Assessing the Effects of Ethanol Addition on Particulate Matter Emissions in GDI Engines

by

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ABSTRACT

Previous research on the effects of ethanol addition on particulate matter (PM) emissions in GDI engines show diverse results. In this thesis, an overview on three major aspects, PM formation, effects of engine operating conditions, and ethanol effects, unveils the large number of factors that can simultaneously affect PM emissions from gasoline-ethanol blends in GDI engines, partially explaining the reasons for the diverse results from previous research. A further experimental work was conducted to assess three potential ethanol effects, displacement effect, evaporative cooling effect, and oxygen content effect. The displacement effect is based on PM Index (PMI) in the literature. Ethanol has very low PMI and thus very low propensity to form PM. Therefore, the addition of ethanol replaces the high-PMI components in the gasoline, lowering PM emissions. Although the PMI value incorporates species reactivity and volatility, it does not take latent heat of vaporization (HOV) into account. The high HOV of ethanol suppresses the fuel evaporation and potentially causes more liquid fuel films, which serve as sources for PM emissions. This evaporative cooling effect was assessed along with the oxygen content effect, a widely used effect in the literature to explain why ethanol lowers PM emissions. Through the method of control variables, the displacement effect and oxygen content effect were separated out and could be assessed individually. The existence of the displacement effect was confirmed. It was also found that the oxygen content effect was negligible, while the evaporative cooling effect changed PN emission significantly. The extent of the evaporative cooling effect depended on operating conditions, such as fuel injection timing, engine coolant temperature, and load.

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Chapter 1: INTRODUCTION

Direct injection spark ignition (DISI) engines are gaining popularity these years. DI can enable higher volumetric efficiency and raise knock limit because there is no fuel vapor to displace the air in the intake manifold and fuel vaporization lowers the charge temperature [1,2]. Combining with turbochargers, direct injection engines can achieve much higher fuel economy than conventional port fuel injection (PFI) engines [3]. Despite these benefits, DI engines have shown to have higher particulate matter (PM) emission than PFI engines [4]. In a PFI engine, burned gas flows back into the intake manifold through valve overlap. This backflow blows fuel droplets onto hot intake manifold surfaces which assist fuel evaporation [5]. The hot flow itself also helps fuel evaporation and mixing of air and fuel [6]. Unlike PFI engines, DI engines lack time for fuel evaporation, often resulting in liquid fuel on combustion chamber surfaces and inhomogeneous air-fuel mixture [4]. These two undesirable characteristics lead to high PM emissions [7-11].

Regulations have been imposed on PM emissions from spark ignition (SI) engines. Specifically, Euro VI imposed a limit of $6 \times 10^{11}$ particles/km on solid particle number to be achieved by 2014 [12,13]. California Air Resources Board (CARB) LEV III and Tier dictated a PM mass limit of 3 mg/mile by 2017 [7]. The LEV III also proposed an optional limit of $1.9 \times 10^{12}$ particles/km on particle number by 2017 [14] and a limit of 1 mg/mile on PM mass by 2025 [7,15]. These regulations have been a strong driving for global automotive industries to lower PM emissions from DISI engines.

Ethanol is gaining momentum as an alternative fuel in SI engines. Unlike fossil fuels, ethanol can be produced from renewable agricultural feedstock [16]. The 2007 Energy Independence and
Security Act thus dictated the use of ethanol from 9 billion gallons per annum to 31 billion gallons per annum by 2022 [1]. In addition, ethanol can be used as a knock suppressor in SI engines because it has high octane number [4]. The high heat of vaporization (HOV) of ethanol lowers the charge temperature and increases the volumetric efficiency in DI engines [10]. Moreover, ethanol has shown to have more complete combustion and lower hazardous gas emissions [16,17].

The emergence of both trends makes the effects of ethanol addition (in gasoline) on PM emissions in DI engines an interesting research area. Previous research on this topic showed mixed results. Catapano et al. found that accumulation mode particulate number (PN) decreased linearly with the percentage of ethanol added because ethanol is an oxygenated fuel which reduces soot tendency of the blend [10]. Dimou et al. stated that PN was significantly reduced as ethanol was added, but the reduction was not sensitive to the percentage of ethanol added [18]. Chen et al. mentioned a factor of 25-65 reduction in PN and a factor of 2-10 reduction in particulate mass (PMM, to distinguish from PM) with the addition of E10 [19]. However, they also noted that the high heat of vaporization of ethanol might cause inhomogeneous mixture and led to more PM emissions [19]. Storey et al. concluded that ethanol did not strongly affect PN concentrations during cold start, but E10 and E20 reduced PN concentrations during hot start [20]. Karavalakis et al. found that ethanol reduced PN and ascribed this reduction to the oxygen in ethanol [7]. Ojapah et al. observed that PN decreased while particulate matter mass (PMM) increased with ethanol content [21]. As summarized here, the previous results are diverse. Many results even contradict each other.

An important contribution to relating fuel composition to PM emissions is the PM Index (PMI) proposed by Honda. PMI indexes different fuels according to their potentials to form PM emissions
[22]. The higher the PMI of a fuel is, the more PM emissions are likely formed. Ethanol has extremely low PMI (much lower than typical gasoline PMI), so the addition of ethanol to gasoline should reduce PM emissions. However, PMI does not take HOV into account. Ethanol has very high HOV, which impedes fuel evaporation and increases PM emissions [19]. These two contradicting effects, PMI and HOV, are of interest in this research. Engine experiment work was conducted to study these two effects in detail.

Overall, this thesis is an effort to unveil the reasons for the diverse results from previous research and study ethanol effects on PM through experimental work. The thesis firstly reviews PM formations in DI engines, engine hardware and operating condition effects on PM emissions, and potential ethanol effects on PM emissions. The review not only shows the large number of factors that can affect PM emissions but also serves as a background to support how the experiment was designed. After the review, the thesis explains the experiment methodology and presents the results of the experiment.
Chapter 2: PM FORMATION IN DI ENGINES

In order to illustrate how PM is formed, the following topics are reviewed in this section: introduction to PM, PM formation process and chemistry mechanisms, nucleation versus accumulation mode, particulate mass (PMM) versus particulate number (PN), and PM formation in DI engines.

2.1 INTRODUCTION TO PM

PM is known to be the solid materials in the exhaust gas that can be collected on a filter. Such substances include solid-phase particles, volatile organic particles, and ash from lubricate oil and materials from wear [23]. The solid phase particles majorly consist of aggregates of spherical carbon particles, also known as soot [24], with low volatility hydrocarbons (HCs) condensed and absorbed onto these solids [25]. The organic fraction (extractable by the use of a solvent) in PM mainly consists of polycyclic aromatic compounds which originate from partially oxidized fuel and lubricant [26].

2.2 PM FORMATION PROCESS AND CHEMISTRY

There were many attempts to model the formation of PM. Most empirical models only include two processes, soot formation and oxidation, which are both modeled as Arrhenius processes [27]. More sophisticated models include inception, condensation, surface growth and oxidization, and coagulation [27,28]. Maricq established four stages, soot inception, surface growth and agglomeration, oxidization, and soot release [29]. All of these models share many similarities. Among them, a comprehensive one is presented in [30], where five steps are identified. These are
formation of aromatics, growth of aromatics, nucleation, surface reactions, and particle coagulation.

Formation of aromatics: Formation and growth of aromatics in general is highly dependent on Hydrogen-abstraction-carbon-addition or Hydrogen-abstraction-acetylene-addition (HACA) process. This process involves two major steps, abstracting a hydrogen atom from an HC molecule by a gaseous hydrogen atom and adding a gaseous acetylene to the HC radical site [30]. HACA is the key to forming polycyclic aromatic hydrocarbons (PAH), which is generally regarded as soot precursor species [27,31,32]. Aromatics are also oxidized while they are formed. The main oxidizer is O₂, while OH only has a minor oxidation effect [30]. In short, the increase of gaseous hydrogen atoms results in more aromatics production and the increase of O₂ and OH results in more aromatics oxidization [33].

