM response to injection timing also differed from expectations informed by [25], [26], as it initially exhibited little change and then began to increase with retard. Taken together, these two results indicate a difference in the source of particulate. In the wall-guided system, piston impingement and subsequent pool diffusion burning was a major contributor to total PM but it appears that this was not the case for the spray guided engine because it did not benefit
from timing retard, a change designed to reduce impingement, and actually suffered slightly due to the reduced mixing time [33].

The other major consideration in mixture preparation is whether an engine operates with homogenous or stratified charge combustion. Choi et al. compared PM from three vehicles, a wall-guided Hyundai Sonata, an air-guided Audi A5, and a spray-guided stratified injection BMW 330i [37]. Over the NEDC, they produced $1.48 \times 10^{12}$#/km, $6.3 \times 10^{11}$#/km, and $3.17 \times 10^{12}$#/km, respectively. The negative effect of stratification turned out to be larger than the benefit of spray guidance as the BMW had the highest PN. This is not surprising since a spray-guided stratified system has a central multi-hole injector and injection just prior to ignition like a diesel engine. With such a setup, somewhat diesel-like PM is to be expected and that is what occurred in terms of number, mass, and size distribution [34].

2.4 Fuel Composition Effects

Fuel properties impact net PM production by influencing fuel-air mixing and subsequent chemical reactions. Injection sprays are characterized by spray penetration, angle of fuel spread, and degree of atomization. Spray penetration in conjunction with injection timing determines the degree of piston wetting. The angle of fuel spread affects the amount of cylinder wall fuel impingement. Atomization is a required step for mixing and complete combustion. The most important fuel property for all these spray features is volatility, often expressed by Reid Vapour Pressure (RVP). Many studies have shown that increased volatility reduces PM emissions by accelerating vaporization thereby reducing impingement and improving mixing [38]–[41]. For example, Khalek et al. saw a 66% PM number and 82% PM mass reduction in vehicle out emissions by switching from a low volatility to high volatility commercial fuel [38]. The relationship is not entirely consistent with some exceptions in the literature. In one experiment under superheat conditions, flash boiling caused the injection spray to break up and there was rapid vaporization of some components but some liquid droplets actually appeared to penetrate further with the result being that a high volatility fuel produced more PM than a low volatility fuel [42]. There has also been speculation that low boiling point components like pentane can lead to more sooting pool fires. This was presented as an explanation for pentane leading to more PM than iso-octane or other longer alkanes [43].
The effects of ethanol are somewhat of an exception to the volatility trend as well. It has a relatively low boiling point and vapour pressure but it has a high enthalpy of vaporization which inhibits fuel atomization under certain conditions [44]. Ethanol’s net effect on PM cannot be deduced by this feature alone however, as it also has competing chemical effects. Due to its oxygen content, it promotes complete combustion and this effect can dominate the negative effect on vaporization under certain conditions including high temperatures where there is excess energy for vaporization, fuel rich operation since there is an oxygen deficit, and late injection timings because there is not enough time to access air-oxygen [45].

The leading effects of fuel composition on soot formation reactions are believed to be related to the “HACA” (H-abstraction-C2H2-addition) mechanism [46] detailed below. \( A_i \) represents an aromatic molecule.

\[
A_i + H \rightarrow A_i^- + H_2
\]

\[
A_i^- + C_2H_2 \rightarrow \text{products}
\]

The aromatic reactant is a limiting factor. It is either sourced from the breakdown of alkanes (longer alkanes breakdown more readily into methyl and \( \text{CH}_2 \) that form aromatics [47]) or directly from fuel. Therefore aromatic content is the key property of fuel composition. Tests of fuels with equal volatility but varying aromatic content have shown a very strong correlation between PM emissions and % aromatics [[41], [48]].

Fuel additives also impact PM emissions but to a lesser extent than aromatics and with less predictable results because their composition is often proprietary. Methyl tert-butyl ether (MTBE) is a common octane improvement additive that would be expected to reduce PM over a wide range of operating conditions because it contains oxygen which promotes oxidation and it doesn’t have the high vaporization issue of ethanol. There is limited data available but one study showed no discernible MTBE effect on PM in a wall-guided GDI engine over the FTP cycle [49]. Other types of additives do have strong effects but the mechanism is not as clear. A polyolefin amine additive was shown to increase PN by an order of magnitude over an unadditized version of the same base fuel at 15km/hr and by 40% at high speeds but actually had a slightly positive effect at mid-speed conditions [50]. For proprietary additives, a range of responses from order of magnitude increases to 50% decreases appear in the literature [50], [51].
Summarizing all these effects, researchers have found that aromatic content and volatility have the strongest relationships to PM [39], [48]. Aikawa et al. developed a model of the effect of fuel composition on PN and particulate mass in PFI vehicles that incorporates these two variables through inclusion of RVP and double-bonded equivalent (the degree of saturation of a component) [39]. They later showed applicability of this model, the PM Index, to GDI vehicles [38]. Other researchers built upon this work and made slight modifications for better correlation with the PN emissions of their test engine and dubbed their model the PN Index [48]. The two indices are presented as Equations 2.1 and 2.2 below.

\[
PM\ Index = \sum_{i=1}^{n} \left[ \frac{DBE_{i}+1}{VP_{i}(443K)} \right] W_{ti} \quad [37]
\]

\[
PN\ Index = \sum_{i=1}^{n} \left( \frac{DBE_{i}+1}{DVPE} \right) V_{i} \times 100 \ kPa \quad [46]
\]

where:
- \( DBE_{i} = \frac{2C-H-N+2}{2} \), the double-bonded equivalent of the ith component (C, H, and N are the number of atoms of each element in molecule of the component)
- \( VP_{i}(443K) \) – the vapour pressure of the ith component at 443 K
- \( W_{ti} \) – the mass fraction of the ith component
- \( DVPE \) – treated as equivalent to RVP in original work
- \( V_{i} \) – the volume fraction of the ith component

In an extensive survey of global fuels, the average PM index was found to be 2.12 with a standard deviation of 0.81 and the relationship to PM was approximately linear [39].

### 2.5 Sampling Considerations

Due to the lack of standard testing methods for dealing with particulate matter, it has been difficult to reconcile data generated from different laboratories and make general conclusions. To address this issue, there has been an EPA sponsored project to review diesel sampling methods and many independent reviews with suggestions for appropriate sampling methodology. Some of the topics that covered include: comparisons and evaluations of in-lab and on-road PM size
measurements, comparisons of atmospheric and current lab dilution processes, and sampling system best practices.

The first step in any system is sampling and dilution. The sampling and dilution system is required to reduce concentrations to manageable levels for measurement, reduce temperature, control condensation and nucleation, and avoid losses. At this point, experimenters must decide whether “wet” or “dry” measurements are desired. As discussed earlier, particles can be divided into two categories: nucleation mode, mostly volatile particles, and accumulation mode, almost entirely solid particles. The health effects of solid particles are better understood than those of volatiles. Solid particles are also more stable than volatiles which are highly sampling system condition dependent. However, by mass, the majority of engine-out PM is volatile organic material [11]. This leaves a difficult choice between two options for reproducible results, eliminating the condensable volatiles to achieve a dry measurement or trying to condense all particles through a wet measurement. The PMP, EU Particle Measurement Program, has recommended the dry method in order to measure the solid fraction number concentration and mass consistently and this has been incorporated into forthcoming regulations [52]. By comparing PM emissions from field tests and engine dynamometer studies, Wang et al. has shown that the existing PMP protocol may be adequately represent field measurements under low temperature conditions [53].

To avoid nucleation and condensation, high temperatures and dilution ratios (DR) are needed that keep the saturation ratio low. Nucleation is especially difficult to prevent with just dilution so “hot” dilution or thermodilution, diluting cold and allowing particles and then heating to evaporate them, is needed. Another method is to remove the volatiles altogether with sacrificial carbon, known as a thermodesorber, but this is more complicated. The main dilution systems are the full exhaust flow dilution tunnel (FEFD-tunnel), more commonly called the constant volume sampler (CVS), or the partial exhaust flow dilution tunnel (PEFD tunnel). CVS systems take the whole flow so they are large expensive systems that don't have built-in heating. PEFD systems are partial and therefore cheaper but the total flow must be known to determine what % is being sampled and this can be difficult during transient operation. There are also some constant dilution ratio techniques such as ejector and rotating disk dilution which are becoming increasing popular for their lower cost and flexibility. Ejector diluters use a venturi nozzle system for dilution and are small enough for convenient heating and cascading for high dilution
ratios. The downside is that they are inlet pressure dependent. Rotating disk systems allow fine control of ratio and dilution air and sample temperature but only work at low flow rates and are not reliable for large particles, >1μm, due to impaction losses [54]. When setting dilution ratios, consideration must be given to the volatile precursors initially in a gaseous state form the SOF of PM via adsorption / absorption or nucleation. There are theoretical models available to predict this behaviour. It has been found that as the saturation ratio, S, partial pressure of a condensable species vs. local vapor pressure, increases nucleation begins to dominate. The highest values have been found for dilution ratios of 5 to 50:1. Interestingly, the ratios common to dilution tunnels (3 to 20:1) are within this range while atmospheric values are thought to be much higher.

Once the gas has been sampled and diluted, measurements must be taken with the highest priority being mass, number concentration, and size distribution according to the PMP recommendations. Gravimetric analysis is very common for total mass but as mentioned it has run into detection limit problems. To address this, organizations like the EPA have recommended new filter media, higher resolution scales, and tighter tolerances on sampling conditions but there are still concerns with repeatable vapor collection. Much lower masses than the previous method have been found and this has been attributed to the media difference effecting volatile collection efficiency. Another gravimetric issue is that detection limits necessitate lower dilution ratios which makes comparison to particle number results difficult. Past work has shown increases in PM by as much as a factor of 6 associated with some dilution ratio changes [55]. Care must be taken to ensure that the dilution system provides consistent results. For their experiments, Chan et al. used two systems, a PMP compliant at a high dilution ratio and second setup fed by a Dekati Thermodeneuder at 300 °C at a low dilution ratio for particle size and mass data [34]. The measurements from these systems were in agreement over the course of their extensive testing program. When such elaborate measures are not available or different information is required there are alternatives to gravimetric analysis. A popular one is thermal mass analysis which first oxidizes OC and sulfur to CO2 and SO3 in order to use mass spectrometry but this method cannot detect ash. Online quantification of opacity has also been used, but light extinction is not uniquely dependent on total carbon mass. For particle number, condensation particle counters (CPC) are ubiquitous. The CPC's only drawback is a minimum detection size of 3 to 15nm which can be affected by maintenance. The best means to address this is just comparison between multiple machines. The major concern with particle number is not based on the measurement system but designing a sampling to address coagulation number changes and avoid nucleation and diffusional losses. Size distribution is done using an ELPI or the more recently
through the quick scanning of SMPS. A new novel approach is based on diffusion, the electrical diffusion battery (EDB). The particles entering the battery are charged which leads them to enter different stages and the resulting current at each stage is used to make a distribution based on the known relationship between average size and particle charge. Current work is looking into new optical techniques and combinations to yield unique indicators that account for morphology.

For each stage of the measurement process, the sample exhaust needs to be handled in a manner that minimizes the effects on PM. A number of best practices have been established to this end. During dilution, beyond controlling DR, temperature, and humidity, experiments have shown that the dilution air should be filtered to remove ambient PM and the residence time after final dilution should be minimized [54]. Prior to sampling, all lines should be heated to avoid condensation, line lengths should be as short as possible and conducting lines are useful to minimize electrostatic loses. Test conditions including fuel details and previous operating conditions should be noted as they can have a strong impact.

Overall, sampling conditions can be seen to have a major effect on the characteristics of the PM being studied. The major findings so far are that the critical dilution ratio range for nanoparticle nucleation as exhaust gases cool is 5 to 50:1. Therefore, dilution ratios should be set above that range for PN measurement. Since gravimetric analysis necessitates lower dilution ratios to collect adequate sample mass, care must be taken when comparing mass and number results, and sampling lines should be heated to near exhaust temperature and line lengths should be minimized.
Chapter 3
Experimental Rationale and Objectives

As discussed earlier, experimental research on PM production from GDI engines focuses on the effects of operating parameters, mixture preparation, and fuel composition effects. At the University of Toronto Engine Research and Development Lab (ERDL), the focus to date has primarily been on fuel effects. This is a logical topic choice because it is the initial factor for PM production that interacts with the other variables. Another consideration is that it has the greatest potential for an immediate large impact given that any developments have the potential to affect the millions of GDI vehicles already in-use in addition to future designs that will utilize new engine technology.

3 Previous Work

A number of tests on a variety of gasoline fuel blends have already been conducted at ERDL by Ramos and Mireault [11], [20]. Through these tests, they have developed and refined laboratory methods, compared emissions instruments, and made preliminary observations on the effects of ethanol and toluene on PM emissions. Most of their observations regarding fuel effects corroborate what has been seen by other researchers such as ethanol reducing PM under hot conditions or toluene increasing it, but they also had novel observations regarding PM variability [44], [48]. Both witnessed substantial variation in PM emissions between tests conducted on the same fuel and a gradual increase in the rate of emission, even at steady state operating conditions, over the course of individual tests.

3.1 Investigation by Mireault

In his investigation of this observed variability, Mireault pursued engine stability, complications associated with using an Engine Exhaust Particle Sizer (EEPS) to measure particle number, unaccounted for variations in the dilution ratio produced by the lab’s TSI branded rotating disk diluter, and the influence and source of brief sudden spikes in PM emissions well after reaching steady operating conditions.

The fuel tanks initially installed in ERDL allowed the engine to operate at the production vehicle’s highway cruise conditions - the approximate load and engine speed needed to travel
100 km/h, for 70 to 80 minutes. Great care was taken in selecting operating parameters and targets that would indicate that the engine had reached steady state conditions. Based on the fact that the engine’s cooling system begins to regulate the coolant temperature at 90°C, 90°C was selected as the steady state coolant temperature [56]. The engine was instrumented to the greatest extent practically possible including a scanner for the On-board diagnostics (OBD) data that the engine itself produces and the installation of multiple thermocouples for temperature measurements. Over the course of the first 19 reported tests, all engine temperatures, the throttle output as measured by the throttle position sensor, and the air mass flow rate measured by the engine’s mass air flow sensor had a relative standard deviation of less than 1% [20]. Therefore, it was concluded that engine instability was not a significant influence on PN variability. Mireault recommended monitoring fuel flow rate, fuel temperature, and ambient humidity for future study.

The EEPS, and particle measurement instruments in general, are still primarily limited production research tools so their reliability and robustness is not as well-known as commercially used devices like oxygen sensors and thermocouples. As a result, there was concern that the EEPS output could be sensitive to particulate build-up or fluctuations in sample temperature, pressure, or flow rate. Periodic cleaning of built-up PM on the internal parts of the EEPS is required to reduce output signal noise which suggests that PM build-up could be a factor in the increase in measurements witnessed during steady state tests and the variability between tests conducted on the same fuel only days apart. This theory was tested in two ways: increasing dilution ratio to reduce the particulate concentration flowing through the device and thus the rate of deposition within it, and intermittently running HEPA filtered air through the EEPS during engine testing as HEPA air has been shown to be able to clean the EEPS. If dirtying of the EEPS over the course of tests was the primary cause of the drift in PN measurements, these methods would be expected to reduce if not eliminate the issue. Instead, the drift continued apparently unaffected [20]. Fluctuations in EEPS operating conditions were also discounted as a factor. Sample pressure and flow remained stable over the course of testing and sample temperature, while somewhat variable, did not correlate with the particulate number results [20].

After tackling the EEPS, the study moved upstream in the particle sampling setup and looked at the influence of the TSI rotating disk diluter that provides the EEPS its sample flow. Four diluter parameters were considered: temperature stability, dilution ratio stability, particle
buildup, and dilution air humidity. Intentional changes were made to the temperature of the diluter head using a fan but no corresponding effect on particle measurements occurred, thereby eliminating temperature as possible cause. The dilution ratio setting of the device was verified using a CO\textsubscript{2} monitor upstream and downstream of the diluter. While the dilution ratio setpoint was inaccurate and inconstant, the temporal drift in PN was still present even after the actual dilution ratio calculated from the CO\textsubscript{2} monitor data was applied as a correction factor. Particle impaction is always a concern with rotating disk diluters due to the small crevices and fast moving parts in contact with the gas stream [54]. If these impacted particles were to then be released gradually as the test proceeds, that could help explain the gradual increase in particle number. To test this theory, a Dekati ejector diluter, which has far less particle impaction due to its use of a venturi system with no moving parts, was used. Particle number and particle mass increases were still measured using the EEPS and gravimetric analysis respectively. Dilution air humidity is known to be a large factor in measured PN due to increased humidity leading to increased nucleation of water/sulfuric acid particles [50], [52], [57]. The dilution air for the TSI diluter was taken directly from the surrounding room and not a conditioned air supply so it was subject to changes in ambient humidity. This was clearly a source of potential day-to-day variability but it could not be responsible for the drift given that dry air supplied to the Dekati diluter reproduced the phenomenon. A shift in particle size distribution to the nuclei mode, as would be expected if the drift was an artifact of nucleation promoting dilution humidity increases, was also not witnessed [20].