Growth of aromatics and particle nucleation: Particle nucleation is a result of both chemical growth, where PAH species gain more mass, and physical growth, where PAH molecules and clusters collide with each other, forming larger clusters [30]. Nucleation of gaseous PAH species (soot precursors) is an Arrhenius process, whose rate is proportionally scaled with the amount of PAH species and is exponentially dependent on temperature [34].

In a burner experiment done by Maricq, the nucleation of incipient particles was found over a range of height in the flame [29]. The incipient particles formed lower in the flame underwent agglomerations later on, while incipient particles formed later did not have time to agglomerate and were released directly. This explains the bimodal size distribution of soot emissions [29].
Surface growth and oxidation: The particle nuclei undergo surface growth and oxidation. Acetylene is the surface growth precursor [27,30]. Aromatics are also the surface growth species. Hypothesis of chemical similarity assumes that surface reactions on soot particles are similar to the surface reactions on PAHs as discussed in “formation of aromatics”. According to this hypothesis, HACA mechanism also drives the surface growth of incipient particles [30]. As particles grow, the decrease in both hydrogen atoms and number of reaction sites on soot particles leads to a decrease in growth rate and eventually leads to an equilibrium [30]. In other words, the abundance of HCs and the amount of particle surface area strongly relate to the amount of mass acquired [34].

Offsetting the effects of surface growth, surface oxidization by O₂ and OH radicals reduces particle size and mass [30]. Surface oxidization is of Arrhenius type [34]. High exhaust gas temperature and excessive oxygen enhances oxidization [31].

Particle coagulation: Collisions between particles produce larger particles. Initially, surface growth rate is large enough to merge two collided particles and coalesce them into a spherical particle. This regime is called coalescent growth, whose rate is a function of pressure (or the ratio of the mean free path to the particle diameter). [30] Agglomeration regime happens next. During agglomeration, surface growth rate is not fast enough to merge the two particles, so particles collide to form a chain-like fractal shape [30]. In the particle coagulation stage, growth is quadratically dependent on the number of incipient particles nucleated [34].
The formation mechanisms of PM are easily confused with the formation mechanisms of HCs. Some sources of HCs, such as incomplete combustion, liquid fuel, and incomplete oxidization, are also the sources of PM. Therefore, to some extent, the increase in HCs predicts an increase in PM. However, the correlation between HCs and PM is weak [34]. A major mechanism of HCs is the unburned fuel-air mixture in crevice volume. This mechanism only provides HCs to be absorbed onto existing PM particles, but does not enhance PM nucleation. In general, PM has to be produced in some chemical reactions such as gas-phase nucleation, but HCs can be produced simply because fuel-air mixture bypasses chemical reactions [34,35].

2.3 PARTICULATE MASS (PMM) AND PARTICULATE NUMBER (PN)

PMM and PN were found to be highly correlated. An increase in PN often implied an increase in PMM and vice versa [4,7]. However, as discussed in section 2.2, PN is largely controlled by particle nucleation and coagulation. Surface growth and oxidization, which have minor effects on PN, instead strongly affect PMM [30].

Kittelson mentioned two subtle mechanisms that can cause discrepancy between PMM and PN [36]. First, a decrease in PMM comes with a decrease in surface area available to absorb soluble organic fraction (SOF). The excessive SOF species that are not absorbed will raise PN. Second, intensive carbon oxidation, which reduces PMM, can also fragment coagulated particles, increasing PN.
2.4 NUCLEATION MODE VERSUS ACCUMULATION MODE

PM is commonly observed in two modes, nucleation mode and accumulation mode. Nucleation mode represents small particles that have sizes typically less than 30 nm in diameter [14,37]. The mean particle diameters were observed to be 5 – 10 nm [14,38]. This mode includes condensed volatile substances, such as HCs and sulfate, and solid particles which are hypothesized to be mainly metallic ash from lubricant [14,29,37]. For the condensed volatile substances in the nucleation mode, high volatility substances largely come from unburned fuel, and low volatility substances are hypothesized to come from lubricant [38].

Accumulation mode represents particles that have sizes above 30 nm in diameter [14,37]. The mean diameters were observed to be 30 – 80 nm [14,38]. The great majority of the particles in the accumulation mode is soot (aka. carbon black particle mass or carbonaceous agglomerates) [14,21]. When PM is measured from exhaust, it has a clear bimodal size distribution due to the presence of the two modes [36].

Some researchers used organic carbon (OC) and elemental carbon (EC) to describe PM [6,31]. In general, EC is a measure of soot, roughly corresponding to the accumulation mode, and OC is a measure of semi-volatile organics, roughly corresponding to the nucleation mode. [20].

Temperature only has minor effects on the accumulation mode particles, because accumulation mode does not contain a significant portion of volatile materials [29]. Condensates of volatile species in the gaps of the fractal-shape particles in the accumulation mode are affected by temperature [29]. However, the absence of these volatile materials in the gaps does not change the
mobility diameters of the particles, which modern instrument usually measures. On the other hand, temperature has significant influence on nucleation mode particles because they are majorly volatile materials [29].

The Euro VI regulation (limiting PN emissions to $6 \times 10^{11}$ particles/km) measures solid particles within diameters of 23 – 2500 nm using the particle measurement protocol (PMP) [39]. The particles are thus mostly in the accumulation mode [36]. The experiment part of this thesis will thus emphasize the accumulation mode particles.

2.5 PM GENERATION IN DI ENGINES

Many researchers concluded two major mechanisms of PM generation in DI engines, combustion of inhomogeneous mixture in the combustion phase and pool fires originated from liquid fuel films on a piston head in the post-combustion stage [7-11]. The two mechanisms were found in both spray-guided DI engines [9] and wall-guided DI engines [8,11].

Unlike PFI engines, where backflow from cylinders helps fuel vaporization in the intake, DI engines have shorter time for fuel evaporation and fuel-air mixing, which leads to mixture inhomogeneity [5,31]. The mixture inhomogeneity creates locally fuel rich regions, burning of which generates soot [7,8]. Optical research found soot radiation early in the combustion process (around 10˚ CA BTDC) [8,10]. This part of soot generation was attributed exactly to the combustion of the locally rich regions [9,10]. However, soot formed in this stage is easily oxidized by the oxygen in the neighboring lean regions in the hot early-combustion environment. This part of soot thus does not contribute significantly to engine-out PM emissions [8,28].
In addition to mixture inhomogeneity, liquid fuel films are easily formed on a piston head and cylinder liner due to impingement of fuel spray onto these areas in DI engines [31,40]. Experiments on optical engines confirmed the existence of liquid fuel on a piston head [41,42]. Pool fires created by these liquid fuel films were optically observed in the late expansion stroke (post-combustion, around 35° CA ATDC) [1,9,41]. The yellow luminosity of the pool fires was considered to be soot radiation, and thus demonstrated the soot formation mechanism due to liquid fuel films and pool fires. [8,41]. The soot generated by pool fires is rarely oxidized because of low temperature and low level of oxidizers in the post-combustion environment, being the major engine-out PM emission source [28].

A subtlety here is the liquid fuel on intake and exhaust valves [11,41]. In PFI engines, such liquid fuel is caused by injection during valve opening [41]. In wall-guided DI engines, early fuel injection in the intake stroke when the piston is high causes fuel spray to be reflected from the piston head onto the valve areas [11]. The liquid fuel on the valve areas may also form soot.

There are two schools of thoughts regarding how liquid fuel is transformed into soot (or how pool fires are produced). One party deemed that diffusion burning generated soot from liquid fuel [8,10,29,41]. However, Ketterer et al. pointed out that diffusion burning is unlikely to happen in the post-flame environment where pool fires were observed because of the lack of oxygen [11]. They attributed soot generation to the pyrolysis of vapor flume evaporated from the liquid fuel [11]. Dimou et al. shared the same thought with Ketterer et al. [18].
The chemistry of soot generated by diffusion flames has been well studied in diesel engines. On the other hand, the chemistry of the pyrolysis hypothesis is that HCs are first decomposed into smaller structures and radicals in a relatively hot environment without oxygen [21,31]. One of the key products of the decomposition is acetylene, an important soot precursor as discussed in section 2.2 [21,31]. The soot formation mechanisms are then initiated by the acetylene and follow the steps as described in section 2.2.
Chapter 3: EFFECTS OF ENGINE HARDWARE AND OPERATING CONDITIONS ON PM EMISSIONS

This chapter discusses the effects of engine hardware and engine operating conditions on PM emissions. Factors of engine hardware include spray-guided versus wall-guided DI, injectors, and catalyst converters. Operating conditions include speeds and loads, equivalence ratios, residuals (or valve timings), engine coolant temperature (ECT), spark timings, start of injection timings (SOI), multiple injections, and fuel pressure.

3.1 SPEEDS AND LOADS

Engine speeds mostly affect the mixing of air and fuel. Higher speeds increase turbulence, and thus reduce wall wetting, better preparing the mixture [5]. Therefore, an increase in speed reduces PM emissions [1]. However, not many researchers mentioned that time for mixture preparation is reduced as speed increases, which harms mixture preparation. High turbulence causes higher heat transfer loss which may also take away the heat for in-flight fuel evaporation.

Increasing loads increases in-cylinder temperature. High temperature results in high PM nucleation rate, because PM nucleation is Arrhenius type [43]. At high loads, more fuel is injected, so there is more liquid fuel in the cylinder, leading to high PM emissions [5,35]. Counterbalancing the tendency of increasing PM, high temperature also facilitates oxidation of PM [35]. However, PM was observed to generally increase with an increase in load [4]. In terms of vehicle tests, a widely accepted perspective is that acceleration events and cold start phase produce most of the PM [4,14,31].
In He et al.’s experiment, nucleation mode dominated PM emissions at idling, whereas accumulation mode dominated at high engine load above 6 bar NIMEP [44]. This observation might be explained by the pressure dependence of particle coalescence discussed in section 2.2, because in-cylinder pressure is higher at high load.

3.2 EQUIVALENCE RATIOS

PM emissions increase sharply as the fuel-air equivalence ratio (φ) increases [2010-2117]. An experiment conducted on a DI engine which nevertheless ran premixed charge showed that air-fuel equivalence ratio (λ) of 0.8 was a threshold, below which PM emissions increased almost exponentially [5]. Another experiment on a PFI engine showed that PM increased in both directions as equivalence ratio increased and decreased [35]. For rich air-fuel mixture, PM increased due to the excessive HCs and the fact that in-cylinder temperature peaked at a slightly rich condition. High temperature assisted in PM nucleation. For lean mixture, PM was formed mostly by the diffusion burning of liquid fuel, which is so called pool fires as discussed in section 2.5. The excessive oxygen in the lean mixture enabled diffusion burning [35].

3.3 RESIDUALS

The use of early EVC to trap residuals and late EVC to recuperate exhaust both reduced PN [31]. As concluded by Kayes et al. [35], This observation was the result of conflicting effects. Internal EGR has higher temperature than fresh charge, helping fuel evaporation and reducing liquid fuel. Less liquid fuel causes less particle nucleation and smaller nuclei sizes. On the other hand, more EGR aggravates partial burning and reduces post-flame temperature because the residual gas acts as a thermal sink. The consequences are increased amount of HCs due to partial burning and lower
post-flame temperature, and thus less post-flame oxidation due to lower temperature. Less oxidation was shown to be a minor effect since PM was observed to generally reduce with more EGR. However, the large amount of HCs encourages particle growth. The net effect of less liquid fuel and more HCs was that particles in nucleation mode became even smaller but particles in accumulation mode became even larger [35].

3.4 ENGINE COOLANT TEMPERATURE

Many research results have indicated that engine coolant temperature has nontrivial influence on PM emissions. In general, PN decreases exponentially with an increase in coolant temperature because fuel evaporation (vapor pressure) is exponentially related to temperature [18,38]. Test results showed that raising coolant temperature from 25 °C to 90 °C eliminated 90% of the PM [17]. In addition, vehicle tests also showed that cold start phase released the largest amount of PM [4,14,31].

The reason for reduced PM with temperature increase is that hot cylinder walls promote fuel vaporization and cause liquid fuel to better evaporate [11]. A test of liquid fuel evaporation on a hot plate showed that liquid fuel film reduced by a factor of 15 as plate temperature increased from 120 °C to 160 °C [42]. The engine coolant effect is more pronounced when direct injection happens early in the intake stroke when the piston is high, because the fuel spray is reflected by the piston onto the valves and cylinder head, whose temperature is close to the coolant temperature [11].
3.5 SPARK TIMING

Advancing the spark timing results in higher peak cylinder temperature, less time for fuel evaporation and mixing, and lower exhaust temperature. Higher peak temperature increases both PM nucleation and oxidation, which are Arrhenius processes [35]. Impeded fuel vaporization and mixing cause liquid fuel and mixture inhomogeneity [35]. The lower exhaust temperature reduces post-flame oxidation of PM and HCs, exaggerating PM growth and accumulation [35]. The net result of advancing spark timing was found to be PM reduction [35] and PM increase [19]. The conflicting results were due to the contradicting effects of spark advancement as mentioned above. Retarded spark timing improves post-flame oxidation of PM, and thus reduces PM [19]. Post-flame oxidation is more important than the other factors because the main source of PM, pool fires, happens late in the expansion stroke.

3.6 START OF INJECTION

Start of injection (SOI) is one of the most important factors that affect PM emissions. Early SOI in the intake stroke is associated with high PM emissions. Specifically, injection earlier than 60° CA aTDC creates high PM emissions [1]. At early SOI, fuel spray impinges on the piston and gets reflected onto cylinder head and valves. Liquid fuel is thus accumulated on these areas, which subsequently forms PM [11,18,44]. Fuel spray was found to be visually longer and slimmer at a cylinder pressure of 12 bar than how it looked at 16 bar. From this observation, it is imaginable that fuel penetration could substantially increase in the intake stroke when pressure is low [9]. This aggravates piston impingement, which causes liquid fuel at early SOI.
SOI at around mid-intake stroke causes a trough in PM emissions [42]. Piston instantaneous speed is the highest around mid-stroke. The induced charge motion thus contains high kinetic energy and creates highly-mixed air-fuel mixture. The high turbulence simultaneously increases heat transfer rate and thus helps fuel evaporation [11,35]. Relatively long time before sparking also permits more complete fuel evaporation. The piston is away from the injector at mid-intake stroke, so less fuel impingement on the piston occurs [11]. All these factors lead to a low PM level. This low PM level sustains until around mid-compression stroke when the piston becomes close to the injector again. After mid-compression, PM rises sharply due to liquid fuel on the piston crown because of the lack of time for mixing [11,18].

An interesting point is that retarding SOI to avoid piston wetting may intensify liner wetting, which also causes PM emissions. The reason is that, with a retarded SOI timing, fuel is injected when tumble, which deflects fuel spray away from the liner, has decayed [1].

In terms of fuel sensitivity to SOI, Tanaka et al. found that fuel with high aromatics and low volatility is more sensitive to SOI [42]. Fatouraie et al. observed that ethanol gasoline blends are more sensitive to SOI than gasoline alone [17].