Rare and unexplained spikes in PN without a corresponding change in engine throttle position occurred late into many tests. These events were not frequent or sustained long enough to be a major contribution to the gradual PN increase or test-to-test variability directly, but understanding them could provide clues as to the types of processes that affect PM emissions. As usual, instrumentation was examined first and multiple combinations of equipment were used to confirm that spikes were “real” engine out increases. Next, pre-programmed PCM fuel injector responses similar to what is done in many vehicles to warm up oxygen sensors were considered. This was eliminated from contention by the lack of any noticeable change in equivalence ratio (\(\phi\)) or short-term fuel trim (STFT). With the control and instrumentation possibilities rejected, only in-cylinder processes such as injector deposit dislodgement and piston ring alignment, could be envisioned as possible sources. The growth of injector deposits is a well-documented issue in
GDI engines [58]. Over time, the injector face can become fully coated and dry out, leaving brittle flakes that can fall into the cylinder at any time [59]. When this occurs, the flakes themselves are not expected to register as particulate matter because they would likely be too large to be quantified by the EEPS. However, they could disrupt steady-state PM production by introducing a fuel rich pockets in-cylinder as the solid pieces desorb the vapours collected on the injector tip. Unfortunately, no method to test this theory could be devised. The final potential cause of the spikes, piston ring alignment, is similarly difficult to test because equipment for measuring crankcase blow-by flow or crankcase pressure was not available. It is speculated that the gaps on the three piston rings may momentarily align allowing a sharp increase in blow-by flow that would lead to more oil and fuel vapour being recirculated and potentially partially burnt to produce PM [60]. In addition to the potential for recirculation, alignment also permits more fuel vapor and oil interaction or even back flow from the crankcase to the combustion chamber. Both in-cylinder theories were considered promising and left for further study [20].

While not pursued by Mireault, an interesting offshoot of the investigation of the two potential in-cylinder PM spike sources is their apparent application to the overall emissions variability. Injector coking is clearly a gradually developing process that can affect PM in more ways than flaking deposits. Berndofer et al. used optical investigations to show that injector coking can potentially disrupt the injection process and lead to the formation of a persistent sooting diffusion flame post-injection [58]. Parameters describing the sooting flame, size and duration, showed a very strong correlation with total PM emissions. This indicates that the influence of injector coking supported diffusion flame soot production is large enough to explain the temporal increase in PM observed by Mireault and Ramos. The only caveat is that Berndofer’s testing was done with a spray guided engine, which produces less total PM so the source might make up a smaller proportion in ERDL’s wall guided Ford engine.
Looking at the work of Mireault as whole, the following areas warranted further study:

- Test operating conditions including fuel temperature, fuel flow rate, dilution air humidity, and ambient humidity
- Fuel-oil film interaction and the build-up and exit of rich vapour pockets from piston crevices
- The influence of crankcase gases
- The influence of injector deposits

### 3.2 Investigation by Ramos

Ramos began his work once questions regarding the impact of the emissions instrumentation had been conclusively answered, so he was able to move straight to studying systematic sources of variability arising from test conditions, engine hardware, and later fuel composition.

The test conditions considered were dilution air humidity, oil and fuel temperature, and oil age. Dilution air humidity was studied by changing the TSI rotating disk diluter’s air supply from ambient air to a filtered dry source. The result of this change was a statistically significant reduction in particle count and relative standard deviation of that count over sets of three tests on the same fuel blends. Based on this improvement, the use of dry dilution air was incorporated into all future testing. Reduced fuel temperatures have been shown to reduce engine out PM [61]. This was verified by an engine test where the running fuel tank was changed to one with a temperature 7 °C lower. An approximately 4% reduction in PM out was observed as the switch was made. The magnitude of the reduction, though perceptible, was not large enough to explain any of the larger variability questions being studied. Nevertheless, use of the fuel cooler was made permanent as a test improvement. In the same spirit, an oil cooler was also added with the expectation of better oil temperature control. The effect of oil age was checked by comparing the results of the first four runs following two oil changes for any signs of PM stabilization. No significant change was seen between run 1 and run 4 leading to the conclusion that oil age is not a key factor [11].

The emphasis of the engine hardware investigation was the intake deposits arising from the positive crankcase ventilation (PCV) system with some attention also given to injector deposits. The crankcase ventilation system returns blow-by gases to the intake manifold to be
consumed by the engine. These blow-by gases are comprised primarily of air, but also contain fuel-oil vapours and combustion products that can form deposits in the intake system. When checked, substantial deposits were present on the intake valves and runners that could potentially cause air flow disturbances or vapour desorption that lead to PM. To address this possibility, a thorough cleaning was conducted and an aftermarket PCV filter system was added to the test stand. Pre-and-post-cleaning-and-filter-installation results were not generated on the same gasoline batch so it is difficult to isolate the impact but the temporal and test-to-test variability remained. In the course of the PCV work, significant injector deposits were also found but they proved more difficult to deal with. Fuel filtering would not be effective because the deposits form through in-cylinder processes and cleaning injectors was not possible because the seals required for re-installation after removal for cleaning could not be procured. Instead, to the extent possible without disassembly, images of the deposits were taken using a borescope to check for stabilization. It was determined that deposits did not grow appreciably over the course of two months of testing so the effect on the injection streams and thus PM production was deemed minor. Despite confidence in this conclusion, limitations in the approach were recognized and further study was recommended [11].

The second half of Ramos’s work dealt with fuel blend testing. Testing began with a base gasoline, E0, and then progressed to ethanol blends, E10 and E30, toluene blends, 10% toluene and 10% toluene with E10, and finally a return to pure gasoline, E0 return. The significance of this work as it applies to the study of variability is the comparison between the E0 and E0 return results. The difference in average PN concentration emitted during those tests was actually larger than the difference between the E0 and E10 tests confounding any attempt to draw conclusions regarding the effects of ethanol and toluene. The result was initially mystifying but a pronounced difference in aroma during the E0 and E0 return tests was recalled which led to suspicions of a change in the aromatic content of the two batches of pump gasoline purchased at the same station only a few weeks apart. Unfortunately, gasoline samples weren’t available to complete a detailed hydrocarbon comparison so speciation of the gaseous emissions was used as an approximation. Of the gaseous species measured, toluene had the largest positive correlation with PM and isobutylene had the largest negative correlation. On the basis that toluene reflects higher fuel aromatic content and isobutylene reflects higher vapour pressure, an adjusted PN index was calculated and applied to the all the fuel blends tested. The results were dramatic as shown in
The adjustments were able to explain all apparent deviations from the PN index in the original results, making inadvertent gasoline composition changes the best explanation of test-to-test variability to date [11].

Figure 3.1 PN concentration at end-of-test for each fuel blend with PN Index and Corrected PN Index overlain [11].

Ramos was successful in gathering preliminary evidence for a very promising explanation for day-to-day variability but it still needed verification and work was still required to explain the PN drift. In keeping with these aims, the future work in the following areas was suggested:

- Development of a proxy gasoline using pure hydrocarbons to establish a baseline fuel for future studies
- Parametric fuel studies to determine the relative influence of vapour pressure and double bonds

3.3 Experimental Objectives

Building on the work done previously at ERDL by Mireault and Ramos, the research priority for this thesis is to better understand PM emissions variability, both temporal and test-to-test. The
areas for investigation listed below draw heavily from a review of the gaps in knowledge in their work and their recommendations in pursuit of that overall objective.

- Extended length testing to assess the occurrence and contribution of late deposit, PCM, and fuel stabilization to the previously documented gradual increase in particulate matter emissions over the course of individual tests.

- Formulation of a surrogate gasoline from pure hydrocarbons to establish test repeatability, verify the influence of inadvertent gasoline changes, and characterize the sensitivity of PM to different fuel properties.
Chapter 4  
Experimental Setup

4  GDI Test Stand and Emissions Measurement Equipment

The GDI engine test stand and methods at ERDL were developed over the course of two previous graduate research projects. The foundation was laid by Mireault and refinements were added by Ramos [11], [20]. At the start of this research project, a mature experimental system was inherited and maintained where possible. A summary of the system is presented here with an overview given in figure 4.1. The description of the system from Ramos’s work is repeated here for areas where no changes have been made [11]. Italicics indicate repeated material. The non-italicized material in sections 4.1.3 and 4.1.6 describes modifications made during this study.

![Figure 4-1 Overview of GDI test stand and emissions sampling setup](image)

**Figure 4-1 Overview of GDI test stand and emissions sampling setup**

4.1 Research Engine

The engine used in this research is a pre-production four-cylinder GDI engine used in the 2012 and newer Ford Focus. It employs side mounted, wall-guided direct injectors and is naturally
aspirated. Table 4.1 lists some of the major specifications of the engine. A stock ECU - known as a Powertrain Control Module (PCM) within Ford - electronically controls the operation of the engine, and in production vehicles the transmission and other drivetrain components. It has the ability to read on-board sensor data, look up predetermined engine maps, and adjust them according to the current conditions. Parameters such as spark timing, injection timing, valve timing, and many more, are directly controlled by this unit and can be varied in real-time. A custom dyno-wiring harness interfaces the ERDL-made engine control panel with the stock PCM and engine wiring harness.

<table>
<thead>
<tr>
<th>Table 4-1 Research Engine Specifications</th>
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<tbody>
<tr>
<td><strong>Displacement</strong></td>
</tr>
<tr>
<td><strong>Bore x Stroke</strong></td>
</tr>
<tr>
<td><strong>Compression Ratio (r.c)</strong></td>
</tr>
<tr>
<td><strong>Horsepower</strong></td>
</tr>
<tr>
<td><strong>Torque</strong></td>
</tr>
<tr>
<td><strong>Redline</strong></td>
</tr>
<tr>
<td><strong>Fuel Injection</strong></td>
</tr>
<tr>
<td><strong>Valvetrain</strong></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td><strong>Block and Head Material</strong></td>
</tr>
<tr>
<td><strong>Recommend Fuel</strong></td>
</tr>
<tr>
<td><strong>Emissions Control</strong></td>
</tr>
<tr>
<td><strong>Emissions Standards</strong></td>
</tr>
</tbody>
</table>

4.1.1 Powertrain Control Module

The PCM was supplied with a non-production engine calibration. Discussion with Ford has indicated that this PCM was used in durability testing campaigns and has a slightly rich tune and is not configured for proper catalyst function. Indeed, wide-band oxygen sensor readings showed a fuel-air equivalence ratio of approximately 1.015 at steady conditions. However, the exact calibration of the PCM is not known and it is currently unmodifiable.
4.1.2 Engine Exhaust System

A standard equipment exhaust manifold was used in this set-up, which normally has an incorporated TWC see Figure 4.1. However, given that the PCM is not configured to run with a TWC, the exhaust manifold was modified to remove the stock exhaust after-treatment. This was accomplished by cutting open the catalyst can, removing the catalytic core and re-welding the can back together. Keeping an otherwise stock exhaust manifold will permit future work on this engine to look at catalyzed vs. uncatalyzed emissions under an identical set-up. The exhaust manifold was joined to the exhaust tube, which in turn feeds the raw engine exhaust to the sampling tube at a typical tail-pipe distance. The exhaust system and sampling tube were designed in accordance to US EPA guidelines [15].

4.1.3 Fuelling System

A custom fuel system was implemented here, as the use of a stock fuel system would not be appropriate. Figure 4.2 shows a schematic diagram of the fuelling system. Two fuel tanks hold the test fuel and are selected via two three-way solenoid valves, which control the flow path of the outgoing and return fuel. A coarse filter removes large debris from the ow to protect the low pressure fuel pump, while a fine filter is employed to prevent any smaller debris from entering the high pressure loop on the engine side. A pressure regulator ensures that fuel at 55 psi is continuously supplied to the high pressure fuel pump, with unused fuel being returned to the appropriate tank. A fuel cooler was added in this investigation to control the fuel temperature being fed to the high pressure loop. The fuel temperature is measured at the exit of the pressure regulator before the fine filter. A custom fuel-to-water cooler was made to provide control over the fuel temperature. Measured in-tank fuel temperature was found to increase steadily with run time, due to the fact that the low pressure fuel pump is cooled by the fuel that is continuously pumped in the low pressure loop. Figure 4.3 shows a cut-away view of the fuel cooler. The custom fuel cooler amounts to a single shell, single tube heat exchanger. With an annular cross-section, fuel is pumped through the centrally mounted tube, while city water is counter-owed through the shell side. A ball valve controls the water ow upstream of the cooler, while a precision needle valve regulates the outow of water from the cooler. The ball valve allows the user to disable the cooler and the precision needle valve controls the fuel temperature.
Figure 4-2 Fuelling system flow diagram. [11]

Figure 4-3 Cross-sectional view of fuel cooler. Red arrow indicate fuel flow path and blue arrows indicate water flow path. [11]

The inherited fueling system was modified by replacing fuel tank 2 with a large Jugs 16 gallon fuel cell (part# 555-15376) to enable extended length testing.

4.1.4 Dynamometer

A GO-Power D-557 water brake dynamometer was used to apply a load on the engine. The water brake dynamometer works by transferring the mechanical energy of the engine to the water due to friction and turbulence generated between the rotor and stator. The rotor is coupled to the engine, while the stator is coupled to the dynamometer stand. A strain gauge measures the
force applied to the stator by the rotating fluid in the internal cavity. Water is supplied at a pressure that is regulated down from building pressure; the amount of water flowing to the dynamometer is controlled via the dynamometer controller (see Section 4.2.2).

4.1.5 Oil Cooler

A sandwich type oil cooler from a 2012 Ford Focus ST (turbocharged, high performance variant of this research engine) was installed for this work. Figure 4.4 shows the installation location and the relevant flow paths. The oil cooler works by owing engine coolant through a heat exchanger that is seated above the oil filter. Pressurized oil is forced through this cooler before continuing through the filter and back to the engine block. The oil cooler was installed in the typical coolant loop location for the heater core on a production vehicle. This location ensures that coolant flows through the oil cooler at all times while the engine is turning over because the coolant path for the heater core is unobstructed by the thermostat. By having coolant owing at all times, the cooler works to both heat the oil more quickly in cold conditions and cool the oil when the engine is fully warmed. A ball valve downstream of the oil cooler allows disabling of the unit by preventing coolant flow to it.

Figure 4-4 Schematic of oil cooler. Note: oil flow paths do not intersect. [11]
4.1.6 Crankcase Ventilation Filter

A crankcase ventilation system is designed to recycle engine blow-by gases (combustion products and unburnt fuel vapours that escape the combustion chamber through the piston rings) back into the induction system of the engine so that it may be combusted with incoming fuel-air charge. This prevents the uncontrolled emission of these gases to the atmosphere, and is part of emissions control packages on vehicles. In the case of this engine, a positive crankcase ventilation (PCV) system is utilized; vacuum generated by the engine in the intake manifold draws in the crankcase air and blow-by gases. This crankcase ventilation is regulated by a PCV valve that also reduces the vacuum from inHg in the manifold to inH2O in the crankcase. The stock engine design incorporates an oil separator onto the engine block that functionally prohibits the ingestion of crankcase oil into the induction system via this ventilation system but visual inspection showed that some oil escaped. As a result, a MANN+HUMMEL ProVent200 oil separator filter for closed crankcase ventilation was installed. An exploded diagram of the filter is provided in Figure 4.5. The filter was fitted downstream of the stock PCV valve and upstream of the intake manifold. A coalescing filter element absorbs oil vapours and liquid oil being pulled by the vacuum of the intake manifold.

![Exploded view of the MANN+HUMMEL ProVent200 oil separator filter](image)

During initial testing, it was discovered that the filter still allowed some oil droplets and vapour to return to the intake manifold. To gauge the influence of this material, a 3-way valve was
installed with one branch returning to the engine and another directed out of the test cell. The branch that diverted the blow-by gases included a Thomas Industries 917CA18TFEL-B pump and a NDS rotameter to maintain the crankcase evacuation flow. This addition allowed operators to isolate the engine from blow-by gases as desired.

4.2 Engine Controls

A custom made engine control panel operates the major electrical control functions for the engine. These include the starting system, the fuelling system, the PCM system, and the emergency stop system. The control panel is the same one used in the first study on this engine by Mireault [20]; specific details are omitted here for the sake of brevity.

4.2.1 Throttle Control

An ECM appsCAN throttle pedal simulator was used to simulate the throttle pedal signals to the PCM. Modern vehicles make use of throttle-by-wire systems, where an electrical sensor measures the throttle position at the pedal and relays that to the PCM. The PCM then performs the necessary calculations to select the appropriate throttle plate angle given the commanded throttle position and other critical parameters; the PCM physically controls the throttle plate angle with a servo motor. As owner safety is of utmost importance to auto manufacturers, the throttle pedal actually has two sensors that must mathematically correspond to each other; the PCM reads both values and should one not correspond to the other a fault is triggered and the vehicle enters what is known as “limp-mode”. Therefore, the coordination of these two signals is necessary for proper engine operation. The appsCAN provides a synchronous output of signals in a stand-alone fashion required to operate the throttle. This throttle pedal simulator represents a modification from the original throttle control used by Mireault [20], which amounted to a servo-controlled throttle pedal. The need for this change was borne out of improving the repeatability of the throttle control process, which would be a requirement for future drive cycle work. Therefore, the appsCAN module was installed to satisfy this requirement as well as to better automate the control of the research engine. Specific to this research engine, the throttle pedal outputs two position signals, APPS1 and APPS2, based on its current position to the PCM. Measurement of the signals showed that APPS2 is 50% of APPS1 at any given position. As such, the appsCAN module was set to run in ratiometric mode, where the two desired outputs would run at a fixed percentage of an input voltage signal. A 0-10 V input signal
from the NI DAQ (see Section 4.4.1) was used to control the appsCAN which in turn provided two signals at 50% and 25% of the original input. Note that the signal was scaled in the Labview program to fit the required signal range of the pedal to a 0-100% scale (i.e. a 0 % selection in the program would yield a 1.6 V output to the module, which corresponds to the 0% pedal position for sensors APPS1 and APPS2). Further logic was incorporated to read throttle ramps from a file, as well as provide for certain fail safes.

4.2.2 Dynamometer Control

A Digalog 1022A Dyno Controller was used to provide control of the water brake dynamometer mentioned in Section 4.1.4. The dyno controller reads engine speed from a magnetic pick up on the dynamometer, as well as the strain voltage (calibrated for torque loading) from the strain gauge. The dyno controller has the ability to control the load and speed set-points given these two readings by controlling the amount of water entering the dynamometer through a compressed air controlled water valve. Essentially, this works by regulating the amount of compressed air supplied to open the water control valve. This is done with an on-board closed loop PID controller, which was re-calibrated along with the stain-gauge prior to start of this work. In this investigation, the controller was set to control the engine speed, the set-point of which was controlled by analog voltage signals from the NI DAQ (see Section 4.3.1).