3.7 MULTIPLE INJECTIONS

Multiple injections are a strategy to stabilize the combustion at cold start when the spark is retarded to raise exhaust temperature for the catalytic converter light-off [11,31]. The first injection creates a globally lean mixture and the second injection creates a locally rich mixture around the park plug for flame initiation [11,31]. Multiple injections split one injection so that fuel penetration length
for each injection is shorter. Shorter spray reduces piston wetting, valve wetting and liner wetting, which reduces PM [45]. However, because the second injection is late in the compression stroke, it still creates liquid fuel on piston top due to lack of time for mixing [11]. Therefore, multiple injections tend to increase PM emissions compared to a single injection (at a reasonable SOI) [45]. PM is increased as the second injection is retarded [11].

3.8 FUEL PRESSURE

Better fuel atomization can be achieved by higher injection pressure. Better atomization improves mixture homogeneity and combustion completeness, which reduces PM [31,45] This reduction was reported to be mostly in the nucleation mode [31]. However, higher fuel pressure can increase fuel spray penetration and adversely make more wetting area and more PM [1]. In practice, fuel pressure can be optimized with SOI to achieve better PM emissions [1].

3.9 INJECTORS

Injector deposits are a dominating factor that increases PM. Injector deposits can deviate fuel spray from its original direction [6], and accumulate liquid fuel at nearby areas [45,46]. Through a comparison test with a clean injector, an injector with deposits was found to greatly increase PM emissions. The intensity of diffusion-like flame near a coked injector (an injector with deposits) was also found to correlate with PM emissions [45]. Ethanol-gasoline blends were found to reduce injector deposits [47].

Another aspect of injector is the opening and closing events. Opening and closing events of a multi-hole injector were associated with larger fuel droplets, which caused locally rich mixture
and high PM emissions [31,45]. This phenomenon was especially significant for short injection pulse width [31]. Outwardly open injectors greatly reduced fuel droplet sizes [31].

3.10 SPRAY-GUIDED VERSUS WALL-GUIDED INJECTIONS

In a spray-guided design, the injector is located near the center of the cylinder head close to the spark plug. Correct air-fuel ratio is achieved because of the closeness between the injector and the spark plug. In a wall-guided design, the injector is mounted on the side of the cylinder head at an angle pointing downward. Correct air-fuel ratio is achieved by using a bowl-shape feature on the piton top to reflect fuel spray towards the spark plug [7]. Although tumble flow during intake stroke can effectively deviate the fuel spray away from the liner to reduce liner wetting in a wall-guided design [19], the use of piston head to reflect fuel spray greatly increases piston wetting [7,31], which is the major source of pool fires mentioned in section 2.2. Therefore, wall-guided injections tend to generate more PM than spray-guided injections [7]. However, spray-guided injection was reported to generate high PN in the nucleation mode [19].

3.11 CATALYTIC CONVERTERS

Catalytic converters reduce volatile particles (i.e. nucleation mode PM as discussed in section 2.4), while accumulation mode PM does not change significantly with the addition of a catalytic converter [19,44]. The main reason is that condensed volatile materials in the nucleation mode could vaporize in a catalytic converter. The vaporized substances are subsequently oxidized [44]. Oxidation of HCs in a catalytic converter does not have a significant effect on PM sizes, because the reduction in particle growth due to less HCs is confronted by more particle accumulation due to the residence time in the converter [34]. In addition, the effect of a catalytic converter to reduce
nucleation mode is more prominent at idling when particles stay for a longer time in the converter [44].
Chapter 4: ETHANOL EFFECTS

Ethanol has both positive and negative effects on PM emissions. The oxygen content of ethanol is widely mentioned as a reason for ethanol-gasoline blends to reduce PM [4,10,40]. The replacement of high-soot-tendency unsaturated HCs originally in gasoline by ethanol is another widely used reason [6,33]. Ethanol can also reduce the boiling temperature of ethanol-gasoline blends so that the blends are better vaporized and less prone to form soot [4,6]. Some adverse effects include high heat of vaporization (HOV) which impedes fuel evaporation and a low heating value which increases the volume of fuel injected at a given load [19]. Some other minor effects include the reduction of injector deposits [6], and the elimination of carbon from soot reactions by forming carbon monoxide [33].

Some researchers observed that ethanol greatly changed PM in a particular mode, either accumulation mode [10], or nucleation mode [48]. In addition, researchers found ethanol effects to be strongly dependent on start of injection (SOI) timings [10,42]. They thought that this was due to the conflicting effects of high HOV and oxygen content [10]. It was mentioned that ethanol could increase harmful unregulated formaldehyde and acetaldehyde [49], though they are not relevant to PM formation.

This chapter discusses each major effect of ethanol separately. The effects being discussed are replacement effect, distillation characteristics, oxygen content, heating value, and heat of vaporization.
4.1 DISPLACEMENT EFFECT: PM INDEX

Numerous research results indicate that aromatics content is highly correlated with PN [4,18,7,19,42]. In addition to aromatics content, low-volatility components are another key factor responsible for PN emissions [4,42], because low volatility leads to more liquid fuel. It is the small amount of low-volatility aromatics in gasoline that produces most of the PM emissions [4]. Addition of ethanol displaces these heavy components so that PM is reduced.

Honda invented PM Index (PMI) to capture the above observations regarding aromatics content and volatility [22]. The equations to calculate PMI are shown below.

\[
P_{MI_i} = \frac{DBE_i + 1}{V.P_i (kPa @ 443K)} \quad \text{Eq. 4.1}
\]

\[
DBE_i = (2\#C_i + 2 - \#H_i)/2 \quad \text{Eq. 4.2}
\]

\[
P_{MI_{fuel}} = \sum_i P_{MI_i} \times (wt\%)_i \quad \text{Eq. 4.3}
\]

Equation 4.1 is used to calculate the PMI of each component in the fuel. In the numerator, double bond equivalent (DBE) roughly represents aromatics content. From its formula, Equation 4.2, it can be seen that DBE essentially gives a sense of what type of bonds (single bonds, double bonds, triple bonds, and etc.) there are in a HC molecule. For paraffins, which only have single bonds, DBE is zero. For mono-olefins, which only have one double bonds, DBE is one. For benzene, which has a benzene ring, DBE is four. Aromatics thus have high DBE values. The addition of
one in the numerator in Equation 4.1 is to allow PM formation from paraffins [22]. No physical and chemical theories directly explain relation between DBE and PM, so it is an empirical term [46]. It is noted that DBE does not contain information of chemical structures, such as straight or branched chains, or oxygen content [46].

In the denominator of Equation (1), vapor pressure represents volatility. The vapor pressure is taken at 443 K so that the calculated PMI has a good empirical correlation with actual PM emission results from experiments [22]. In the paper, Honda also provides a correlation between normal boiling pressure and vapor pressure at 443 K for most fuel substances [22].

The total PMI of a fuel is a simple mass-weighted sum of the PMI of each fuel component, as shown in Equation 4.3. Thus, PMI of a fuel does not contain any information about the cross-interactions of fuel components.

The relationship between the fuel PMI and PN emissions was originally obtained from tests on PFI cars, for which gasohol fuel was used in the test matrix [22]. It was verified on DI cars in subsequent research efforts [50]. PMI showed a linear relationship with PM emissions (both PMM and PN) with $R^2$ values to be generally above 0.95 [22]. The $R^2$ values were lower for DI cars [50].

PMI is dominated by the least volatile aromatics [46]. Barrientos et al. reported that volatile components of a U.S. certified gasoline only have 3% PMI contribution, while low-volatility aromatics contribute 94%. This matches the widely-accepted understanding that aromatics and low-volatility components are the key sources of PM emissions [46].
Ethanol has zero DBE and vapor pressure of 1573 kPa at 443 K, which essentially make its PMI negligible. The addition of ethanol simply displaces the components with high PMI in gasoline. This displacement effect (or dilution) of ethanol should lower PM emissions.

4.2 DISTILLATION CHARACTERISTICS

Alcohols enhance the evaporation of lighter components in gasoline at low temperature [4,10]. This means that the volatility of gasoline-alcohol blends is higher than the volatility of the individual alcohol or gasoline at low temperature [51]. This cross-interaction phenomenon is not included in PMI.

In the low temperature range, the gasohol evaporation is nearly at constant temperature; the behavior is similar to the evaporation of pure substances [52,53]. This phenomenon is described as near-azeotropic mixture of gasoline and alcohols [10,21].

Andersen et al. presented a report on gasohol distillation curves [54]. To illustrate, take Figure 2A in ref. [54] as an example. The initial boiling point of the ethanol-gasoline mixture is insensitive to ethanol content up to 85% [54]. However, the evaporation at mid-range volume fractions is enhanced even with small addition of ethanol. For example, gasoline evaporates about 25% at the ethanol normal boiling point, 78 °C, where the horizontal line is in Figure 2A [54]. Assume 100% of ethanol is evaporated at 78 °C. For E15, this means that 21% (25%×85%) gasoline and 15% ethanol which is in total 36% of the mixture should evaporate at 78 °C if there are no cross-interaction effects. However, the figure shows that about 50% of the mixture is evaporated, so the
mixture evaporation is actually enhanced. Another way to look at this is that the initial distillation curve of E15 is below the distillation curves of both ethanol and gasoline.

The mid-range part of the curves looks very flat, which demonstrates the aforementioned near-azeotropic mixture of gasoline and ethanol [54]. This part of the curves has important implications on engine cold start behaviors as the temperature is low [55]. Following the mid-range enhanced evaporation, a rapid increase of boiling temperature can be seen after 78 ºC. The rapid increase is due to the absence of ethanol, which is already evaporated [54].

The physics behind the azeotropic mixture is that the polar alcohol molecules due to hydrogen bonds interact with non-polar HCs [56]. Polarity and boiling point are related to aliphatic chain length [54]. As aliphatic chains in alcohols become longer, the boiling point increases and polarity decreases [54]. Methanol has the shortest chain length so it has the lowest boiling point (most volatile) and highest polarity [54].

Vapor pressure is another measure of volatility, treating the fuel as a whole. Accompanying Andersen et al.’s work on distillation curves, vapor pressure curves are reported in [56]. The general observation is that vapor pressure reaches a maximum at E10 (10% ethanol by volume) [6,21,57].

The effects of distillation characteristics of gasohol on PM will be discussed together with heat of vaporization in section 4.5.
4.3 OXYGEN CONTENT

The oxygen contained in alcohols helps oxidation of HCs and reduces soot precursors [21,58]. Besides oxygen content, the structure of an oxygenated fuel is also important for soot reduction. Alcohols have straight chains and oxygen atoms at the periphery of the structure. Therefore, its oxygen is easily accessible for soot precursor oxidation [46].

4.4 HEATING VALUE

Ethanol has a lower heating value than the heating value of gasoline. In order to keep the same engine load, more gasohol fuel has to be injected, so the injection duration is longer. Long injection duration can cause similar effects as a retarded SOI discussed in section 3.6. In general, it tends to cause more liquid fuel and mixture inhomogeneity that increase PM [4,6].

4.5 HEAT OF VAPORIZATION

Ethanol has a high heat of vaporization (HOV) value. For the same mass of fuel, HOV of ethanol differs from HOV of gasoline by a factor of 2.6, while the factor is 4.6 for the same mass of stoichiometric mixture [6,46]. As ethanol evaporates, it takes away a large amount of heat and lowers the temperature, so the high HOV impedes fuel evaporation and causes more PM emissions [19,59]. Some researchers observed a decrease in NOx emissions with addition of ethanol and attributed the reduction of NOx to high HOV of ethanol which reduced flame temperature [40,48]. Therefore, the high HOV of ethanol may even have influence on PM nucleation and oxidation during combustion, which are both Arrhenius processes (section 2.2).
The change of distillation characteristics (section 4.2) itself may not seem to increase PM, because it beneficially enhances fuel evaporation. However, when combining the distillation characteristics with high HOV, the net effect is adverse. As gasohol fuel evaporates, lighter components in gasoline and alcohol quickly evaporate at low temperature and take away a large amount of heat. The remaining heavy components are more difficult to evaporate given that the environment temperature has dropped due to the heat loss [40,46]. These heavy components form liquid fuel and are the main soot source [1] as discussed in sections 4.1 and 2.5.
Chapter 5: METHODOLOGY

In the previous chapters, effects of engine and operating conditions (Chapter 3), and ethanol effects (Chapter 4) on PM emissions have been discussed based on the mechanisms of PM formation (Chapter 2) and literature. Although the existence of so many factors that can simultaneously affect PM emissions partially explains why literature gives diverse results regarding ethanol effects on PM, there is a need to explore more deeply how the two main ethanol effects, the replacement effect and the evaporative cooling effect, affect PM emissions. This is the main topic of the subsequent experiment work reported in this thesis.

This chapter explains the experiment methodology, including experiment reasoning and design, experiment matrix, experiment conditions, apparatus, and experiment procedures.

5.1 EXPERIMENT RATIONALE AND DESIGN

The overall design of the experiment and reasons for the design choices are given in this section. The experiment was performed on a commercialized General Motors LTG direct injection engine (specifics will be given in section 5.4) to be representative of modern mass-production engine technology. Fleet testing was avoided because it is difficult to separate different effects in fleet testing. The gasohol fuels used contained 25% alcohols by volume. Below 25% it might be difficult to discern any effects from alcohols. The engine is designed for gasoline, so above 25% it might cause artifacts due to improper engine design to affect PM.
Among all the five ethanol effects, replacement effect, evaporative cooling effect, and oxygen content effect will be assessed through experiments, because these three effects are deemed as the dominating effects.

The effect of distillation characteristics alone is difficult to assess because in-cylinder temperature is hard to measure due to significant nonuniformity of temperature. As discussed in section 4.5, the net effect of evaporative cooling and distillation characteristics is that the heavier components in gasoline become even more difficult to evaporate. In addition, because the underlying physics of both the high HOV of alcohols and the near-azeotropic property of gasohol is related to hydrogen bonding, alcohols with higher HOV tend to enhance the evaporation of lighter components in gasoline more than alcohols with lower HOV do. For example, methanol has higher HOV than ethanol. M10 (10% methanol) has T40 (temperature where 40% mixture is evaporated) around 65 °C while E10 (10% ethanol) has T40 around 78 °C [54]. Both distillation curves of ethanol and methanol after these two temperatures rapidly approach the curve of gasoline, so there is not too much difference between the two curves after the 40% threshold [54]. Therefore, methanol aggravates the difficulty in evaporation of heavier components more than ethanol because of two concurrent properties, higher HOV and stronger enhancement of lighter component evaporation (These two properties cause a large amount of heat has been taken away before the heavier components start to evaporate). In conclusion, distillation characteristics are a minor effect. A single term, HOV, may be enough to represent the effects of both evaporative cooling and distillation characteristics because of the similarity of the underlying physics.
Another effect being neglected is the heating value effect (section 4.4). In our experiments, only 25% volume fraction of alcohols was added to gasoline. 25% is not large enough to make an overwhelming change in injection durations. In addition, from the calculation results and experiment practice in section 5.2, the actual changes in injection durations were small, especially in terms of crank angle (only around 2 °CA).