4.3 Engine Data Acquisition and Control

Critical engine parameters, temperatures, and pressures were recorded using two independent data acquisition systems. Engine specific parameters were recorded using the high-speed controller area network (CAN) bus that is standard to production vehicles and known as the on-board diagnostic version 2 (OBD-II). The other acquisition unit—a National Instruments CompactDAQ-measured temperatures, pressures, and other analog signals, as well as outputted control signals. This data stream was recorded using a modified version of the Labview program used by Mireault [20].

4.3.1 National Instruments Compact DAQ

A National Instruments (NI) CompactDAQ (cDAQ-9174) populated with four modules captured analog data such as temperature, pressure, and load. Two NI-9211 thermocouple modules provided acquisition of temperature data, while an NI-9205 module collected analog sensor
data. A single NI-9263 module handled analog outputs used to control the throttle simulator (Section 4.2.1) and the dyno controller (Section 4.2.2) for the load and speed set-points, respectively. Table 4.2 lists all the sensor data collected and the analog outputs controlled by the DAQ. All thermocouples used were Omega K-Type grounded thermocouples (HGKQSS-18G-12). Pressure measurements were made with engine manifold air pressure sensors (MSD Ignition 2312).

Two independent Labview programs were used with the DAQ for data recording and output control. The main program for recording purposes is a modified version of the original program used by Mireault [20]. The above inputs from the NI DAQ, as well as inputs from the standard emissions bench (Section 4.5.3) over TCP/IP, are read and written to a file at 5Hz and 1Hz, respectively. Modifications to this program include the addition of the previously excluded emissions analyzers and the calculation of corrected emissions from the standard emissions bench. The second program controls the throttle (load) and engine speed set-points for the throttle and dyno controllers, respectively. Manual control or pre-developed load and speed ramps are available for selection by the user.

<table>
<thead>
<tr>
<th>NI Module</th>
<th>Recorded/Outputted Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>9211 (2)</td>
<td>TC1 - Exh. Temperature (°C)</td>
</tr>
<tr>
<td></td>
<td>TC3 - Exh. Temperature (°C)</td>
</tr>
<tr>
<td></td>
<td>Ambient Air Temperature (°C)</td>
</tr>
<tr>
<td></td>
<td>Oil Temperature (°C)</td>
</tr>
<tr>
<td>9205</td>
<td>Abs. Ambient Pressure (kPa)</td>
</tr>
<tr>
<td></td>
<td>Engine Speed (rpm)</td>
</tr>
<tr>
<td></td>
<td>Fuel-Air Equivalence Ratio (ϕ)</td>
</tr>
<tr>
<td>Outputs</td>
<td>9263</td>
</tr>
<tr>
<td></td>
<td>Throttle Position (%)</td>
</tr>
<tr>
<td></td>
<td>Engine Speed Set-point (rpm)</td>
</tr>
</tbody>
</table>

### 4.3.2 OBD-II

Data from the OBD-II CAN bus was gathered using a generic after market OBD-II reader. The reader contains an ELM-327 chip which is widely used to decode CAN messages over the OBD-II protocol-known as parameter IDs (PIDs)-and interface with computer software via USB. As the OBD-II standard is made to provide a minimal level of access to diagnose issues with vehicles, this chip can only decode those CAN values deemed essential for troubleshooting by regulatory agencies. However, manufacturers do employ proprietary CAN messages which are
only decodable with proprietary readers. A list of the available PIDs recorded during this investigation is provided in Table 4.3.

<table>
<thead>
<tr>
<th>Table 4-3 PIDs recorded from OBD-II data stream.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Engine Speed (rpm)</td>
</tr>
<tr>
<td>Intake Air Temperature (°C)</td>
</tr>
<tr>
<td>Air Flow Rate (g/s)</td>
</tr>
<tr>
<td>Accelerator Pedal Position (%)</td>
</tr>
<tr>
<td>Fuel Rail Pressure (kPa)</td>
</tr>
<tr>
<td>Long Term Fuel Trim (%)</td>
</tr>
</tbody>
</table>

4.4 Particle Matter Sampling

The following section will detail the particulate matter sampling apparatus used in this investigation. The two dilution systems are discussed first, followed by the instruments used to analyze size, mass, and composition of the particles. All referenced instruments were serviced at acceptable intervals prior to and during data collection per manufacturer recommendations.

4.4.1 TSI Rotating Disk Thermodiluter

A TSI 379020A Rotating Disk Thermodiluter supplied diluted exhaust gas to the particle sizer used in this study (see Section 4.4.4). The 379020A is controlled and fed dilution air from a combination of a TSI 379030 Thermal Conditioner Air Supply and a Matter Engineering MD19-3E Raw Gas Diluter; this latter unit will henceforth be referred to as the `diluter box'. This diluter is capable of achieving DRs between 15:1 to 3300:1 at flow rates between 0.5-20 lpm [62]. The 10-cavity rotating disk mixes fixed volumes of exhaust gas with the primary dilution air. The par-diluted sample is sent to a thermal conditioner and thermodenuder, before being cooled by the secondary dilution [62]. Through results obtained by Mireault, the diluter was found to produce stable DRs; however, true DRs were found to be consistently under the set-point desired. As a result, the true dilution ratio was measured using CO2 as a tracer gas. Modifications were made by Ramos to the diluter box in order to accept a dry supply of dilution air. This consisted of plumbing flexible tygon tubing from the HEPA filter inlets to the top of the unit, where a connection was made to a line of dry pressurized air (see Section 4.4.3). The pressurized air is supplied at ambient pressure by venting any excess to ambient. A small additional modification was made during this study to move the HEPA filters from inside to
the box the top of the unit connection to the dried air because the temperatures inside the box occasionally melted the filters closed.

4.4.2 Dekati FPS 4000 Diluter

The Dekati Fine Particle Sampler (FPS) 4000 provided diluted exhaust sample for the filter collection cart (Section 4.5.5). The unit is capable of supplying 60-160 lpm of diluted sample at DRs of 20-200 [63]. The Dekati incorporates two stages of dilution to achieve the desired dilution ratio. The first stage of dilution occurs through a perforated tube, where the dilution air is drawn into the sample stream through a porous metal tube; the second stage is an ejector type diluter. The DR is controlled by the amount of dilution air owed, which the unit controls via several solenoid valves and critical orifices [63]. A primary dilution air heater and a dilution probe heater allow for adequate dilution temperature control. A calculated dilution ratio is provided by on-line measurement of temperature and pressures through the system, though its accuracy has been put into question by previous work at the ERDL [11], [20]. Therefore, as with the rotating disk thermodiluter, the true dilution ratio was measured using CO2 as a tracer gas.

4.4.3 Dry Air Supply

Dry dilution air was supplied to both the Dekati diluter and the rotating disk thermodiluter via a system of filters and desiccant driers on the building's pressurized air line. This dry air supply meets or exceeds the specifications required by the Dekati. This dry air supply was also used to provide the dry air needed for the emissions bench (HFID and HCLD analyzers)—see Section 4.5.3. The filters were cleaned and the desiccant was re-dried prior to the start of this study.

4.4.4 Engine Exhaust Particle Sizer

A TSI 3090 Engine Exhaust Particle Sizer (EEPS) provided total PN concentrations and particle size distribution characterizations of the engine exhaust. Particles are characterized by their electrical mobility in 32 discrete bin sizes from 5.6 to 560 nm [64]. The EEPS works by charging incoming exhaust particles to a known level with a corona charger [64]. The charged particles then flow through the column with a centrally mounted, positively charged electrode repelling the particles radially where the electrometers are located. The electrometer that any given particle impacts is related to its electrical mobility and therefore, its particle size. These
electrometers measure the charge of the impacted particle allowing both size and concentration data to be extracted simultaneously. Data was logged using the proprietary TSI software at a rate of 2Hz. The EEPS measured diluted exhaust from the aforementioned TSI Rotating Disk Diluter (Section 4.4.1).

4.4.5 PM Filter Collection Cart

An ERDL designed and built filter collection cart was used in this study to collect PM laden filters for gravimetric and compositional analyses. Figure 4.6 shows a schematic configuration of the filter collection cart. Diluted exhaust sample is drawn through the filter cart via two vacuum pumps—one for each filter cassette holder. A cyclone removes particles greater than 10 nm upstream of the filter holders, which hold the filter cassettes that collect the PM on each filter. Sample collection is controlled by two, three-way solenoid valves, which when selected to sample connect the exhaust flow path through the filter cassette holders. The cart includes a bypass section, whereby the sample pumps would continuously pull on the Dekati diluter irrespective of the solenoid valve position. A Parker-Balston 58N Engine Exhaust Filter (with a 100-12-404 filter element) is in this bypass flow path to remove particles and to protect the mass flow controllers. A Neptech Inc. Hot Pocket custom heater blanket (52C-AN-CUSTOMKN-V) is installed on the cyclone separator to help keep the exhaust sample in the desired temperature range. The Hot Pocket was custom sewn for the cyclone shape and incorporates a heater cord in an insulation wrap. An Omega CN7533 PID temperature controller controls the temperature set-point of the hot pocket with feedback from an embedded thermocouple.

4.4.6 Gravimetric Filter Analysis

Gravimetric filter analysis was conducted according to the procedure detailed in the US EPA’s Standard Operating Procedure [65]. All gravimetric measurements were conducted in a class 100 clean room using a Sartorius SE-2F Microbalance, which meets the US EPA specifications. NIST traceable calibration weights were used to verify the accuracy of the microbalance on an ongoing basis. An electrostatic neutraliser was used to neutralise filter samples prior to taking measurements. The clean room was maintained at a temperature of 22±1 °C and a relative humidity of 45±5 %. Gravimetric measurements were carried out on 47 mm Pall Teflo filters. Their specification are provided in Table 4.4.
4.5 Gaseous Sampling

The following section discusses the four instruments used for gaseous sampling in this investigation. An FTIR provided gaseous speciation, while a standard emissions bench gave regulated emissions concentrations. A small CO2 monitor was used to measure dilution ratios of the two diluters and an AFR sensor provided corrected fuel-air equivalence ratios for the fuel used. Figure 4.1 shows the arrangement of the equipment used.

4.5.1 Fuel-Air Equivalence Ratio

The research engine is nominally equipped with a wide-band oxygen sensor that provides the PCM with a reading of the AFR for closed loop control. However, an additional, highly accurate and stand-alone AFR sensor system was employed to gather independent AFR data from the exhaust stream. This was done with an ECM 2400E-1 wide-band oxygen sensor in conjunction with an ECM AFRecorder 2400 to provide real-time AFR data. The main benefit of this system is that the AFRecorder can be configured for different fuel compositions in order to display a corrected AFR reading [66].

4.5.2 FTIR

An MKS 2030HS Fourier Transform Infrared Spectroscopy (FTIR) was used to perform gaseous speciation of the exhaust gas in real time. Raw exhaust is drawn from the sample tube through a heated filter that removes exhaust particles from the sample stream. A heated sample line carries the remaining gas phase species to the FTIR analyzer. Both the heated filter and the heated sample line were operated at 191 °C. Data was recorded using the MKS supplied FTIR software at 2 Hz. The software permits the off-line reprocessing of spectral data for different “recipes”-pre-selected lists of compounds for analysis. The FTIR operates on an infrared light absorption measurement technique, not dissimilar to Non-Dispersive Infrared emissions analyzers. They

<table>
<thead>
<tr>
<th>Table 4-4 Filter specifications for Pall Teflo Filters [65]</th>
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</thead>
<tbody>
<tr>
<td><strong>Material</strong></td>
</tr>
<tr>
<td>Nominal Diameter</td>
</tr>
<tr>
<td>Aerosol Retention</td>
</tr>
<tr>
<td>Pore Size</td>
</tr>
</tbody>
</table>
differ, however, in the number of gaseous species they are capable of analyzing; where an emission analyzer is typically limited to a single compound (single wavelength), an FTIR can analyze any compound that falls within its spectrum. In this case, the FTIR operates in the mid-infrared region of 2-20 μm and any compound that absorbs infrared radiation in this region can be measured [67]. An interference pattern is passed through the gas sample and the resulting light is measured and converted to an absorbance spectrum using Fast Fourier Transform mathematics [67]. Using reference files for pure species, the instrument deconstructs the spectrum based on a preselected batch of species assumed to be in the sample; known as the ‘recipe’. The development of the recipe is of utmost importance to the operation of the instrument. Including compounds not present in the sample, or conversely, excluding compounds actually present, will result in erroneous readings. The FTIR recipe used in this investigation is detailed in Section 5.2.1.

4.5.3 Standard Emissions Bench

An emissions bench measured raw exhaust concentrations of the standard (regulated) emissions. These include total hydrocarbons (THC), oxides of nitrogen (NOx), carbon dioxide (CO2), oxygen (O2), and carbon monoxide (CO). Data was logged using the Labview program through the TCP/IP protocol; a network switch connected all four analyzers to the logging computer. Table 4.5 summarizes the analyzers including the ranges used and their respective calibration cylinders. All analyzers were zeroed with emissions grade nitrogen (N2). The four analyzers were made by California Analytical Instruments (CAI) and they each conform to US EPA guidelines for measuring their respective species. The same dry air supply used for the aforementioned diluters was also used for the emissions bench (see Section 4.4.3)

The exhaust sample is drawn in through the sample probe at the heated filter head. A filter removes particles from the exhaust stream while maintaining the sample temperature at 180 °C. A heated 3/8 in. Teflon sample line carries the exhaust sample to the emissions bench from the heated filter, where it is teed off to the different analyzers. The two heated analyzers (THC and NOx) have internal sample pumps which pull the sample through their respective heated sample lines (each set to 149 °C). The two unheated analyzers (CO2/O2 and CO) use an external sample pump which passes the sample through two chillers to remove water (a source
of interference in these analyzers). A calibration flow drawer controls the flow of calibration and sample gases to the probe; the exact calibration method is described in Section 5.2.2.

Table 4-5 Emissions analyzers summary

<table>
<thead>
<tr>
<th>Model No.</th>
<th>Analyzer Type</th>
<th>Species</th>
<th>Ranges</th>
<th>Concentration</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAI 600</td>
<td>Heated Flame Ionizer Detection</td>
<td>THC-C₃</td>
<td>300 ppm 3000 ppm</td>
<td>203 ppm 2000 ppm</td>
<td>C₃H₆/N₂</td>
</tr>
<tr>
<td>CAI 600 HCLD</td>
<td>Heated Chemiluminescence Detection</td>
<td>NOₓ</td>
<td>100 ppm 1000 ppm 5000 ppm</td>
<td>89.7 ppm 900 ppm 4063 ppm</td>
<td>NOₓ/N₂</td>
</tr>
<tr>
<td>CAI 601P*/602 NDIR</td>
<td>Non-Dispersive Infrared and Paramagnetic*</td>
<td>CO₂</td>
<td>14% 1.1%</td>
<td>13.7% 0.99%</td>
<td>CO₂/N₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O₂*</td>
<td></td>
<td></td>
<td>O₂/N₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CO</td>
<td>15000 ppm 14500 ppm</td>
<td></td>
<td>CO/N₂</td>
</tr>
</tbody>
</table>

**THC Analyzer**

The THC analyzer (600 HFID) is a heated flame ionization detector, which is the accepted technique for measuring hydrocarbon constituents of vehicle exhausts according to the US EPA [68]. It operates by detecting the ions formed during the combustion of organic species in a hydrogen flame [6]. These ions are formed proportionately to the hydrocarbon concentration in the sample stream [6]. Effectively, this analyzer counts the reduced carbon atoms in the flame and reports it as an equivalent concentration of hydrocarbons; in this case on a C₃ basis. That means that for every three ions detected (or three carbon atoms), one hydrocarbon is reported. Being a heated analyzer, the internal sample components are maintained at 190 °C to prevent condensation [69].

**NOₓ Analyzer**

The NOx analyzer (600 HCLD) operates on the principle of chemiluminescence, the acceptable method for measuring this species per the US EPA [70]. Incoming NO species are reacted with ozone (O₃) to form NO₂ molecules that are electronically excited [6]. As they decay, they release radiation which is detected by a photomultiplier; the amount of radiation is proportional to the amount of NO in the sample [6]. This instrument also has the capability to convert the NO₂ in the exhaust to NO by decomposition, before being reacted with the ozone [71]. The reported concentration in this configuration, as used in this investigation, is therefore NOₓ (NO
+ NO2). The internal temperature of components in contact with sample gas are maintained above 68 °C [71].

**CO2/O2 and CO Analyzers**

Two unheated analyzers were used for the remaining three gases of the emissions bench: 601P NDIR for CO2/O2 and 602 NDIR for CO. Both analyzers operate on the principle of non-dispersive infrared analysis, with the CO2 analyzer having an optional paramagnetic analyzer for O2. These are both accepted practices for measuring these species according to the US EPA [72], [73]. The NDIR analyzer operates on the principle of infrared absorption where the radiation absorbed in a sample cell is compared to a reference cell [6]. Radiation not absorbed by the exhaust sample is absorbed by one side of the detector, while the radiation not absorbed by the reference gas is absorbed by the other side [6]. Different amounts of absorption in the two halves causes diaphragm distention from the resulting difference in pressure [6]. A micro-flow detector measures the induced ow between the two halves, which is converted to species concentration using the calibration as a reference [74]. As water causes a large interference in the infrared spectrum for the above compounds, it must be removed from the sample before being analyzed (see Section 4.5.3).