Now that the parameters subject to study have been determined, experiments can be designed by the method of control variables. The first step is to study oxygen effect. The control variables are PMI and HOV. The experiment should compare PN emissions from a gasohol fuel and gasoline which both have the same PMI and HOV. Figure 5.1 below shows how this is achieved.

![Figure 5.1. A diagram illustrating the experiment on oxygen content effect](image)

In Figure 5.1, at point 1, PN from gasoline is measured. 25% (by volume) Methyl Tertiary Butyl Ether (MTBE) is added to the baseline gasoline at point 2. PN from MTBE25 (25% MTBE + 75% gasoline) is measured. The HOV of MTBE is very close to that of gasoline as seen in Table 5.1. Therefore, there are PMI effect and oxygen effect at point 2. At point 3, 124-Trimethylbenzene
(124TB), which has a high PMI and a similar HOV (Table 5.1), is added to MTBE25 to bring the PMI back to the original level. Through calculations, the composition to achieve this goal is 25% MTBE + 66% gasoline + 9% 124TB (section 5.2). Point 1 and point 3 now have similar PMI and HOV. The only difference is that the doped MTBE25 at point 3 contains the oxygenated fuel, MTBE. The difference in PN between point 1 and 3 should only come from the oxygen content effect.

The choice of MTBE is due to its long chain. As discussed in section 4.2, a longer chain makes the alcohol molecule less polar, so its distillation characteristics and HOV more resembles those of HCs in gasoline.

Table 5.1. Properties of the fuels used. The gasoline (US EPA Cert. Fuel 96 Ron) composition was identified via chromatography by Saybolt Petroleum Services (This composition information used to determine its PMI can be found in Appendix I). The gasoline density was also provided by Saybolt Petroleum Services. The structure was calculated based on the mole fractions of the species in the gasoline. The HOV is taken at 298 K. NBP is taken at one atmosphere pressure.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Gasoline</th>
<th>MeOH</th>
<th>EtOH</th>
<th>MTBE</th>
<th>124TB</th>
</tr>
</thead>
<tbody>
<tr>
<td>DBE</td>
<td>C\textsubscript{72}H\textsubscript{13.1}</td>
<td>1.67</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>NBP (K)</td>
<td>-</td>
<td>338</td>
<td>352</td>
<td>328</td>
<td>442</td>
</tr>
<tr>
<td>HOV (kJ/kg)</td>
<td>350</td>
<td>1170</td>
<td>921</td>
<td>338</td>
<td>367</td>
</tr>
<tr>
<td>LHV (kJ/kg)</td>
<td>43.7</td>
<td>21.1</td>
<td>27.7</td>
<td>35.2</td>
<td>41</td>
</tr>
<tr>
<td>Density (kg/m\textsuperscript{3})</td>
<td>0.717</td>
<td>0.792</td>
<td>0.789</td>
<td>0.74</td>
<td>0.876</td>
</tr>
<tr>
<td>Molar mass (g/mol)</td>
<td>100</td>
<td>32</td>
<td>46.1</td>
<td>88.2</td>
<td>120</td>
</tr>
<tr>
<td>VP @443K (kPa)</td>
<td>-</td>
<td>2130</td>
<td>1570</td>
<td>1400</td>
<td>103</td>
</tr>
<tr>
<td>PMI</td>
<td>1.49</td>
<td>0.047</td>
<td>0.0636</td>
<td>0.0714</td>
<td>4.86</td>
</tr>
</tbody>
</table>

In the study of evaporative cooling effect, the control variables are PMI and oxygen content. However, oxygen content is an inherent property of alcohols, so there is no way to eliminate
oxygen content. The hope is that the oxygen effect can be concluded as a trivial effect from the previous experiment, so it does not affect the measure of evaporative cooling effect. This postulation is reasonable because the engine is run stoichiometric and there is no extra oxygen. It is only a matter of where the oxygen is, in the air or in the fuel. Figure 5.2 shows how the experiment assesses the evaporative cooling effect.

Figure 5.2. Diagrams illustrating the experiment on evaporative cooling effect

The experiment design is similar to the previous experiment. At point 1, PN from the baseline gasoline is measured. At point 2, 25% alcohol, either ethanol or methanol, is added to gasoline. The alcohols used should have much higher HOV than gasoline (Table 5.1). It is wise to use different alcohols with different HOV values to conduct multiple experiments, so the evaporative cooling effect is more evident. The PN at point 2 is affected by the low PMI of alcohols, the high HOV, and the possibly negligible oxygen effect. By adding a dopant, 124TB, the PMI at point 3 is brought back to the level at point 1. The difference of PN between point 1 and point 3 only comes from evaporative cooling if the oxygen effect is negligible. The fuel composition at point 3 is 25% alcohol + 10% 124TB + 65% gasoline (section 5.2).
In addition to controlling ethanol effects, various effects of operating conditions should be controlled as well. Specifically, SOI, equivalence ratio, coolant temperature, valve timing, fuel pressure, spark timing, load, and speed, should be controlled constant in a set of comparison experiments. The settings of these operating conditions will be discussed in section 5.3.

5.2 EXPERIMENT MATRIX

In this section, calculated property values of the blends used in our experiments are presented. Table 5.2 shows the experiment of oxygen effect.

Table 5.2. Properties of the blends used in the experiment of oxygen content effect. HOV is taken at 298 K. Sample calculations are in Appendix II.

<table>
<thead>
<tr>
<th></th>
<th>Gasoline</th>
<th>MTBE</th>
<th>124TB</th>
<th>PMI</th>
<th>HOV (kJ/kg fuel)</th>
<th>Relative injection duration at $\lambda = 1$</th>
<th>Relative heat of vaporization per unit fuel energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Step 1</td>
<td>100%</td>
<td>-</td>
<td>-</td>
<td>1.49</td>
<td>350</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Step 2</td>
<td>75%</td>
<td>25%</td>
<td>-</td>
<td>1.13</td>
<td>347</td>
<td>1.05</td>
<td>1.04</td>
</tr>
<tr>
<td>Step 3</td>
<td>66%</td>
<td>25%</td>
<td>9%</td>
<td>1.49</td>
<td>349</td>
<td>1.06</td>
<td>1.06</td>
</tr>
</tbody>
</table>

As seen in Table 5.2, the PMI at step 2 is 1.13 which is much lower than the PMI at step 1. However, the PMI at step 3 is 1.49 which is the same as the original PMI at step 1. The HOVs at all the three steps are comparable. Oxygen to carbon ratio has increased by 0.04 from step 1 to step 3. The PN difference between step 1 and 3 should come from this difference in oxygen content.

As discussed earlier in section 5.1, injection duration changes due to different heating values of the fuels are not significant. The typical low-load (4 bar NIMEP per cylinder) injection duration is 1500 $\mu$s. At 1500 rpm (0.009 °CA/$\mu$s), given the normalized injection duration values in Table
the difference between injection duration step 1 and step 3 is 0.54 °CA, which is negligible. The actual difference during the experiments was a little larger. For example, running gasoline at the low load condition and 60 °CA aTDC SOI required 1283 μs injection duration to keep the NIMEP at 4.08 bar. Running ethanol also at the low load condition and 60 °CA aTDC SOI required 1360 μs injection duration to keep the NIMEP at 4.08 bar. The injection duration difference caused by the heating value difference was 77 μs (0.69 °CA) in this case. The changes in injection duration were below 1 °CA, so the heating value effect is negligible.

Table 5.3 shows the experiment of evaporative cooling effect. Two fuels with different HOVs, methanol and ethanol, were used. For both M25 and E25 with dopant at step 3, the PMIs are similar to the PMI of gasoline. However, the HOV of E25 plus dopant is 516.43 kJ/kg and that of M25 plus dopant is 615.89 kJ/kg compared to the baseline case, 350 kJ/kg. Thus, the difference in PN between step 1 and step 3 is caused by the evaporative cooling effect (if the effect of oxygen content is negligible).