**4.5.4 Mini CO2 Monitor**

A LI-COR LI-840A CO2/H2O analyzer (CO2 monitor) was used to measure diluted CO2 concentrations to calculate true dilution ratios of the two diluters. The CO2 monitor operates on the principle of NDIR [75], just as the analyzer in the emissions bench does. A small sample pump draws the diluted exhaust stream to the analyzer through 1/4 in. Teflon tubing. The unit incorporates a water sensor that corrects the CO2 reading for water interference [75], so no chiller is necessary.

**4.6 Test Fuels**

Both commercial gasoline and custom hydrocarbon blends were used in engine testing. Details of each are provided in the following sections.
4.6.1 Gasoline Batches

Four batches of gasoline were tested for this thesis. A batch refers to a quantity of gasoline purchased from a gas station at one time. Local fire regulations limiting the quantity of gasoline that may be stored in the engine lab necessitate frequent purchases of gasoline in smaller quantities. Most gasoline in Ontario contains ethanol due to renewable fuel mandates. For this research program, an ethanol-free gasoline was desired as a baseline for the studies of mixtures of pure hydrocarbons. Only one commercially available ethanol-free gasoline could be identified. Thus, all gasoline used in these tests was Shell 91 octane, which contains no ethanol.

An initial batch of gasoline, “gas1”, was tested primarily to confirm that all equipment and methods were still operating well. A second batch of gasoline, “gas 2”, was consumed in tests to assess the impact of crankcase ventilation system cleaning. A sample from the “gas2” batch was sent for detailed chemical analysis. Two additional batches, “gas 3” and “gas 4” were purchased and used to assess the impact of diverting blow-by gases in both standard length and extended tests. An H/C ratio of 1.85 is used for all gasoline batches based on EPA guidelines [76].

4.6.2 Custom Blends

The chemical analysis of the “gas2” batch provided a frame of reference for developing custom fuel blends of pure hydrocarbons. Table 4-6 summarizes the results of the chemical analysis of the “gas 2” batch. Appendix A1 contains full details of the analysis. Paraffin hydrocarbons make up the largest proportion of the fuel at 45.4% (v/v), followed by aromatic hydrocarbons at 43.8% (v/v) and olefins at 5.5% (v/v). Table 4-6 also shows that most of the components are in the C5 to C9 molecular size range. For paraffins, C5 and C8 make up the largest share, while C8 is the largest share for the aromatics. It should be noted that the high volatility C4 and C5 paraffins are used to adjust the vapor pressure of the gasoline to facilitate cold starting. Thus, the amounts of these species in gasoline varies seasonally. The “gas2” batch was purchased in July and is therefore a summer gasoline.
Table 4-6 Comparison of custom blends and analyzed gasoline

<table>
<thead>
<tr>
<th>Test Blend</th>
<th>PM Index</th>
<th>Paraffins % Volume</th>
<th>Aromatics % Volume</th>
<th>Olefins % Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C4</td>
<td>C5</td>
<td>C6</td>
</tr>
<tr>
<td>Commercial Gasoline</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>gas2</td>
<td>2.385</td>
<td>2.15</td>
<td>15.2</td>
<td>8.51</td>
</tr>
<tr>
<td>Custom Blends</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>I65T35</td>
<td>0.592</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>I65T35 + Oil</td>
<td>0.592</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>TMB</td>
<td>0.839</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Nap60g</td>
<td>0.869</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Heavy Solvent</td>
<td>0.878</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Both Solvents</td>
<td>1.393</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>7-Parts</td>
<td>1.552</td>
<td>-</td>
<td>-</td>
<td>35.5</td>
</tr>
<tr>
<td>7-Parts + Sulfur</td>
<td>1.552</td>
<td>-</td>
<td>-</td>
<td>35.5</td>
</tr>
</tbody>
</table>

*The PM index of 2.385 for the gasoline was calculated on 10-component simplification of the analyzed data*

Ideally, custom blends would be created using pure hydrocarbons in each category to match the commercial gasoline. However, there are limitations arising from the availability and the cost of pure hydrocarbon components, especially as molecular size increases. Aromatic hydrocarbons are known to facilitate particle formation. Thus, representing the aromatics content of the “gas2” batch is particularly important. The following components were identified for use in the test program:

- **Hexanes** (C₆H₁₄) – The pure hydrocarbon Pentane (C₅H₁₂ - paraffin) would be a very logical component to include as the “gas2” blend had 15.2% (v/v) of C5 paraffins. Unfortunately, at the time of testing, pentane had a very long lead time and could not be procured. Thus, hexanes (a 98.5% ACs grade mixture of isomers) was used to represent lighter paraffins, recognizing that it has lower vapor pressure than pentane.

- **Isooctane** (C₈H₁₈ – paraffin). Reagent grade, ≥99%, 2,2,4-Trimethylpentane (isooctane). Isooctane is the reference fuel for octane rating (isooctane = 100 octane) and thus a great basic building block for constructing surrogate gasoline blends.
- Toluene ($C_7H_8$ - aromatic). Laboratory grade, $\geq 99.3\%$. Toluene is a widely available and is key component of gasoline (19%) in the “gas2” blend.

- Mixed Xylenes ($C_8H_{10}$ – aromatic). This blend of xylene isomers (ACS reagent grade, $\geq 98.5\%$) was used to represent C8 aromatics.

- Trimethylbenzene ($C_9H_{12}$ – aromatic). Details – 1,3,5-trimethylbenzene (mesitylene), Sigma-Aldrich Product# M7200, 98%. The “gas2” blend contained significant amounts of C9 aromatics and trimethylbenzene is a key component in that category.

- Naphthalene ($C_{10}H_8$ – aromatic). Naphthalene is readily available representative of a polyaromatic hydrocarbon structure. It is a C10 two-ring aromatic structure.

- Heavy aromatic hydrocarbon mixtures. Two aromatic solvent blends containing mixtures of heavier aromatics were identified, Sun 100 and Sun 150. Data sheets for the two solvents are included in Appendix A.
  - Sun 100 is a C8 aromatic hydrocarbon mix
  - Sun 150 is mixture of C9-C10 aromatic hydrocarbons.

Custom blends of these available components were created in an attempt to match the general features of the gasoline such as the % aromatic, starting with only two components and then adding progressively more components in order to better recreate the “gas2” composition. A comparison of the composition of the custom blends to the analyzed “gas2” gasoline is provided in Table 4.6. Each custom blend is described below. The description also includes the hydrogen to carbon ratio that blend that is needed for input into ECM AFRecorder that measures air/fuel ratio (see section 4.5.1). A sample calculation of the H/C ratio is presented in Appendix A3.

- **I65T35** - A simple two-component mixture, “I65T35”, was created by mixing 65% isooctane (2,2,4-trimethylpentane) and 35% toluene by volume. This is a very rough approximation of “gas2” as it includes readily available components that match the most prevalent carbon number for the alkane and aromatic groups in the analyzed batch. It is also a blend composition tested in work by Stone et al. [48]. The H/C ratio of this blend is 1.74.
• **TMB** - The “TMB” blend is a mixture of 61.75% isoctane, 33.25% toluene, and 5% 1,3,5-trimethylbenzene by volume. Trimethylbenzene, a C9 aromatic, was added to the original blend to try to incorporate some of the larger aromatics seen in the gasoline. Based on the PM Index formula (equation 2.1), addition of TMB was expected to encourage particle formation. The H/C ratio of this blend is 1.72.

• **Nap80g** - The “Nap80g” blend is a three component mixture consisting of 10 L of the I65T35 blend with 80g of naphthalene (99%, reagent grade) added. This was created as a follow-up to the TMB blend. After seeing the effects of a trimethylbenzene, a C9 aromatic, the next step was to assess the effect of a C10 polyaromatic, naphthalene. The H/C ratio of this blend is 1.73.

• **Heavy Solvent** - The “Heavy Solvent” blend is a three component mixture consisting of 62.8% isoctane, 33.8% toluene, and 3.4% SUN 150 solvent. Heavier aromatics were tested individually in the previous two blends, but gasoline includes a range of C9-C10 aromatics so an attempt was made to emulate that mix with a C9-C10 aromatic solvent. The H/C ratio of this blend is 1.73.

• **Two Solvents** - The “Two Solvents” blend is a five component mixture of 57.2% isoctane, 30.8% toluene, 0.3% naphthalene, 8.3% SUN 100, and 3.4% SUN 150. This blend was made as a follow-up to the “Heavy Solvent” test and included a wider range of aromatics through addition of SUN 100, a C8 aromatic solvent mix. Two sets of tests were conducted on this fuel to assess the repeatability of blended fuel engine testing. The second set is labeled “Two Solvents 2”. The H/C ratio of this blend is 1.70.

• **7-Parts** - The “7-Parts” blend is a seven component mixture of 19.9% isoctane, 18.9% toluene, 0.3% naphthalene, 8.0% SUN 100, 3.3% SUN 150, 14.2% mixed xylenes, and 35.5% n-hexane. Here, the amount of toluene (C7 aromatic) was reduced and mixed xylenes (C8 aromatic) was added instead to more closely represent “gas2”. In addition, a large amount of n-hexane was added to increase the vapour pressure of the blend in an attempt to mimic the light alkane portion of gasoline (The C3-C6 paraffins). The C3-C6 hydrocarbons were not a priority in constructing the custom blends because the PM Index would suggest that the inclusion of light alkanes would reduce PM and previous blends
were already emitting far less than the target gasoline. This blend was the most complete attempt to duplicate the composition of the analyzed gasoline.

All of the custom fuel blends are summarized in Table 4-6.

An additional test was conducted on this blend with added sulfur as commercially available gasoline contains some sulfur from the refining process. The H/C ratio of this blend is 1.77.

**Additional Blends**

Three additional blends were created to study the effect of fuel interaction with the lubricating oil as well as to the effect of two minor fuel fuel components - namely sulfur and a fuel detergent additive.

**Lubricating oil interaction** - Fuel sprays are known to impinge on the cylinder wall and interact with the lubricating oil film on the cylinder wall. The interaction can facilitate the entrainment of lubricating oil into fuel rebounding or evaporating from the cylinder wall. To examine this situation, a test was conducted with a fuel blend consisting of 3 ml of motor oil mixed into 10 L of the “I65T35” test fuel. The motor oil used was 5W-20 synthetic, the same oil used in the engine crankcase. This custom fuel blend is identified as “I65T35+Oil”.

**Sulfur** - To investigate the effect of the sulfur in the fuel, another custom blend “7 Parts + S” was created by mixing 1 ml of thiophene into the “7 Parts” test fuel. The thiophene was Sigma-Aldrich T31801, ≥99%. The resulting blend has a sulfur content of approximately 64 mg/kg, substantially higher than the gasoline limit of 30 mg/kg at the time the testing was conducted (the limit has been revised to 10 mg/kg post-2017) [77].

**Fuel detergent** - Gasoline incorporates a chemical additive that helps prevent/remove intake system and valve deposits, as well as deposits of GDI fuel injectors. A sample of a commercial additive consisting was obatined. Complete product details were not available due to confidentiality concerns but the additive’s safety data sheet indicates it consists of “polyisobutylamine, polyether, and hydrocarbons.” A custom blend “TMB+add” was created by mixing 1ml of detergent additive into 10 litres of the “TMB” custom blend.
The composition of these fuel blends will form an important part of the discussion of results in Chapter 6. First however, the procedure followed for the tests is presented in Chapter 5.
Chapter 5
Experimental Methods

5 Test Procedures

This section describes the experimental procedures employed during this research project. As with the test stand setup, the methods inherited from Mireault and Ramos were largely maintained for comparability [11], [20]. Details on the rationale for procedures are found in the earlier work.

5.1 Engine Testing

The test engine was put through transient start-up and steady-state highway cruise operating conditions. The cold start conditions were developed by Mireault to simulate starting a vehicle on a cold day and the hot start conditions were meant to simulate quickly restarting a vehicle after a brief stop [20]. The hot start was also meant to apply to an automatic shutdown and restart in a vehicle equipped with a stop-start system. The highway conditions were based on road load power calculations for a 2012 Ford Focus travelling at 100 km/h.

5.1.1 Pre-test Procedures

One day prior to every engine test, the engine battery’s voltage is checked and a battery charger is connected if necessary. Starting about 1 hour before the start of a test, the following series of tasks are completed:

- The dyno controller is turned on and the dyno is activated to warm-up.
- The water supply and air supply to the dyno is opened.
- The engine coolant heat exchanger and dyno are flushed with water.
- The PCV filter element and housing is cleaned and the system’s 3-way valve is set to return or bypass.
- The fuel tanks are filled.
- The OBD-II program, DAQ, throttle controller, and ECM AFRecorder are turned on.
5.1.2 Transient Start Procedures

Both the cold and hot start procedures last two minutes and are conducted at idle speed with no applied load. Their defining characteristic is their engine coolant temperature at the beginning and end of the two-minute period. Cold starts begin with an engine coolant temperature of 20 ± 2 °C and end at 28 ± 2 °C. Hot starts maintain an engine coolant temperature of 90 ± 2 °C for the entire period. To achieve this temperature, hot starts are conducted by running a full length test and then bringing the engine to idle speed and operating there until the exhaust temperature reaches 130 °C. At that point, the engine is shutoff for 15 seconds so that the exhaust temperature reaches 125 °C before it is restarted. Engine coolant temperature is maintained at 90 ± 2 °C during this entire process. Two consecutive full tests, a cold start followed by a hot start are plotted in figure 5.1.

5.1.3 Steady-state Testing Procedures

After 6 to 7 minutes of runtime, the engine is ramped to highway cruise conditions. The ramp is programmed to take 33 seconds to reach a throttle output of 22.9%, which typically results in an engine speed of 2600 rpm. The ramp rate starts fast and decays over the 33 seconds and occasionally some manual adjustment is needed to reach and maintain the target operating conditions in table 5.1. Of those targets, oil temperature takes the longest to achieve, typically just under 10 to 15 minutes.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>Speed</td>
<td>2600 ± 25 rpm</td>
</tr>
<tr>
<td>Load</td>
<td>41 ± 1 lb-ft</td>
</tr>
<tr>
<td>Coolant Temperature (ECT)</td>
<td>90 ± 2 °C</td>
</tr>
<tr>
<td>Oil Temperature</td>
<td>98 ± 2 °C</td>
</tr>
<tr>
<td>Fuel Temperature</td>
<td>22.5 ± 1.5 °C</td>
</tr>
</tbody>
</table>
Figure 5-1 Example of engine speed and load over two consecutive standard length tests. The first test began with a cold-start and the second began with a hot start.

For a standard length test, highway cruise is continued for 90 to 100 minutes of elapsed time from engine start. For extended length tests, the fuel tank that the engine is running from is switched at 90 to 100 minutes and the test is continued for an additional 320 minutes for a total test length of 420 minutes (6 hours). The test is ended by gradually reducing the throttle controller output and removing the load to return to idle conditions. Once engine coolant temperature is below 60 °C and oil temperature is below 75 °C, the ECU is turned off to shut the engine down.

5.2 Gaseous Emissions Sampling Procedures

This section provides details on the operation of the FTIR, emissions bench, and LICOR mini CO₂ monitor for gaseous emissions measurement during engine testing.

5.2.1 FTIR

The FTIR was used for chemical speciation of exhaust gas samples. The species recipe used was identical to the one used by Ramos except for the inclusion of trimethylbenzene for extended length tests [11]. This recipe is listed in table 5.2 below. Trimethylbenzene was added as a marker of whether the lighter components of gasoline were evaporating mid-test.
Table 5-2 Compounds included in FTIR speciation

<table>
<thead>
<tr>
<th>Nitric Oxide (NO)</th>
<th>Carbon Monoxide (CO)</th>
<th>Carbon Dioxide (CO2)</th>
<th>Water (H2O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen Dioxide (NO2)</td>
<td>Methane (CH4)</td>
<td>Ethane (C2H6)</td>
<td>Pentane (C5H12)</td>
</tr>
<tr>
<td>Nitrous Oxide (N2O)</td>
<td>Ethylene (C2H4)</td>
<td>Propylene (C3H6)</td>
<td>Isobutylene (C4H8)</td>
</tr>
<tr>
<td>Acetylene (C2H2)</td>
<td>1,3-Butadiene (C4H6)</td>
<td>Benzene (C6H6)</td>
<td>Toluene (C7H8)</td>
</tr>
<tr>
<td>Formaldehyde (CH2O)</td>
<td>Acetaldehyde (CH3CHO)</td>
<td>Methanol (CH3OH)</td>
<td>Trimethylbenzene (C9H12)</td>
</tr>
</tbody>
</table>

Before running the FTIR, the gas cell heater temperature and gas inlet heater temperature should already be set to 191 °C. After this is checked, the FTIR is filled with approximately 5L of liquid nitrogen. Next, an MKS diagnostic daily checklist is conducted to ensure that parameters like laser voltage are within their normal operating range. If everything is within specifications, N2 from a calibration cylinder is flowed through the instrument and a background reading is taken. The FTIR is then ready for an engine test.

Measurements on the exhaust stream are not taken until after the engine has reached highway cruise conditions and the exhaust temperature is above 300 °C because a warm sample stream is needed for the instrument to maintain optimal internal operating temperatures. To begin sampling, all that is required is changing a flow selection valve, turning on a pump, and initiating the device’s software.

5.2.2 Emissions Bench

The emissions bench is used to measure standard emissions, CO, CO2, O2, NOx, and total hydrocarbons using the four analyzers described in section 4.5.3. The sampling system utilizes heated lines and a heated filter that are on continuously to avoid a long warm-up period. Once all systems are warm, the air supply to the HCLD and HFID is opened. The HFID also requires a helifuel (40% hydrogen, 60% helium) supply for ignition. These two analyzers and the NDIR analyzers are then set to sample room air and left to warm up for at least 30 minutes.