The increase in oxygen to carbon ratio is still present due to the addition of alcohols. If the previous experiment shows that oxygen effect is negligible, the only effect will be evaporative cooling. The assumption is that oxygen effect of MTBE is similar to the oxygen effect of both methanol and ethanol. The injection duration difference for methanol is larger. However, the difference is only 1.9 °CA, being still negligible.
Table 5.3. Properties of the blends used in the experiment of evaporative cooling effect. HOV is taken at 298 K.

<table>
<thead>
<tr>
<th></th>
<th>Gasoline</th>
<th>EtOH</th>
<th>124TB</th>
<th>PMI</th>
<th>HOV (kJ/kg fuel)</th>
<th>Relative injection duration at $\lambda = 1$</th>
<th>Relative heat of vaporization per unit fuel energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Step 1</td>
<td>100%</td>
<td>-</td>
<td>-</td>
<td>1.49</td>
<td>350</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Step 2</td>
<td>75%</td>
<td>25%</td>
<td>-</td>
<td>1.11</td>
<td>503</td>
<td>1.1</td>
<td>1.59</td>
</tr>
<tr>
<td>Step 3</td>
<td>65%</td>
<td>25%</td>
<td>10%</td>
<td>1.51</td>
<td>502</td>
<td>1.12</td>
<td>1.60</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Gasoline</th>
<th>MeOH</th>
<th>124TB</th>
<th>PMI</th>
<th>HOV (kJ/kg fuel)</th>
<th>Relative injection duration at $\lambda = 1$</th>
<th>Relative heat of vaporization per unit fuel energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Step 1</td>
<td>100%</td>
<td>-</td>
<td>-</td>
<td>1.49</td>
<td>350</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Step 2</td>
<td>75%</td>
<td>25%</td>
<td>-</td>
<td>1.1</td>
<td>570</td>
<td>1.16</td>
<td>1.89</td>
</tr>
<tr>
<td>Step 3</td>
<td>65%</td>
<td>25%</td>
<td>10%</td>
<td>1.5</td>
<td>568</td>
<td>1.17</td>
<td>1.89</td>
</tr>
</tbody>
</table>

5.3 EXPERIMENT CONDITIONS

Three conditions, fast idle, low load, and high load, were tested to represent normal engine operation regions. The specifics of these conditions are summarized in Table 5.4.

Table 5.4. Three operating conditions tested in the experiments

<table>
<thead>
<tr>
<th></th>
<th>Fast idle</th>
<th>Low load</th>
<th>High load</th>
</tr>
</thead>
<tbody>
<tr>
<td>Engine speed (RPM)</td>
<td>1200</td>
<td>1500</td>
<td>1500</td>
</tr>
<tr>
<td>NIMEP (bar)</td>
<td>2</td>
<td>4</td>
<td>8</td>
</tr>
<tr>
<td>Spark timing (°CA aTDC)</td>
<td>-35</td>
<td>-25</td>
<td>-18</td>
</tr>
<tr>
<td>Engine coolant temperature (°C)</td>
<td>25</td>
<td>80</td>
<td>80</td>
</tr>
<tr>
<td>Gasoline injection duration (µs)</td>
<td>780</td>
<td>1280</td>
<td>2120</td>
</tr>
<tr>
<td>Gasoline injection duration (°CA)</td>
<td>5.6</td>
<td>11.5</td>
<td>19.1</td>
</tr>
</tbody>
</table>

PN was measured for each test point in Figure 5.1 and Figure 5.2. Namely, gasoline, E25, E25 + 124TB, M25, M25 + 124TB, MTBE25, and MTBE25 + 124TB were each run through all the three
conditions several times to collect statistically significant data. Comparisons were made between different fuels for each condition.

5.4 APPARATUS

Apparatus in this experiment includes a direct injection engine, intake and exhaust systems, dynamometer, fuel supply system, coolant circulation system, PN measuring instrument, engine control system, data acquisition system, in-cylinder pressure sensor, manifold air pressure sensor, lambda sensor, and fuel pressure sensor. A schematic of the whole setup is shown in Figure 5.3. Details of each system will be discussed next.

![Figure 5.3. A schematic of the experiment setup](image)

The engine used is a General Motors 2014 LTG direct injection engine (EcoTec Gen III) with variable valve timing. The engine specifications are in Table 5.5. Only the cylinder on the timing
chain side was firing during the experiments. The other cylinders did not fire. The exhaust and intake systems were modified so that the exhaust and intake for the running cylinder was separated from the rest (Figure 5.4). The turbocharger, coolant compressor, starter, generator, and other unnecessary accessories were removed. The lubricant circuit was unmodified.

Table 5.5. Engine specifications

<table>
<thead>
<tr>
<th>Configuration</th>
<th>inline 4-cylinder</th>
</tr>
</thead>
<tbody>
<tr>
<td>Displaced volume</td>
<td>1998 cc</td>
</tr>
<tr>
<td>Stroke</td>
<td>86 mm</td>
</tr>
<tr>
<td>Bore</td>
<td>86 mm</td>
</tr>
<tr>
<td>Connecting Rod</td>
<td>145 mm</td>
</tr>
<tr>
<td>Compression ratio</td>
<td>9.5:1</td>
</tr>
<tr>
<td>Number of Valves</td>
<td>4</td>
</tr>
<tr>
<td>Exhaust Valve Open</td>
<td>52°CABDC @ 0.2 mm lift</td>
</tr>
<tr>
<td>Exhaust Valve Close</td>
<td>10°CATDC @ 0.2 mm lift</td>
</tr>
<tr>
<td>Inlet Valve Open</td>
<td>11°CATDC @ 0.2 mm lift</td>
</tr>
<tr>
<td>Inlet Valve Close</td>
<td>61°CABDC @ 0.2 mm lift</td>
</tr>
</tbody>
</table>

Figure 5.4 (a). Modified intake system to run a single cylinder
Figure 5.4 (b). Modified exhaust system to run a single cylinder

The in-cylinder pressure transducer (Kistler 6052) was mounted through a customized partially threaded hole through the engine head. A photo of the mounting is shown in Figure 5.5. The transducer is connected to an amplifier (Kistler 5010B) which is connected to a data acquisition system.

Figure 5.5. Mounting of the in-cylinder pressure transducer
The engine control unit (ECU) was removed. Instead an in-house control system was used. The control system ran on a C++ program. The system was able to control spark timing, injection duration, start of injection (SOI), exhaust valve timing, and intake valve timing.

The intake system is shown in Figure 5.6. It has filters, compressors (and surge tanks to simulate boosting conditions; they are not relevant in this project), electrically controlled throttle (Bosch 0280750148 32mm bore), pre-mixed charge injection system (not relevant in this experiment), and a manifold air pressure (MAP) sensor (Omega). The MAP sensor is mounted after the throttle as shown in Figure 5.7.
The dynamometer (Digalog AE 150 HS) connects to a motor (LEESON C215T17FB43C). They are shown in Figure 5.8. The motor was responsible for engine start-up, fast idle and low load conditions, where the single cylinder was not powerful enough to overcome the friction of the entire engine. The dynamometer was used to take away extra power and maintain the engine at a constant speed. The speed of the engine was controlled by the dynamometer and the motor.
High-pressure fuel supply was done by pressurizing a cylinder that has a piston inside. A schematic of the system is shown in Figure 5.3 and a photo of the system is in Figure 5.9. When the cylinder was supplying pressurized fuel, compressed nitrogen was used to pressurize the volume above the piston so that the fuel contained below the piston was also pressurized. The fuel pressure could be controlled by the regulator on the nitrogen gas cylinder. The fuel pressure was measured by an Omega PX309-3KG5V pressure transducer. When refilling the cylinder, a pump was used to pump the fuel into the cylinder with no nitrogen pressure. The fuel line connected to the original fuel rail of the engine. The injector used was a state-of-the-art GM proprietary injector which was able to provide better fuel atomization.