The calibration process for the emissions bench is time consuming but it consists of a few repeated steps. First emission grade N2 is flowed through the system and a zero measurement is set on all four analyzers. Then, each calibration cylinder in table 4.5 is connected, the pressure of gas flowing in the machine is set to 10 psig with the emissions bench rotameter, the flow is given
about one minute to stabilize, and lastly, the value is saved as the span for its respective analyzer and range. The sample system is the set to room air so that the next cylinder can be connected and the process repeats until all ranges are calibrated.

To begin sampling exhaust, the sample valve at the heater filter is switched to the exhaust stream and all analyzers are switched from cal to measurement mode. Data is recorded and displayed live via the LabVIEW program described in section 4.3.1. Adjustment of some of the data for water content and correction of the O2 data is also performed live by the program (calculations are available in Appendix A6)

The emissions bench is shutdown by first sampling room air for at least 30 minutes following the end of the engine test to avoid moisture buildup. The HFID is shutdown by closing the helifuel supply so that its burner extinguishes and then setting it to standby mode along with the other analyzers.

5.2.3 LiCor Mini CO2 Monitor

The LiCor CO2 monitor was used to calculate the true dilution ratio of the Dekati and TSI diluters. Comparison of the CO2 concentration measured by the monitor downstream of the diluters and the CO2 concentration from the emissions bench enables the calculation of a true dilution ratio (see Appendix A7 for details). The unit has its own sample pump and data acquisition software which are turned on 30 minutes prior to engine testing to warm up. Two minutes of dry dilution air CO2 measurements gathered prior to every test as his data is needed as a baseline for the dilution calculations. During engine testing, the monitor is switched between the outlet of the EEPS, which is a TSI diluter stream, and a branch from the Dekati diluter depending on which dilution system’s ratio is being checked.

5.3 Particulate Matter Sampling and Measurement

This sections details the use of the diluters, EEPS, filter cart, and gravimetric analysis setup for PM sampling and measurement.
5.3.1 Rotating Disk Thermodiluter

The rotating disk thermodiluter was used to supply the Engine Exhaust Particle Sizer with a diluted exhaust sample with a particle concentration in a manageable range that would not foul the equipment.

Prior to every test, the diluter disk is cleaned and the diluter head is drained of water. The diluter is then turned on and set to target conditions in table 5.3 which were inherited from Ramos and Mireault [11], [20]. Once the diluter is stable, a green “ready” led is illuminated. At this time, the dry filtered air supply to the box is opened slowly until the attached ambient air flow meter decreases from its starting point of 15 L/min to 0 L/min which means that the 15 L/min of ambient air that was being used for dilution has been displaced by the filtered dilution air. The ambient air filter is then removed and the filtered air supply is opened up slightly more so that there is an excess flow of about 3 L/min which is necessary to maintain dilution stability [20]. The diluter can now be connected to the EEPS for testing.

<table>
<thead>
<tr>
<th>Table 5-3 Diluter box settings</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameter</td>
</tr>
<tr>
<td>Speed</td>
</tr>
<tr>
<td>Load</td>
</tr>
<tr>
<td>Coolant Temperature (ECT)</td>
</tr>
<tr>
<td>Oil Temperature</td>
</tr>
<tr>
<td>Fuel Temperature</td>
</tr>
</tbody>
</table>

At the end of the engine test, the diluter gas temperature is elevated to 150 °C and it is run for an additional 30 minutes with the engine off to remove water that builds up in the diluter head. The dry air supply is then closed gradually and the ambient air filter is reinstalled. Lastly, the diluter box power is switched off.

5.3.2 Dekati Diluter

The Dekati ejector diluter was used exclusively to supply the PM filter collection cart with a sample exhaust stream. The operating procedure and settings used duplicated those employed by Ramos [11]. The first step after turning the Dekati on is to adjust the supply pressure to 4.5 bar. Next, the dilution ratio control settings are entered. Medium flow is selected along with diluter
valves 2 and 3 (this results in a nominal dilution ratio of approximately 10). The final step is the temperature setpoints. The dilution air temperature heater is set to 250 °C in 50 °C increments to avoid overshooting the temperature and the probe is set to 125 °C. Once these temperatures are reached, dilution conditions are considered stable and sampling can begin. For shutdown, the dilution air temperature controller is set to 0 °C and once the reading is below 150 °C, the unit is turned off.

5.3.3 Engine Exhaust Particle Sizer (EEPS)

The EEPS was used to measure live exhaust particle size distributions and total particle number concentrations. When not being used for engine tests, the EEPS is left on to sample room air through a HEPA filter. This filtered air flushes out residue from past tests and reduces the need for periodic disassembly and manual cleaning. Leaving the EEPS on also has the added benefit of making it continuously available for engine testing.

During testing, the EEPS only needs to have its inlet connected to the TSI diluter and its outlet connected to the CO₂ monitor to begin sampling. To log data, the provided software must be opened and set to record. A maximum of 1.5 hours can be recorded in a single continuous file so multiple files are needed for most engine tests. For repeatable transitions, each file was typically set to one hour and 28 minutes to allow for a two-minute transition [11].

5.3.4 Filter Cart

The filter cart was used to collect PM on Teflo filters for post-test gravimetric analysis. An extensive procedure for operating the filter cart is provided in an appendix of Mireault’s thesis [20].

Warm-up and calibration of the cart’s flow meters is required. The flow meters are turned on one hour before testing so that their flow signals can decay to zero. Once this is achieved, the flow controllers are set to 7 slpm and the sample pumps are turned on with carts in “bypass” mode and the cart is ran at these conditions for 5 minutes. The pumps are then shut off, the flow meters are set to 0, the flow is set to sample, and the sample port cap is closed. After two minutes elapse, the flow meter zero values are saved. Calibration is complete.
In preparation for an engine test, the cart’s cyclone heater is set to its operating temperature of 55 °C, the cart is connected to the Dekati, put in bypass mode, and its sampling flow is set to 33 lpm. The cart is ran at these sampling conditions to maintain warm filter holders.

Filters are collected only once exhaust temperatures are stabilized which is usually about 10 to 15 minutes after beginning highway cruise. To collect a filter, a used filter is installed and ran first until the post-filter temperature on the cart reaches 30 °C. At that point, the dummy filter is switched with a filter for gravimetric analysis and PM is deposited for as long as desired before the filter cassette is removed. When not installed in a filter holder, all filters that are intended to be weighed should be stored in their own clean filter cassettes within a sealed container.

5.3.5 Gravimetric Filter Analysis

Ramos [11] developed the ERDL gravimetric analysis procedure in accordance with EPA guidelines. Filters for PM collection are required to be weighed in the lab’s class 100 clean room before and after being used in engine testing. A class 100 compliant full body suit is always worn in the clean room’s changing area (behind one door) before entering the main clean room (behind a second door). All filters must first equilibrate to the clean room for approximately 2 weeks before use.

Pre-test weighing is done on filters that have equilibrated before they can be used in engine tests. To weigh a filter, it is first held under an electrostatic neutralizer with the clean room tweezers for 10 seconds and then flipped and held for an additional 10 seconds. The lifter is then placed in the enclosed Sartorius SE-2F Microbalance. After two minutes on the scale, the mass reading is recorded on a laptop that never leaves the clean room but has internet access. The laptop is also used to countdown the two-minute waiting period. This process is repeated daily for every lifter until the difference between replicate weights is less than 5 µg. Once that is achieved and the day of engine testing arrives, the lifters are placed in their cassettes and put in a sealed box in the clean room change room until the immediately before the test is to begin.

The post-test process is largely the same. The sealed container with the used filters is brought into the clean room change room where it is wiped down with an alcohol / de-ionized water wet wipe and then brought into the main clean room to equilibrate for one day. The next
day, daily weighing begins following the same process as the pre-test lifters (daily weighing until the difference is below 5 µg).
Chapter 6
Results and Discussion

6 Study of PM Emissions Drift and Test-to-test Variability

This section details the results of tests conducted for understanding the GDI PM emissions variability phenomena that have occurred during research projects conducted by multiple researchers in the Engine Research and Development Lab at the University of Toronto. Findings are organized by the type of variability being studied and are presented roughly in the order they occurred to give a sense of the reasoning behind testing decisions. All graphs of particle counts measured by the EEPS have been corrected using the procedure developed by Zimmerman et al. unless otherwise noted [78]. All standard errors are calculated based on three tests conducted on the same fuel unless otherwise noted.

6.1 Investigation of the Gradual Increase in PN Emissions during Steady State Tests

Extended length testing was used to consider three potential sources of PN drift (increase): blow-by gas derived intake system deposits, changes in fuel properties over the course of testing due to elevated fuel temperatures, and PCM adjustments to the short-term fuel trim. As noted in section 4.6 (Test Fuels), four different batches of commercial gasoline were used for these tests. The fuel batches used for investigation of each of the three effects studied in this section are summarized in Table 6.1, along with other data that will be discussed subsequently.
Table 6-1 Fuel Batches used for Section 6.1 Tests

<table>
<thead>
<tr>
<th>Test Group</th>
<th>Test Length (min)</th>
<th>Fuel Batch</th>
<th>PCV Diverted?</th>
<th>Total # of Tests</th>
<th># of Steady State Only Tests</th>
<th># of Cold Starts</th>
<th># of Hot Starts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas 1</td>
<td>100</td>
<td>gas 1</td>
<td>No</td>
<td>3</td>
<td>3</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>GC/MS Gas (Pre-cleaning)</td>
<td>100</td>
<td>gas 2</td>
<td>No</td>
<td>2</td>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Extended GC/MS</td>
<td>420</td>
<td>gas 2</td>
<td>No</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Post-Cleaning PCV (GC/MS gas)</td>
<td>100</td>
<td>gas 2</td>
<td>No</td>
<td>2</td>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>PCV Enabled</td>
<td>100</td>
<td>gas 3</td>
<td>No</td>
<td>3</td>
<td>0</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>PCV Diverted</td>
<td>100</td>
<td>gas 3</td>
<td>Yes</td>
<td>3</td>
<td>0</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>PCV Enabled (Extended)</td>
<td>420</td>
<td>gas 4</td>
<td>No</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>PCV Diverted (Extended)</td>
<td>420</td>
<td>gas 4</td>
<td>Yes</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

6.1.1 Crankcase Ventilation System Deposits

The first step taken in studying the effect of intake deposits was to revisit the PCV filter system. Ramos noticed a significant decrease in total PN and an apparent elimination of the drift immediately following intake system cleaning and installation of a PCV filter [11]. After subsequent tests, some buildup in the intake system was found but it was not as extensive as what was seen prior to filter installation so he believed it had minimal impact. To substantiate this judgment as a part of the current thesis, new highway cruise tests were run before and after cleaning the intake system again. The same batch of gasoline “gas1” was used for both tests, before and after. The state of the intake ports is shown in figure 6.1. The PCV filter element was also replaced at the time of the recent intake system cleaning. The image in figure 6.2. clearly show that substantial amounts of fuel-oil vapour were still entering the combustion chamber. The filter to the left was in place for the “before-cleaning” test, while the new filter (right) was used for the “post-cleaning” test.
Figure 6-1 Intake ports of cylinders 1-4 prior to and following cleaning
The results of the engine tests suggested that recirculated blow-by gases remained a contributing factor in PM emissions despite the introduction of the filtered PCV system. In figure 6.3, every 2-minute average data point from the post-cleaning data set was lower than the corresponding data point from the pre-cleaning data set, certainly a statistically significant trend (p<0.01). The drift also appeared to be gone in the post-cleaning results. The dramatic effect of cleaning posed a challenge because it was evidence not only that intake deposits formed by PCV gases could still be the source of particle drift but also that the existing setup was not sufficient to prevent them for future testing. In response, the PCV diversion system described in section 4.1.6 was developed allowing the intake system to be completely isolated from blow-by gases. Once the new system was installed, tests were conducted in triplicate with the system engaged (PCV diverted – blow-by gases diverted) and disengaged (PCV enabled – blow-by gases returned to the engine). The results of these tests are shown in figure 6.4. The average PN mirrors the test trends in figure 6.3 and this fact, combined with a clear post-test visual inspection, demonstrates the effectiveness of the diversion system at keeping the intake clean. One surprising result evident in figures 6.3 and 6.4 is that the post-cleaning tests had a smaller standard error than the pre-
cleaning tests but the PCV diverted tests, which were also done with clean intake ports, had a larger standard error than the unclean PCV enabled tests. An initial reaction might be to suspect engine disturbances caused by the PCV diversion system, but other factors need to be considered first before the system is abandoned. The PCV tests were conducted on a different batch of gasoline than the cleaning tests as detailed in section 4.6.1. This would be expected to shift the total PN and did, but it would not be expected to change how PN responded to the presence of blow-by gas in the intake system so it is an unlikely cause of increased standard error. The next factor is limited data since one test in each set of three had a hot start and was therefore omitted from standard error calculations. With only two tests averaged per test condition, a more suitable metric than standard error was desired to evaluate if the new PCV system disrupted normal evacuation of the crankcase or any other engine processes. Disruption would likely manifest itself as cycle-to-cycle variation within each test so relative standard deviation (RSD) was selected and is displayed in table 6.2. The PCV diverted tests had a lower average standard deviation at each test time confirming that the system did not disrupt the engine in a manner that influences PN. Summarizing the effects of use of the blow-by diversion system, it was demonstrated to lower PN emissions and improve PN emissions rate stability and was consequently incorporated in the test stand permanently and made the subject of further testing.

![Figure 6-3](image.png)

Figure 6-3 Two-minute average total PN / kg-fuel for sets of tests prior to and following PCV and intake cleaning. Shaded areas indicate standard error (note: standard error is from only two tests because the third test in each set was a hot start).
Figure 6-4 Two-minute average PN / kg-fuel for sets of tests with the PCV enabled and diverted. Series labelled “Hot” are single tests that begun with a hot start. Shaded areas indicate standard error. (note: standard error is from only two tests because the third test in each set was a hot start).

Table 6-2 Average Relative Standard Deviation Comparison PCV Enabled and Diverted

<table>
<thead>
<tr>
<th>Run Time (min)</th>
<th>PCV Enabled</th>
<th>PCV Diverted</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>9.84%</td>
<td>8.61%</td>
</tr>
<tr>
<td>30</td>
<td>9.33%</td>
<td>8.69%</td>
</tr>
<tr>
<td>40</td>
<td>9.26%</td>
<td>8.75%</td>
</tr>
<tr>
<td>50</td>
<td>9.49%</td>
<td>8.61%</td>
</tr>
<tr>
<td>60</td>
<td>9.24%</td>
<td>8.32%</td>
</tr>
<tr>
<td>70</td>
<td>9.72%</td>
<td>8.34%</td>
</tr>
<tr>
<td>80</td>
<td>9.95%</td>
<td>8.55%</td>
</tr>
<tr>
<td>90</td>
<td>10.28%</td>
<td>8.93%</td>
</tr>
<tr>
<td>100</td>
<td>16.12%</td>
<td>9.68%</td>
</tr>
<tr>
<td>Avg.</td>
<td>10.36%</td>
<td>8.72%</td>
</tr>
</tbody>
</table>
The PCV diversion system’s arrest of intake deposit formation reduced total PN and appeared to reduce the rate of PN increase across pairs of cold and hot tests. On this basis, two extended length tests were conducted, one with PCV diverted followed by one with it enabled, in the belief that at least the PCV diverted test would demonstrate PN stabilization. The result of those tests defied that expectation completely as shown in figure 6.5. There was a very pronounced increase in PN with time, $R^2=0.98$ and $R^2=0.95$ for PCV Diverted and PCV respectively, over the course of the entire tests. The reduction in PN from PCV diversion that was witnessed in the standard length tests was still present and even more significant from a statistical standpoint given the increased number of datapoints ($p<0.01$).

Figure 6-5 Two-minute corrected total PN / kg-fuel for single extended tests with the PCV enabled and diverted. Shaded areas indicate standard error using data from 100 minute PCV testing.
For further understanding of the effects of PCV diversion, the particle size distributions were compared beginning with the standard length tests shown in figure 6.6. Note that returning blow-by gas did not affect the number of sub 50 nm particles or the overall shape of the binomial distribution but it decreased the particle counts in the accumulation range. Moving on to the extended length tests, since drift was the primary interest, the change in size distribution was illustrated by plotting the a sample every 100 minutes, refer to figures 6.9 and 6.10. Comparing 6.9B and 6.10A shows that gasoline batches can differ in particle size distribution in addition to the differences in total PN mentioned earlier. The diameters of the modal and median size bins of the GC/MS gasoline (the PCV was enabled at that time) extended run are 92 nm and 60.4 nm at 100 minutes and they increase to 139 nm and 69.8 nm respectively at 400 minutes. The diameters of the modal and median size bins of the PCV enabled gasoline extended run are 139 nm and 69.8 nm at 100 minutes and they increase to 201 nm and 168 nm respectively at 400 minutes. All extended runs exhibited a gradual shift in distribution toward larger sizes which indicates that the particles added due PN drift are mainly in the accumulation mode. The actual number of nuclei mode particles did not decrease significantly during the three tests so it appears that a new source or sources of particles develops that is more favourable in terms of time or environment to particle coagulation. The transition to larger particles was slower in the test with blow-by gas diverted, which suggests that blow-by gases support the hypothesized other pathway
of PM formation that is responsible for the bulk of the drift. The slower transition is visible in figure 6.10 but it is clearer in the non-normalized plots in Appendix B.1. If the additional fuel-oil vapours provided by blow-by recirculation contribute to drift it would be expected that fuel properties have an impact.

### 6.1.2 In-Use Gasoline Property Changes due to Evaporation

Ramos speculated that continuous recirculation of fuel from the vented fuel tanks to the fuel regulator and back could lead to evaporation of the light hydrocarbon components [11]. The PN/PM Indices predict that PM emissions would increase as this occurs due to the decrease in fuel vapour pressure. Extended length testing provides an excellent opportunity to test this theory because it provides sufficient time for a start-to-finish change in PM large enough that changes in fuel properties should be discernible if they are the in fact the primary influence. Unfortunately, performing full analysis on multiple fuel samples was not practical so exhaust gaseous species were used as a proxy as was done by past researchers [11].

As an additional check, extended results with and without the Zimmerman EEPS corection factor are plotted in Figures 6.7 and 6.8 to ensure that the per bin coefficients (y=Ax+B) are not skewing the results [78]. A plot of EEPS PN concentration vs. filter mass during an extended test drift in Appendix B.1 also corroborates the drift.

![Figure 6-7 Two-minute average corrected PN concentrations for single extended tests with the PCV enabled and diverted. Shaded areas indicate standard error using data from 100 minute PCV testing.](image-url)
Figure 6-8 Two-minute average raw PN concentrations for single extended tests with the PCV enabled and diverted. Shaded areas indicate standard error using data from 100 minute PCV testing.
Figure 6-9 2-Minute average particle size distributions of extended GC/MS gasoline test measured at 100-minute increments. A) Raw B) Normalized

Figure 6-10 2-Minute average normalized particle size distributions of PCV tests measured at 100-minute increments. A) PCV Enabled B) PCV Diverted
Using the MKS FTIR, isobutylene, toluene, and trimethylbenzene (TMB) sample concentrations were averaged periodically over the course of every extended length test and the correlation with PN was computed, a sample is plotted in Figure 6.11. Those species were chosen based on results from Ramos’s work which showed that isobutylene and toluene had the strongest correlation to PM emissions to the point that multiple linear regressions of those species led to a predictive equation [11]. There is also a theoretical basis for their selection. Isobutylene is a common intermediate product of combustion of medium weight alkanes (C4-C8), formed by H-abstraction and β-scission [46]. Toluene and TMB are both aromatics which are known soot precursors. These traits also play into the PN index as PAHs have more double bonds than alkanes and medium weight hydrocarbons would have relatively high vapor pressures. For a PM increase with time, a decrease in exhaust isobutylene and increase in toluene and TMB would be expected. Overall, there was no correlation between any of three components and PN for complete set of extended length tests. Both strong positive and negative correlations were seen for the same parameter during different tests, as shown in Table 6.3, so in-use gasoline property changes are not likely a factor in PM drift.

Figure 6-11 2-Minute total fuel normalized PN and 2-minute average gas species concentration. Error bars indicate standard deviation of gas concentrations.
Table 6-3 Correlation Coefficients of Selected Gas Species and 2-Minute total fuel normalized PN taken every 10 minutes during various gasoline test series

<table>
<thead>
<tr>
<th>Test Series (Length)</th>
<th>Isobutylene ( R^2 )</th>
<th>Toluene ( R^2 )</th>
<th>Trimethylbenzene ( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>GC/MS (Long)</td>
<td>0.95</td>
<td>-0.97</td>
<td>-0.87</td>
</tr>
<tr>
<td>GC/MS (Standard)</td>
<td>0.15</td>
<td>0.55</td>
<td>N/A</td>
</tr>
<tr>
<td>PCV Enabled (Standard)</td>
<td>0.02</td>
<td>0.88</td>
<td>-0.61</td>
</tr>
<tr>
<td>PCV Enabled (Long)</td>
<td>0.16</td>
<td>0.01</td>
<td>-0.67</td>
</tr>
<tr>
<td>PCV Diverted (Standard)</td>
<td>-0.75</td>
<td>0.90</td>
<td>-0.59</td>
</tr>
<tr>
<td>PCV Diverted (Long)</td>
<td>0.82</td>
<td>0.84</td>
<td>-0.12</td>
</tr>
<tr>
<td>Average</td>
<td>0.23</td>
<td>0.37</td>
<td>-0.57</td>
</tr>
</tbody>
</table>

6.1.3 PCM Adjustments to Fuel Injection

A gradual increase in injection duration at steady-state highway cruise conditions has been proposed as a possible cause of PN drift [11]. If this occurs, it would manifest itself as a change in equivalence ratio and STFT. A desire to capture equivalence ratio changes is part of what motivated the change to reporting PN in emissions factors in section 6.1 instead of concentration as was previously done in ERDL. Comparison of Figures 6.5 and 6.7 shows that switching to \#/kg-fuel results, which would account for additional fuel injection, does not affect the apparent drift so equivalence ratio changes can be discounted. The relationship between PM and short term fuel trim displayed variability similar to its relationship with the gaseous species in Table 6.2. Some tests had a very strong correlation but others had almost no correlation as shown in Table 6.4. Examination of the raw STFT plots makes the reason for this odd relationship clear. As shown in Appendix B.1, the STFT does not have consistent test-to-test behavior. In the GC/MS test (the test with analyzed fuel batch “gas2”) it gradually increased, while in the PCV diverted test it was erratic over a small range, and then in the PCV enabled test it was relatively steady. Regardless of the behavior, the PM emissions gradually increased so STFT is not likely a significant factor.

Table 6-4 Correlation Coefficients of short-term fuel trim (STFT) and fuel normalized PN taken every 10 minutes during extended duration testing using the analyzed fuel batch “gas2”

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Enabled</th>
<th>Diverted</th>
<th>GC/MS</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R^2 )</td>
<td>0.709116</td>
<td>0.10011</td>
<td>0.967006</td>
<td>0.766</td>
</tr>
</tbody>
</table>
6.1.4 Summary and Discussion of PN Drift Findings

Extended length testing was used to investigate PN drift during steady state tests. The investigation was unable to identify a source of the drift but a number of possibilities were eliminated and some revealing characteristics were discovered that will be valuable to future work. In-use fuel property changes and STFT changes during testing had no correlation with PN emissions and are therefore eliminated as potential causes. Intake system deposits and blow-by gas recirculation both had the effect of shifting average PN emissions concentration but they did not eliminate the gradual increase in rate of emissions. Blow-by gas recirculation did appear to slow the PN drift slightly which suggests that source of drift interacts with oil-fuel vapours. Another clue regarding the PN source was provided by the particle size distribution. Nearly all the particles added after 100 minutes of testing were above 100 nm with the peak being around 200 nm.

PM from GDI engines at steady state is known to originate from 4 areas: fuel rich pockets in the combustion chamber due to poor mixing, oil-fuel film interaction in the piston-cylinder crevices, “pool fires” on the piston surfaces, and vapour desorption from injector deposits [4], [79]. If the typical size of particles formed in each of these areas was known it might be possible to pinpoint the source of the drift PM. Unfortunately, a complete description of GDI particle size by origin could not be found in the literature but fragments are available that can form a partial picture. During cold starts, an initial burst of larger (100-200 nm) particles is followed by sustained emission of nucleation mode particles that doesn’t decay until engine temperature stabilizes [55]. Hot starts have a similar initial burst but do not have the sustained nucleation mode particles because engine temperature rises much more quickly [20]. Taken together, the PM emissions behavior of the different temperature starts suggests poor mixing stemming from inhibited fuel vaporization, likely the effect of cold temperatures, leads to nucleation mode particles. Therefore, fuel rich pockets in the combustion chamber due to poor mixing are not likely responsible for the larger accumulation mode particles that make up the bulk of the drift. The lubricant oil contribution to drift can be similarly discounted. Using hydrogen powered engines, lubricant produced soot has been isolated and it found to be primarily in the 18 to 31 nm size range, much smaller than the drift particles [80]. The magnitude of the lubricant contribution is also generally believed to be too small to account for the particulate added by the drift during
ERDL tests [81]. There has been some concern that the recent widespread adoption of oil squirting nozzles in GDI vehicles may lead to more oil-derived PM than without nozzles but preliminary research indicates that it has not had an impact. Researchers at the DOE found negligible amounts of lubricant derived hydrocarbons on soot samples from a modern GM vehicle equipped with piston cooling oil nozzles [82]. The final two possible origins of the drift particles, “pool fires” and injector deposit vapour desorption, are the most promising and most researched. Optical engine studies have shown that homogenous charge engine PM is dominated by “pool fires” [83]. The formation of pools can be avoided by careful selection of injection time at least in laboratory spray guided engines but the ERDL Ford engine is wall-guided and designed to meet existing regulations and consumer preference not PN limits. The typical particle size also matches with the range added by the drift [84]. Injector deposits were considered by Ramos and Mireault but they were limited by hardware availability [11], [20]. In work by Piock et al., a constant increase in emitted PM and PN concentration over a 10 hour period following installation of a clean injector was observed [79]. This severity of the process was also tied strongly to low injector pressure and the pressure used in this thesis was lower than even the lowest pressure tested, 150 bar vs. 200 bar respectively [85]. Still, the applicability of this example to the drift at ERDL is uncertain because the injectors in the lab’s engine have never been cleaned and would be expected to already have reached equilibrium deposit buildup. However, additional buildup is not needed to increase PN since injector deposits have two pathways of influence: disruption of the injection spray(s) by solid deposits and desorption of stored fuel vapour late in the combustion cycle [86]. The latter pathway could foreseeably produce an increasing amount of PM over the course of a test without the need for additional soot buildup depending on how long it takes for existing deposits to become saturated with fuel. The 7-hours of engine operation for each extended length test might be assumed to be enough time but that is unconfirmed.

6.2 Development of a Surrogate Gasoline to Study Fuel Composition Influence on Test-to-Test Variability

Past work at ERDL has exclusively used pump gasoline as the base fuel. This has proven to be untenable due to large and unpredictable differences in resultant PM and exhaust gaseous species that make test comparisons unclear. This section details efforts to create custom blends of pure hydrocarbons to approximate the PN emissions behavior of gasoline so that a consistent fuel can
be used for future studies and the variability believed to stem from pump gasoline batch changes can be avoided. For convenience, Table 6.5 summarizes the custom fuel blends described in section 4.6 (Test Fuels) and also includes information that will discussed in subsequent paragraphs.

### Table 6-5 Summary of custom fuel blends for Section 6.2 (detailed composition given in Table 4.6).

<table>
<thead>
<tr>
<th>Test Group Identifier</th>
<th>Custom Fuel Blend</th>
<th>Total # of Tests</th>
<th># of Steady State Only Tests</th>
<th># of Cold Starts</th>
<th># of Hot Starts</th>
<th>PM Index</th>
<th>PCV Diverted?</th>
</tr>
</thead>
<tbody>
<tr>
<td>I65T35</td>
<td>I65T35</td>
<td>3</td>
<td>2</td>
<td>1</td>
<td>0</td>
<td>0.592</td>
<td>No</td>
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<tr>
<td>I65T35+Oil</td>
<td>I65T35 + oil</td>
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<td>1</td>
<td>0</td>
<td>0</td>
<td>0.592</td>
<td>No</td>
</tr>
<tr>
<td>TMB</td>
<td>TMB</td>
<td>3</td>
<td>2</td>
<td>1</td>
<td>0</td>
<td>0.839</td>
<td>No</td>
</tr>
<tr>
<td>TMB+add</td>
<td>TMB and additive</td>
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<td>1</td>
<td>0</td>
<td>0</td>
<td>0.839</td>
<td>No</td>
</tr>
<tr>
<td>Nap80g</td>
<td>Nap80g</td>
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<td>0</td>
<td>1</td>
<td>0</td>
<td>0.834</td>
<td>No</td>
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<td>Heavy Solvent</td>
<td>Heavy Solvent</td>
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<td>0</td>
<td>1</td>
<td>0</td>
<td>0.878</td>
<td>Yes</td>
</tr>
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<td>Two Solvents</td>
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<td>0</td>
<td>2</td>
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<td>Two Solvents 2</td>
<td>Two Solvents</td>
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<td>0</td>
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<td>1</td>
<td>1.378</td>
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<td>7-Parts</td>
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<td>0</td>
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<td>7-Parts+S</td>
<td>7-Parts+S</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>1.538</td>
<td>Yes</td>
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</table>

### 6.2.1 Transient Start PM Emissions of Pure Hydrocarbon Blends

During engine start and warm-up, emissions characteristics are different than they are after the engine stabilizes and the steady operating conditions are reached. This initial period is the starting point for comparing the effects of pure hydrocarbon fuels and gasoline on PM. Cold and hot starts were conducted in accordance with the methods described in section 5.1.2. Cold-start data for seven fuel blends is displayed in Figure 6.12 below. Transient PN emissions are highly variable, especially during cold starts so there is little that can be concluded from the relatively close single runs displayed. The overall PN vs. time relationship of all fuels follows the trends established in the work of Ramos and Mireault [11], [20] shown in figure 6.13 for reference. Cold starts begin with a large initial PN spike when the starter motor is cranking the engine and fuel is being injected but combustion is not yet stable. This is followed by a secondary smaller spike at approximately 30 seconds as the engine reaches a consistent idle speed and begins to regulate fuel injection based on feedback from the $O_2$ sensor.
Figure 6-12 Fuel blend comparison of average cold-start PN concentration with time.

Figure 6-13 Ramos gasoline-fuel blend cold-start PN concentration with time. [11]
Figure 6-14 PCV Enabled and Diverted comparison of average cold-start PN concentration with time. Errors bars represent standard deviation of two cold starts conducted at each condition.

Figure 6.14 provides some perspective on the extreme variability of cold-start PM emissions. Upon first inspection, the graph seems to show that diversion of the PCV gases increases PM as the PCV diverted series has a nearly 50% higher peak PN concentration but the error bars are large enough that there is almost complete overlap between the two data series over the entire two-minute period. In fact, the error bars around the PN spikes at ~5s and ~30s in figure 6.14 are large enough that they would encompass all the data in figure 6.12, suggesting that fuel composition does not have a significant impact on cold-start PN or at least not an impact comparable to normal start-up variability. This is an agreement with recent literature such as work by Badshah and colleagues that has shown that cold-start GDI PM emissions are driven by the highly unpredictable amount of start-up fuel enrichment to an extent that trends related to other factors can’t be discerned [87], [88]. In figure 6.12, the only difference that is discernible, in that it clearly extends beyond the range of the figure 6.14 error bars, is the PN concentration difference between I65T35 and gasoline post 60s of elapsed time, which is when the engine begins transitioning to steady operation. This result is in agreement with the PM Index model, as gasoline has the highest index of the tested fuels and I65T35 has the lowest. In order to understand the root of the PN concentration difference, it is useful to consider the evolution of the particle size distributions during cold start. Referring to figure 6.15, the initial spike of PM was primarily composed of accumulation mode particles with diameters above 100 nm. The
second spike was made up of smaller nucleation mode particles around 20 nm in diameter. After the two spikes, the more stable portion of the cold start, the region where the statistically significant differences in emitted PN concentration of fuels exists, has a median diameter of 16.5 nm. Particle size profiles were not fuel dependent and other data with similar patterns is available in Appendix B.2. The large discrepancy in particle size between the initial spike in PN and the later period suggests a difference in PM formation. At the beginning of cold start, the starter motor actuates the crankshaft and connected camshafts before consistent combustion is established so some partially burnt fuel would be expected to escape. In the later stage, combustion is steady so this should no longer be the primary source of PM but the engine would still be cold which may lead poorer vaporization and more deposits. Considering the hot start data provides some insight on the effects of temperature on transient PM emissions.

Figure 6-15 Cold-start gasoline particle size profile.

Four hot starts were conducted, three on gasoline batches “gas2” and “gas3” and one on the “Two Solvent” blend. Much like the cold-start data, hot starts began with a large initial spike in PM. No repeat tests with the same fuel and PCV conditions were conducted so it is not possible to rank the test fuels by hot-start PM production. However, the two PCV tests used the same fuel batch and there are a number of factors that suggest that the drastic difference in their emitted PN concentrations cannot be attributed to the change in blow-by configuration. It is more likely an indication of test-to-test hot-start variability. The brief time preceding the initial spike in PM, less than 15 seconds in all four cases as shown in figure 6.16, is likely not sufficient for blow-by gas recirculation to form deposits or even draw significant oil into the intake manifold. The blow-by flow would be consistent over the period of hot start with at most a gradual decline as sealing improves as it is primarily a function of engine speed so any PM effects would not be
confined to the first few fired cycles of the engine. Finally, the presence of blow-by gases would be expected to increase PM as it did during the steady highway cruise portions of the extended tests but the PCV diverted test has a larger PN spike in figure 6.16. Based on these factors, the $1 \times 10^8$ #/cm$^3$ difference in peak particle concentration between the two PCV tests likely represents the PM emissions variability of hot starts. The magnitude of this difference, which is greater than the peak PN concentration during any cold start, makes it difficult to discern the influence of fuel or operating conditions. However, even with this uncertainty, it can be concluded that hot starts on average produce higher peak PN concentrations based on each hot start having a higher peak than the preceding cold start or starts on the same fuel ($p<0.01$). Another glaring difference between the results of the two types of starts is that post 50 seconds of elapsed time the average PN concentration of the hot starts was approximately a fifth of the concentration of cold starts. Taken together, these hot vs. cold observations suggest that the improved atomization that would accompany starting at elevated temperature initially leads to increased escape of partially burnt hydrocarbons and therefore PM but later it improves mixture homogeneity and possibly curbs the formation of liquid films once combustion is stable.

![Figure 6-16 Fuel blend comparison of average hot-start PN concentration with time.](image)

Summarizing the results of the transient testing of pure hydrocarbon blends in relation to the objectives of section 6.2, many of the blends tested appear to be acceptable as a gasoline
alternative especially the “Two Solvents” mixture since it has data for cold and hot starts. In terms of approximating the PM emissions, the pure blends had similar peaks and overall time vs. PN concentration curves while the test-to-test variability did not change drastically. An improvement in variability was desired but its absence is not unexpected given the limited number of tests conducted and recent literature which shows that fluctuations in PM emissions are inherent to transient engine operation [88].

6.2.2 Highway Cruise PM Emissions of Pure Hydrocarbon Blends

The primary operating period of interest for the pure hydrocarbon blend testing was highway cruise since it is the period that was studied by Ramos and Mireault when they described test-to-test variability and identified gasoline batch changes as a potential source [11], [20]. Twenty-two tests were conducted on 11 fuels including different gasoline batches. The results of these tests are summarized in figures 6.17, 6.18, and 6.19 below. To provide a frame of reference for comparison, the dashed line (“Dilution Air Background”) in figure 6.18 shows an exhaust equivalent background particle count. This was obtained by multiplying the EEPS number count measured for filtered dilution air by the dilution ratio to bring the concentration to exhaust levels. This line is added to highlight the fact that the measured pure hydrocarbon blend particle concentrations are relatively low.

![Figure 6-17](image)

Figure 6-17 Two-minute average PN concentration for sets of tests with 3 individual runs for each fuel blend. Shaded areas indicate standard error.
Two-minute average PN concentration for single test fuel blends and a three test average with the TMB blend for reference. Shaded area indicates standard error. The “Dilution Air Background” reference line is the average EEPS particle concentration of the dilution air multiplied by the test dilution ratio.

Figure 6-19 Two-minute average PN concentration for two sets of gasoline test (PCV Enabled and Gas1), a single test with an I65T35 and motor oil blend, and a single test with 7-Part plus sulfur mixture. Shaded area indicates standard error.

As discussed in sections 3 and 4, the fuel blends were chosen to replicate gasoline PM production, first through application of the PM and PN indices and then by emulating the
composition of one of the gasoline batches (“gas2”) used for engine testing. Neither of these methods was able to approach the level of PM production of even the least emitting batch of gasoline as figure 6.19 shows. The 7-Part plus sulfur blend, the most PM emitting gasoline-like hydrocarbon mixture, still had an average particle concentration that was a fraction of that of any pump gasoline tests. It should be noted that the I65T35+Oil test is not seriously considered because its gaseous emissions and particle size distribution were too dissimilar from gasoline. The same trends were also verified by mass measurements available in Appendix B.1 From a PM / PN index perspective, this result is inexplicable. The “7 Parts blend was specifically chosen to emulate the composition of analyzed gasoline batch “gas2” (detailed analysis in Appendix A) with particular attention paid to aromatic content and average carbon chain length because those properties are known to be strongly correlated with the components of the index formulae, double bond number and vapour pressure respectively. In fact, the blend has a higher aromatic content by volume than the analyzed gasoline, 45.6 % vs. 43.8%, and the aromatics used had the same average carbon chain length, namely 7.9.

One possible explanation for the pure hydrocarbon blend vs. gasoline PM discrepancy is that the detailed composition of the gasoline includes very high molecular weight aromatics that have an outsized influence on its true PM Index and subsequent emissions. The PM index of the 7-Part blend was 1.54 which is lower than the average global gasoline PM index of 2.1 but greater than that of both EURO and US emissions certification fuels [39]. Aikawa et al. have shown that index differences in this range, 1.5 to 2.1, can lead to PM increases of nearly 400% at highway cruise conditions so the possibility that the 7-part blend is missing a key component needed to reach the true PM index of the tested gasoline is realistic. This theory can be evaluated through comparison of the Nap80g test to the set of I65T35 tests as they have the same formulation other than the addition of 80g of naphthalene. Naphthalene is a very low vapor pressure compound to the extent that it is actually solid at room temperature and it is a polycyclic aromatic with a high double bonded equivalent of 7 so past research and the PM index would suggest it is a very potent soot precursor [22], [23]. The results shown in figure 6.18 disagree with this hypothesis as the Nap80g test actually produced the same amount of PM within standard error as the base I65T35 tests. Based on the lack of response to naphthalene, it is unlikely that an unaccounted for small quantity of a similar compound in gasoline is responsible
for the gasoline vs. 7-part blend PM discrepancy. The result also indicates some weakness in the PM index model that necessitates further study.

Since the possibility that the fuel properties sought for gasoline levels of PM production are not being achieved due to a lack of some necessary component has been discounted, it follows that the relationship between those desired fuel properties and particulate needs to be reconsidered. An abundance of research has identified ease of vaporization and the presence of double bonds to be the critical characteristics for a fuel’s influence on PM [13], [38]–[40], [44]. The PM index was created to capture these findings in a tool for fuel comparison but there are instances where it is incomplete such as when evaluating ethanol blends which produce amounts of PM that deviate from what the index would suggest [11]. Ethanol adds a complication because its high enthalpy of vaporization inhibits mixing and counteracts its other PM reducing effects [89]. To gauge if the PM of tests conducted for this study were similarly affected by some sort of confounding factor, the particle numbers and PM index values of all blends are displayed in figure 6.20. The correlation is weak with a coefficient of determination of $R^2=0.5479$ compared to greater than 0.99 in the work by Aikawa et al. that created the PM Index [39]. Comparison of the coefficients from two datasets should include the caveats that the Aikawa work encompassed a wider range of particle numbers and was conducted over the New European Drive Cycle so its stronger correlation is not surprising but the gap in coefficients is so large that it still suggests that the Index is not appropriate for pure hydrocarbon blends.

Examining the particle size distributions from the blend tests highlights differences between the pure hydrocarbons mixtures and pump gasoline that are relevant to the huge gap in emitted PM and breakdown of the PM Index model. Figure 6.21 shows that all eight of the pure hydrocarbon fuel blends have similar particle size distributions with their mode diameter bins being 22.1 nm and median particle diameter bins ranging from 22.1 to 29.4 nm. In comparison, gasoline tests had much larger median and mode particle diameters as shown in figure 6.22. The overall trend appears to be an increase in accumulation mode particles as the fuel blends become more complex and closer to the composition of gasoline. This contrasts with the pattern seen during transient operation where particle emissions were largely fuel-independent. Recalling that the PN added due to temporal drift was also primarily in the accumulation mode, there appears to be a relationship between the PM formation mechanism(s) that become more prominent after initial engine warm-up and fuel composition.
Figure 6-20 Two-minute total fuel normalized PN versus PM Index for all custom blended fuels

Figure 6-21 Particle size distributions taken from a series of two-minute averages taken every 10 minutes for tests performed with pure hydrocarbon fuel blends. Error bars indicate standard error.
To examine the possibility of slow developing particle formation sources or mechanisms that are specific to gasoline and gasoline-like complex fuel blends, the particle number emissions of a series of fuels were plotted during the transition from start-up to steady state operation in figure 6.23. As suspected, the emissions rates of the fuel blends relative to that of gasoline decayed gradually and at different rates depending on fuel composition. The approximate parity of particle emissions rate of all fuels during start-up persisted until 5 minutes (all four fuels are within the error bars). The emission rates of the less complex TMB and Two Solvents blends then diverged from the gasoline and 7-part blend at 10 minutes. Finally once steady state was reached at approximately 20 minutes, the gasoline produced an order of magnitude more PM than any of the blended fuels. Another key observation that suggests a change in PM formation mechanism or source is that gasoline was the only fuel that actually saw an increase in emissions going from 10 minutes after start-up to steady state. This suggests that in the case of gasoline tests unlike for other fuels, improved vaporization and mixing due engine warm-up is not the dominant factor on PM emissions as the engines transitions to highway cruise operation so some other fuel composition influenced phenomena must be occurring.
Figure 6-23 Two-minute average PN concentration for selected fuels at 5 minutes, 10 minutes, and average of every of two minutes at every successive 10 minute interval from 20-90 minutes (Avg. Steady). The error bars indicate standard error where three tests on the same fuel were conducted.

Gaseous emissions concentrations are the last available measurements that may provide some clue as to why PM from gasoline, and to a lesser extent the 7-part mix, responds differently to highway cruise operating conditions than the other fuel blends. All the fuels including the gasoline batches had equal concentrations of the H₂O, CO, and CO₂ within standard error. Of the emissions bench measured concentrations shown in figure 6.23, only NOₓ exhibited statistically significant differences between fuels but the differences were still small and not likely meaningful given past results [20], [28]. Looking next at the hydrocarbon emissions as measured by the FTIR displayed in figures 6.25 and 6.26, significant differences exist in methane, ethylene, propylene, toluene, pentane, acetylene, isobutylene, 1,3-butadiene, and benzene. Of these species, toluene, isobutylene, ethylene, propylene, and pentane are of greatest interest based on the magnitude of the differences, past work, and combustion theory [11], [22].
Figure 6-24 Average standard emissions measured by the emissions bench. Error bars indicate 95% confidence interval.

Figure 6-25 Set 1 of 2 of average hydrocarbon emissions measured by the FTIR. Error bars indicate 95% confidence interval.
Ramos [11] used gaseous toluene and isobutylene concentrations as proxies for fuel double bonded equivalent and vapour pressure respectively. These species were selected because toluene is a common gasoline aromatic component and isobutylene is a common product of the combustion of light alkanes so a high isobutylene concentration is expected to coincide with a high concentration of light alkanes in the fuels. The use of proxies was not necessary during this study because the composition of a gasoline batch was analyzed and the other fuel blends had known components. However, comparison of the relative PM production predicted by the input fuel-based PM Index, the gaseous product-based Ramos proxy model, and the measured particle number is still warranted as it may help indicate where the PM Index fails for PN produced by the custom blends. The PM Index values of the custom blends are 0.64, 0.84, 1.38, and 1.54 for I65T35, TMB, Two Solvents 2, and 7-part respectively. Therefore, the Index would predict a substantial increase in PN emissions for the Two Solvents and 7-Part blends relative to the I65T35 and TMB blends but as previously discussed the custom blends all emitted a low level of PM relative to gasoline. Turning to the gaseous products model, the toluene concentrations of tests on all the fuels were within the range of the sets of tests on the two gasoline batches, and the Ramos model coefficient for toluene is only 1/6 that of isobutylene, so the model can be simplified to solely a comparison of isobutylene concentrations. In this model, less isobutylene
represents a less volatile fuel which is thought to lead to poorer mixing and an accompanying increase in PM. On this basis, the isobutylene concentrations in figure 6.26 would predict that I65T35, TMB, and the Two Solvents blends would emit a similar low level of particulate while the 7-part blend would emit a much greater amount of PM close to the amount emitted by gasoline. Like the PM Index, the gaseous model does not match the measured PN, but more interestingly, it differs too with the Index in some cases. The isobutylene concentration of the Two Solvents tests is not significantly different from the I65T35 or TMB tests despite PM Index value being nearly twice as large. Recalling that the Index includes a fuel saturation term in double bonded equivalence and fuel volatility term in vapour pressure, it is perhaps more reasonable to compare exhaust isobutylene and fuel vapour pressure directly since they are meant to represent the same characteristic in their respective models. Still, the disconnect remains as the Two Solvents blend has a lower fuel vapour pressure than even the 7-Part mix despite having more than twice the isobutylene concentration. The implication of this result is that the PM Index’s accounting for the fuel effect on pre-combustion mixing using only vapour pressure is likely insufficient.

Ethylene is a common intermediate molecule that leads to the acetylene necessary for soot formation via the HACA mechanism [22]. The ethylene emissions concentrations produced by the test fuels fall into two major groups: the higher concentration more complex fuel group consisting of the gasoline batches and the 7-part mix at 110-120 ppm and the less emitting simpler fuel group consisting of the I65T35 and TMB blends at approximately 50 ppm. This observed grouping is in line with the PN emissions data during the start-up to highway-cruise transition period discussed earlier that seemed to suggest that the more complex blends have more gasoline like emissions responses.

In contrast, the propylene and pentane concentrations of the simpler fuel blends were actually more similar to that of gasoline than the 7-part blend. Pentane is a light alkane and propylene is an olefin formed as intermediate species during the combustion of light alkanes so it not surprising that the intentionally heavy 7-part mix doesn’t produce as much of these gases as the lighter custom blends or even gasoline which typically includes some pentane and butane components. While expected, this is still a potentially significant result as it confirms that the largest composition discrepancy between the most detailed surrogate blend and gasoline manifests itself in combustion products. It follows that if they are responsible for the largest
noticeable difference in gaseous emissions, the light ends of gasoline could have a large unforeseen impact on particulate emissions.

6.2.3 PM Emissions Repeatability of Pure Hydrocarbon Blends

The motivation for the formulation of a surrogate gasoline from pure hydrocarbon blends was to avoid the poor repeatability of past gasoline tests that is believed to stem from batch-to-batch and/or seasonal changes in pump gasoline. A surrogate blend that reproduced gasoline highway PM results was not yet found but a preliminary assessment of the repeatability was conducted with the caveat that the performance might be influenced by the fact that the custom blends so far only produced a fraction of the PM of gasoline. The analysis should be repeated if a more suitable surrogate blend is found later. For now, two sets of three sets of tests on the Two Solvents blend were conducted with an extended gasoline test and a one week waiting period between them. The results are displayed in figure 6.27 below.

![Figure 6-27 Two-minute total fuel normalized PN for two sets of test the Two Solvents blend. Shaded area indicates standard error.](image)

The error bars for both sets of tests intersect at each 10-minute measurement interval. In comparison, figure 6.19 shows two sets of gasoline tests where one set emitted nearly twice as much as the other and the error bars never intersected. The use of a consistent fuel mixture resulted in a marked improvement in repeatability.
Figure 6-28 Relative standard deviation with test time for 5 custom blends and 4 gasoline batches.

Figure 6-29 Standard deviation over noise (dry dilution air particle concentration) with test time time for 5 custom blends and 4 gasoline batches.

Past work at ERDL used relative standard deviation to assess variability [11], [20]. Figure 6.28 includes relative standard deviations of most blends and gasoline batches at each 10-minute PN measurement interval. By this measure, the second Two Solvents test series and the 7-Part mix were the most variable but the applicability of RSD to a dataset that includes the
custom blends and gasoline batches that have an order magnitude greater PN emissions is questionable. To address this weakness, standard deviation over the dilution air baseline PN is included as a secondary metric in figure 6.29. The baseline is the average emitted PN recorded on the EEPS for a few minutes while it is hooked up to the filtered dilution air before starting each test. Inclusion of noise instead of the test emissions inverts the order of variability with the custom blends now appearing to be the least variable. Overall, the two figures show that any the custom blends have roughly equal variability to the individual gasoline batches but the custom blends are reproducible while the gasoline tests encompass a huge range of variability from Gas 1 to the PCV Enabled sets. Therefore, in terms of having a repeatable long-lasting fuel option, custom blending is superior to pump gasoline.

6.2.4 Low Summary and Discussion of Pure Hydrocarbon Blends Tests

Eighteen standard length tests on eight different fuel blends were conducted with the goal of designing a surrogate gasoline blend made up of pure hydrocarbon components. The surrogate was intended to emulate gasoline performance in terms of transient start and highway cruise PM emissions rate as well at least match emissions repeatability but that was relatively straightforward to demonstrate compared to the former two goals.

The profile of cold-start emissions for all fuel blends began with an initial large spike of PN followed by a secondary smaller spike and ended with a steady portion for the last 80 seconds of the 120-second start. Hot start tests consisted of a larger initial spike in PN than the cold-start tests but a more dramatic decay to a steady emissions rate for the rest of the two-minute period. The PM from both types of start was so variable that it was not possible discern the influence of the fuel blends. This was in agreement with recent literature that suggests that start-up PM is highly inconsistent and largely fuel independent. Based on the transient results and available literature, matching gasoline start-up PM was deemed unlikely to be an issue for a pure hydrocarbon blend.

The highway cruise PN of all custom fuel blends was much lower than that of even the least emitting of the gasoline batches. This was despite the fact that the pure hydrocarbon components were carefully selected, initially using application of the PM and PN Indices and later by matching the composition of an analyzed gasoline batch to the greatest extent possible with available chemicals. A variety of data was presented to investigate this disparity including
particle size distributions, particle counts during the period between start-up and highway cruise, and gaseous emissions data. The custom blends had much smaller mean and median particle diameters during steady-state operation despite being similar at start-up. During the transition period prior to highway cruise, the particle counts from all fuel deteriorated but gasoline and the 7-part mix deteriorated slower. The gasoline tests were also unique in that their PN partially rebounded after 10 minutes and then continued to increase gradually. Gaseous concentrations of ethylene, isobutylene, toluene, and pentane differed substantially from fuel to fuel. Through analysis of all of this data, a number of possible explanations for the custom blend vs gasoline PM gap were discounted and a theory emerged that focused on the light ends of gasoline affecting mixing in ways that are not accounted for by the PM Index.

Support for the theory that high vapour pressure (light) hydrocarbons are necessary for high PM production is found in recent literature. Fuel spray experiments have shown that under certain conditions higher volatility fuels may penetrate further in-cylinder due to a phenomenon referred to as flash boiling [42]. The preferential rapid evaporation of light components breaks up sprays leaving large liquid droplets that deposit onto cylinder walls and piston crowns. Once there, Wary et al. speculated that films containing lighter hydrocarbons might boil instead of steadily evaporating and remixing [43]. They believe that is what led to a higher volatility pentane and toluene mixture producing more PM than an isooctane and toluene blend in their experiments [43]. Ketterer and Cheng had similar conclusions but went even further in terms of the influence of film boiling. They concluded that vapours formed by evaporation from fuel films are the true major source of the PM that has long been misidentified as “pool fires” [68]. Their observations of flame luminosity and PN supported a model where vapour plumes that form above fuel films undergo pyrolysis and form soot due to heat conducted from the surrounding burned gases. The light ends of gasoline are expected to promote the formation and growth of the plumes thereby encouraging particle formation. The relationship between light hydrocarbons and the PM Index has also been examined. Multiple fuel studies have shown that the inclusion of pentane leads to a much stronger correlation between the PM or PN Indices and measured particle counts [48], [89].
Chapter 7
Conclusions and Recommendations

7 PM Variability Findings and Future Work

The overall goal of this study was to understand the temporal and test-to-test PM emissions variability that has been observed in previous work at the University of Toronto. The key findings and recommendations for future work are presented here.

7.1 Conclusions

Exploration of two types of variability, temporal and test-to-test, relied on two experimental approaches: extended length testing and blending of a surrogate gasoline from pure hydrocarbon components respectively. Conclusions from this study are summarized and grouped by these areas of investigation below.

7.1.1 Investigation of Gradual Increase in PN Emissions during Steady State Tests

Earlier gasoline direct injection engine emissions tests have consistently exhibited an unexplained gradual increase in measured particle concentrations with test time at steady-state operating conditions. Using an extended length testing to gain a more detailed picture of this PN “drift” phenomenon, three potential sources were examined: crankcase ventilation system deposits, in-use gasoline property changes due to evaporation, and PCM fuel injection adjustments.

- The presence of crankcase ventilation system deposits significantly increased average particle number concentrations but eliminating them and preventing their subsequent formation through diversion of blow-by gases did not reduce the PN drift. The particle contribution of blow-by gases was primarily in the accumulation mode.
- In-use gasoline property changes correlated with changes in PM emissions quantity were not found. The changes in concentration of the gaseous species of interest, trimethylbenzene, isobutylene, and toluene were subtle and inconsistent with increases and decreases seen during different tests on the same fuel.
PN measurements were expressed on a per kg-fuel basis using the engine’s mass air flow and equivalence ratio to account for any changes in injected fuel quantity but the PN drift remained. The engine’s short-term fuel trim did not behave consistently test-to-test so it was ruled out as an explanation for the very consistent gradual PN concentration increase.

During the course of the source investigation, it was discovered that the majority of particles added due to the drift were accumulation-mode sized and by the end of extended length testing they formed a majority of total particles.

With all of the possible sources of PN drift eliminated, the PM emissions literature was consulted to explain the findings. Based primarily on particle size measurements and the process of elimination, pool fires and desorption of fuel vapours from injector deposits were identified as the most promising areas for further study.

### 7.1.2 Development of a Surrogate Gasoline to Study Fuel Composition Influence on Test-to-Test Variability

To avoid the PM emissions inconsistencies that have been witnessed during past tests on pump gasoline, a reproducible surrogate gasoline composed of known proportions of pure hydrocarbons was desired. Potential surrogate formulas were developed initially using the PM Index as a guide and later by mimicking the composition of an analyzed gasoline sample. Their ability to approximate the transient and highway cruise PM emissions and improve on the repeatability of gasoline was used to evaluate the suitability of the custom blends as a replacement particle emissions fuel.

- Transient particle emissions were found to be largely fuel-independent for both cold and hot starts. The start-up particle emissions followed the same particle size and concentration-time trends as earlier gasoline tests. Therefore, the use of a surrogate custom blend to study start-up PM emissions is viable.

- The highway cruise PN concentrations of all custom blends were less than 25% of even the least emitting gasoline fuel batch tested. The PM Index did not have predictive value for the custom fuel blends. Therefore, fuel vapour pressure and level of saturation is insufficient to describe particle emissions behavior. Adsorption of motor oil into gasoline that does not occur in the blends due their chemistries was discounted as the source of the
particle emissions difference based on a test where a simple custom fuel blend was doped with a small quantity of oil. The possibility that quantities of very high molecular weight aromatics in gasoline may exist that are too small to shift the PM Index but still greatly influence particle counts was deemed unlikely due to the lack of PM response to fuel Naphthalene. Based on gaseous emissions concentrations and PN concentrations during the transition from start-up to highway cruise, a theory emerged that the high vapour pressure components of gasoline affect fuel-air mixing in a manner that promotes PM production.

- The batch-to-batch repeatability of the only custom blend repeated was superior to the repeatability between any two gasoline batches. The PM test-to-test variability was comparable to the least variable gasoline batch tested and repeatable when a new batch of the same composition was blended. Overall, the use of consistent fuel composition resulted in consistent PM results but this should be verified for future blends that approach gasoline particulate emissions levels.

The most significant finding of this thesis was the breakdown of PM Index model for the pure hydrocarbon blends. Some recent literature corroborates the theory that the light ends of gasoline have a negative effect on mixing but more work is required to describe the mechanism by which this occurs.

### 7.2 Recommendations for Future Work

Significant questions remain on the source of the PN emissions drift and some new ones have developed regarding the huge gap in particle concentration between the pure hydrocarbon blends and pump gasoline. Two hypotheses were put forward during analysis of the results: the first is that the drift is caused by injector deposits and the second is that the blended fuel and gasoline PN gap stems from the lack of high vapour pressure components in the custom blends. For verification of these two theories, the following work is recommended:

- Testing of pure hydrocarbon blends that include pentane and/or butane at a range of proportions. Blends with a range of PM Index values and number of components should be tested so that the PM effect of the interaction of light hydrocarbons with a variety of fuel properties can be assessed.
• A series of tests on a single gasoline batch followed by another series of tests on the same batch after it has been vented to remove the light ends. This would demonstrate if C4 to C5 hydrocarbons are necessary for high PM more conclusively than adding pentane to the simpler previously tested blends. The pre-and-post-venting vapour pressure of the gasoline would have to be verified.

• Additional speed and load conditions and if possible a rudimentary driving cycle should be incorporated into the test cycle in order to extend the applicability of future findings.

• The impact of fuel injection deposits should be examined through post-cleaning extended length testing. A second set of injectors and a full fuel rail could be also be purchased which would allow comparison of tests with clean injectors and injectors dirtied by deposits and possibly even enable mid-test switching.

Over the long term, other related topics can be explored depending what capabilities the laboratory is able to add. Some possibilities include:

• The effect of anti-injector deposit fuel additives on PM emissions can be examined if a suitable additive can be procured.

• The PM performance of the previously tested fuel blends and blends with pentane in spray-guided or air-guided configurations can be tested with alternate engines.

• The interaction of injection timing and duration with fuel properties can be studied if access to the PCM is achieved.

• The accuracy of emissions factors calculated using FTIR measured hydrocarbon emissions can be verified if a fuel flow meter is installed for comparison.

• The influence of the oil spray nozzles under the pistons can be discerned by plugging them if this is deemed safe.

7.3 Related Collaborative Research

While carrying out the work in this thesis, testing was also conducted to support a study to assess the effects of GDI emissions exposure on murine lungs. This work resulted in a paper published in the journal “Science of the Total Environment” titled “Murine precision-cut lung slices exhibit pro-inflammatory responses following exposure to gasoline direct injection engine emissions”.

References


[14] B. Liang et al., “Comparison of PM emissions from a gasoline direct injected (GDI) vehicle and a port fuel injected (PFI) vehicle measured by electrical low pressure impactor (ELPI)


[77] Canada Environmental Protection Act, *SOR/99-236 Sulphur in Gasoline Regulations*.


Appendix A Supplemental Setup and Methods Data

A1 Analyzed Gasoline Batch Composition Summary

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# A2 Solvent Certificates of Analysis

## Certificate of Analysis

### Product:
SUN 100

### Sampling Location:
Sarnia Refinery

### Tank #:
131

### Sample Date:
6/26/2015

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<tr>
<th>Method</th>
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<th>Min</th>
<th>Max</th>
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<td>D60</td>
<td>FBP, Deg. C</td>
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<td>D1319</td>
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<td>Sun DHA GC</td>
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Meets ASTM D3734-01 - Standard Specification for Type 1 High-Flash Aromatic Naphthas

### Certificate of Analysis

### Product:
SUN 150

### Sampling Location:
Sarnia Refinery

### Tank #:
129

### Sample Date:
3/10/2015

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<th>Result</th>
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<td>FBP, Deg. C</td>
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Meets ASTM D3734 Standard Specification for Type II High-Flash Aromatic Naphthas.
A3 H/C Ratio Sample Calculation

Sample calculation of hydrogen to carbon ratio for a custom blended fuel.

Ex. I65T35 (65% isoctane, 35% toluene by volume)

Isooctane (\(C_8H_{18}\), H/C = 18/8, molar mass = 114.23 g/mole, density = 0.692 g/cm\(^3\))

Toluene (\(C_7H_8\), H/C = 8/7 molar mass = 92.13 g/mole, density = 0.8669 g/cm\(^3\))

\[
x_{tot} = \frac{x_{tol} \cdot \varphi_{tot} \div M(toluene)}{x_{tol} \cdot \varphi_{tot} \div M(toluene) + x_{iso} \cdot \varphi_{iso} \div M(isoctane) \div M(toluene)}
\]

\[
x_{tot} = \frac{\varphi_{tot}}{\varphi_{tot} + (x_{iso} \cdot \varphi_{iso} \div M(isoctane) \div M(toluene)) \div \varphi_{tot} \div M(toluene)}
\]

\[
x_{tot} = \frac{0.35}{0.35 + 0.65 \times 0.692 \div \frac{114.23}{0.8669 \div 92.13}} = 0.46
\]

\[
x_{iso} = 1 - x_{tot} = 0.54
\]

\[
\frac{H}{C}(I65T35) = x_{tot} \left( \frac{H}{C}(tol) \right) + x_{iso} \left( \frac{H}{C}(iso) \right)
\]

\[= 1.74\]
A4 PM Index Sample Calculations

Sample calculation for I65T35 blend:

\[
DBE + 1_{isoctane} = \frac{2C - H - N + 2}{2} + 1 = \frac{2(8) - 18 + 2}{2} + 1 = 1
\]

\[
DBE + 1_{toluene} = \frac{2C - H - N + 2}{2} + 1 = \frac{2(7) - 8 + 2}{2} + 1 = 5
\]

\[
VP_{iso}(443K), \text{ use Antoine equation with parameters from the NIST Chemistry WebNook}
\]

(https://webbook.nist.gov/cgi/cbook.cgi?Name=Isooctane)

\[
VP_{iso}(443K) = 10^{3.93679 - \left(\frac{1257.84}{443 - 52.415}\right)} = 5.205 \text{ bar}
\]

(https://webbook.nist.gov/cgi/cbook.cgi?ID=C108883)

\[
VP_{tot}(443K) = 10^{4.54436 - \left(\frac{1738.123}{443 + 0.394}\right)} = 4.22 \text{ bar}
\]

\[
W_{ti} = \frac{\varphi_i \times \rho_i}{\sum_{i=1}^{n} \varphi_i \times \rho_i}
\]

\[
W_{tiso} = \frac{0.65 \times 0.692}{(0.65 \times 0.692) + (0.35 \times 0.8669)} = 0.596
\]

\[
W_{ttot} = 1 - W_{tiso} = 0.404
\]

\[
PM \ Index = \sum_{i=1}^{n} \left[ \frac{DBE_i + 1}{VP_i(443K)} \right] W_{ti}
\]

\[
PM \ Index = \frac{5}{4.22} (0.404) + \frac{1}{5.205} (0.596) = 0.592
\]
A5 PN Index Sample Calculations

Sample calculation for I65T35 blend:

\[
PN\ \text{Index} = \sum_{i=1}^{n} \left( \frac{DBE_i + 1}{DVPE} \right) V_i \times 100\ kPa
\]

DVPE is treated as RVP in PN index calculations. The PN index differs from the PM index in that it does not treat the blend as an ideal mixture. Activity coefficients derived from UNIFAC group contribution method are used.

\[
RVP_{I65T35} = \gamma_{iso} x_{iso} RVP_{iso} + \gamma_{tol} x_{tol} RVP_{tot}
\]

The activity coefficients can be calculated from identifying subgroups and referring them to the relevant published lists of interaction parameters or using an online UNIFAC calculator like the AIOMFAC Model (http://www.aiomfac.caltech.edu/model.html) which was used for this work.

Inputting 311 K as the temperature in the model (temperature for Reid Vapour Pressure), results in activity coefficients of

\[
\gamma_{iso} = 1.0596, \ \gamma_{tol} = 1.3709
\]

Looked up from NIST or other sources,

\[
RVP_{iso} = 12.82\ kPa, \ RVP_{tot} = 7.58\ kPa
\]

\[
x_{tol} = \frac{\varphi_{tot} \rho_{tot} \rho_{tol} M(\text{toluene})}{\varphi_{tot} \rho_{tot} \rho_{tol} M(\text{toluene}) + \varphi_{iso} \rho_{iso} \rho_{iso\text{octane}} M(\text{iso\text{octane}})} = 0.46 \ (\text{refer to Appendix A3})
\]

\[
x_{iso} = 1 - x_{tot} = 0.54
\]

\[
RVP_{I65T35} = 1.0596(0.54)(12.82) + 1.3709(0.46)(7.58) = 12.1\ kPa
\]

From Appendix A4, \(DBE + 1_{iso\text{octane}} = 1, DBE + 1_{toluene} = 5\)

\[
PN\ \text{Index} = \left[ \frac{1}{12.1} \times 0.65 + \frac{5}{12.1} \times 0.35 \right] = 19.8
\]
A6 Emissions Bench Corrections

The O$_2$ concentration measured by the emissions bench needs to be corrected. CAI, the bench manufacturer, provides a correction procedure with factors based on the gases present [XX].

\[
\bar{x}^*_{O_2} = \bar{x}^*_{O_2} \left( -\frac{0.29}{100 \times \bar{x}^*_{CO_2}} - \frac{0.07}{100 \times \bar{x}^*_{CO}} + \frac{43}{100 \times \bar{x}^*_{NO_x}} \right)
\]

where:

\(\bar{x}^*_{O_2}\) - corrected dry O$_2$ mole fraction

\(\bar{x}^*_{O_2}\) - dry O$_2$ mole fraction from the emissions bench

\(\bar{x}^*_{CO_2}\) – dry CO$_2$ mole fraction from the emissions bench

\(\bar{x}^*_{NO_x}\) - dry NO$_x$ mole fraction (must be calculated)

\[
\bar{x}^*_{NO_x} = \frac{\bar{x}_{NO_x}}{1 - \bar{x}_{H_2O}}
\]

where:

\(\bar{x}_{NO_x}\) - wet NO$_x$ mole fraction from the emissions bench

\(\bar{x}_{H_2O}\) – water mole fraction (must be calculated)

Formula from Heywood [6],

\[
\bar{x}_{H_2O} = \frac{m}{2n} \left[ \frac{\bar{x}^*_{CO_2} + \bar{x}^*_{CO}}{1 + \frac{\bar{x}^*_{CO}}{K\bar{x}^*_{CO_2}} + (\frac{m}{2n})(\bar{x}^*_{CO} + \bar{x}^*_{CO_2})} \right]
\]

where:

m & n – carbon and hydrogen atoms in the fuel, C$_n$H$_m$

K – empirical constant assumed to be 3.8 from Heywood [6]
A7 Dilution Ratio Calculations

Dilution Ratio is defined as \( \frac{\dot{m}_{\text{exhaust diluted}}}{\dot{m}_{\text{exhaust raw}}} \)

The dilution ratio is calculated through application of conservation of mass:

\[
\dot{m}_{\text{exhaust diluted}} = \dot{m}_{\text{exhaust raw}} + \dot{m}_{\text{dilution air}}
\]

Recalling that we are using the mini CO\(_2\) monitor, we can also apply conservation of species to the CO\(_2\):

\[
\dot{m}_{\text{CO2 exhaust diluted}} = \dot{m}_{\text{exhaust diluted}} \times x_{\text{CO2 exhaust diluted}}
\]

\[
\dot{m}_{\text{CO2 exhaust raw}} = \dot{m}_{\text{exhaust raw}} \times x_{\text{CO2 exhaust raw}}
\]

\[
\dot{m}_{\text{CO2 dilution air}} = \dot{m}_{\text{dilution air}} \times x_{\text{CO2 dilution air}}
\]

Sub in conservation of mass equation so we can collect terms,

\[
\dot{m}_{\text{exhaust diluted}} \times x_{\text{CO2 exhaust diluted}}
\]

\[
= \dot{m}_{\text{exhaust raw}} \times x_{\text{CO2 exhaust raw}} + \dot{m}_{\text{dilution air}} \times x_{\text{CO2 dilution air}}
\]

Collect like terms,

\[
\dot{m}_{\text{exhaust diluted}} \times x_{\text{CO2 exhaust diluted}}
\]

\[
= \dot{m}_{\text{exhaust raw}} \times (x_{\text{CO2 exhaust raw}} - x_{\text{CO2 dilution air}}) + \dot{m}_{\text{exhaust diluted}}
\]

\[
\times x_{\text{CO2 dilution air}}
\]
Divide by $m_{\text{exhaust \; diluted}}$:

$$x_{\text{CO}_2\text{exhaust \; diluted}} = \frac{m_{\text{exhaust \; raw}}}{m_{\text{exhaust \; diluted}}} \times (x_{\text{CO}_2\text{exhaust \; raw}} - x_{\text{CO}_2\text{dilution \; air}}) + x_{\text{CO}_2\text{dilution \; air}}$$

Rearrange for dilution ratio

$$\text{Dilution ratio} = \frac{m_{\text{exhaust \; diluted}}}{m_{\text{exhaust \; raw}}} = \frac{x_{\text{CO}_2\text{exhaust \; raw}} - x_{\text{CO}_2\text{dilution \; air}}}{x_{\text{CO}_2\text{exhaust \; diluted}} - x_{\text{CO}_2\text{dilution \; air}}}$$
Appendix B Supplemental Data and Graphs

B1 Additional Extended Length Tests Data

**Figure B.1** 2-Minute average particle size distribution of extended PCV enabled test measured at 100-minute increments.

**Figure B.2** 2-Minute average particle size distribution of extended PCV disabled test measured at 100-minute increments.
Figure B.3 Extended GC/MS EEPS PN (gas2) vs. Particle Mass. Mass error bars represent acceptable mass variation measuring the same sample on the lab scale. Particle error bars represent standard deviation.
Figure B.4 PCV diverted extended test fuel normalized total particle number and short term fuel trim with time.

Figure B.5 PCV enabled extended test fuel normalized total particle number and short term fuel trim with time.

Figure B.6 GC/MS gasoline extended test fuel normalized total particle number and short term fuel trim with time.
B2 Additional Surrogate Gasoline Development Tests Data

Figure B.7 Cold-start 7-parts particle size profile.

Figure B.8 Cold-start 7-parts particle size profile.
Appendix C Publications