The cooling system has three loops, an engine loop, a dynamometer loop and a building loop, as shown in Figure 5.3. The original loop inside the engine was connected to an external tank and a pump (Figure 5.10) to make an extended loop. The tank was intended to heat up and chill down
the coolant, but these functions were not used in this experiment. The extended loop exchanged heat with another loop (the building loop) which ultimately connected to a chilling tower. Two engine coolant thermocouples were mounted as shown in Figure 5.10. The engine coolant temperature was controlled manually by a valve that closed/opened the stream in the building loop. The control mechanism was similar to a bang-bang controller used in an AC unit.
The exhaust system is shown in Figure 5.11. The lambda sensor mounted on the exhaust pipe was connected to an ETAS LA4 lambda meter. A probe was used to sample the exhaust for PN measurements. The PN measuring instrument was Cambustion DMS500. Its specifications are in [60].

![Figure 5.11. Exhaust system](image)

The working principal of DMS500 is to use size-dependent drag forces and charge-dependent electric forces to separate particles with different sizes [29]. The sample flow first goes through a heated line from the engine exhaust pipe to the instrument. The heated line is used to avoid condensation [40]. After the sample flow enters the instrument, the particles in the flow get charged by a unipolar diffusion charger [19,40]. The particles are then subject to an electric field. The electric forces on the particles are determined by the charge distribution on the particles which is known, while the particles are also subject to drag forces which increase as particle sizes increase [19,29]. Smaller particles thus drift farther. The particles eventually land on a set of electrometer rings in a classifier column. The current through the ring is scaled with the number of particles that
land on the ring [19]. By measuring the current, the instrument can resolve number concentrations and the corresponding sizes of the particles. In this sense, DMS500 actually measures the effective mobility diameter of the particles. The true diameter of a particle and its ability to attach a charge both affect this mobility diameter [5]. The size range being measured is from 5 to 1000 nm [5]. A Bayesian-statistics based algorithm fits the size data to two lognormal distributions, which are the nucleation mode and the accumulation mode [19]. There is no exact cut-off between the two modes due to the use of Bayesian statistics [19], but an empirical cut-off observed in our experiments was 30 nm. The instrument displays real-time size-resolved PN distributions through a customized software.

The data acquisition system used was National Instrument NI cDAQ-9172. It collected common engine operating parameters, such as in-cylinder pressure, NIMEP, PMEP, GIMEP, coefficient of variation, lambda, engine rpm, MAP, fuel pressure, coolant temperature and etc. The acquired data were sent to an in-house LabView program, where data were displayed and recorded. The PN measurements were recorded separately using the customized software for the Cambustion DMS500.

5.5 EXPERIMENT PROCEDURES

A typical experiment trial involved the following steps, fuel blending, fuel line flushing, motoring, firing, conditioning, and data collecting.

Fuel blending: Gasoline and alcohol were splash-blended. The blended fuel was stored in capped containers. All the fresh blends were used within at most two days and usually one day to avoid
evaporation of lighter species. Each type of fuel (alcohols, dopant, or gasoline) had its own designated glassware.

Fuel line flushing: There were three outlets to atmosphere in the fuel line (Figure 5.3 and 5.9). Each outlet was responsible for a segment of the fuel line. Before a different fuel was fueled, the fuel supply system was flushed. A small amount of the new fuel was first pumped into the cylinder (Figure 5.9) to flush the cylinder and the fuel line. The cylinder was then slightly pressurized and the fuel was collected from the three outlets. The fuel used for this flushing procedure was then disposed. This flushing procedure ensured that most of the residual fuel from a last test was flushed out so that the residual fuel did not affect the current experiment.

Motoring, firing, and conditioning: The motor was used to start the engine. In the fast-idle and low load tests, the motor was always on to overcome engine friction, because the power from the single cylinder was not enough to run the whole engine. In the high load tests, the motor was off and the dynamometer was on to take away extra power. The engine was fired after successful motoring. After successful firing, the engine was quickly conditioned to the desired operating conditions and was left firing for 10 minutes to stabilize the operation.

After the engine had reached the desired load, an SOI sweep from 20 °CA aTDC to 160 °CA aTDC with an interval of 20 °CA was performed. Changes in SOI would affect mixing efficiency and combustion efficiency to cause fluctuations in the lambda sensor reading even when all other parameters kept unchanged. The injection duration was usually adjusted to bring the lambda sensor reading back to one (stoichiometric). The throttle was usually kept unchanged unless the load and
lambda reading were completely off the track. The small adjustments in the injection duration would cause slight changes in the load (NIMEP). However, these slight changes were negligible. In order to give a sense of how large the changes in NIMEP was due to the adjustments in the injection duration, some actual numbers during the experiments are given here. For example, running gasoline at 100 °CA aTDC SOI required 2200 μs injection duration to keep stoichiometric at 8.09 bar NIMEP. Running gasoline at 20 °CA aTDC SOI required 2180 μs injection duration to keep stoichiometric at 8.03 bar NIMEP. The differences in injection duration and load were both small.

Coolant temperature in the fast-idle tests was maintained by maximizing the coolant flow in the building loop. The coolant temperature thus depended on the cooling capacity of the chilling tower and the outside temperature. Therefore, coolant temperature in the fast-idle tests fluctuated between the nominal value plus and minus 5 °C. Coolant temperature in the low load and high load tests was controlled manually in a way similar to a bang-bang controller. The temperature was kept at the nominal value plus or minus 2 °C. Although PN was shown to be exponentially dependent on coolant temperature in literature (section 3.4), our experiment practice showed that the errors caused by deviations from the nominal coolant temperature were much less than random noise in the measurements.

Data collecting: The low load and high load tests were run back-to-back because they needed the same coolant temperature. However, the fast-idle tests were only run after the engine was left to cool down (with maximum coolant flow) for at least an hour. Repeated tests on the same fuel
(gasoline, E10, M10, or etc.) were performed on different days to obtain meaningful data that represented the true test-to-test variability.

PN data (collected using the DMS500 software) at each SOI were recorded for 2 minutes, while in-cylinder pressure data (from the NI data acquisition system) were recorded for 80 seconds. After changing to a new SOI, the engine was conditioned for 2 minutes. In addition, data were only recorded when the coefficient of variation (COV) of NIMEP was less than 2.5% unless the engine was running SOI around 80 °CA aTDC, where the engine NIMEP was intrinsically unstable probably due to the high charge motion around mid-stroke.
Chapter 6: EXPERIMENT RESULTS

This section presents the results from the experiments outlined in chapter 5. PN emissions from gasoline at fast idle, low load, and high load are firstly presented to explain the effects of SOI under different operating conditions, which serve as background information for the discussions later. The discussion proceeds to explain oxygen effects using the experiment results of MTBE. The important evaporative cooling effect will be discussed lastly.

In this chapter, all the points on the plots are average values of all the available data except a small number of outliers due to instrument measurement errors. The gasoline points on the MTBE and methanol plots (Figure 6.8 and 6.11(b)) under the high load condition are the averages of the gasoline data collected within the periods when MTBE and methanol tests were performed. Because the time span of the whole project was large, in this way, the gasoline points are more representative of the environment and hardware conditions of the MTBE and methanol tests. The error bars represent standard deviation throughout this chapter.

6.1 OPERATING CONDITION AND SOI EFFECTS

Figure 6.1 and Figure 6.2 show the PN in accumulation mode and nucleation mode respectively from gasoline at the three different operating conditions, fast idle, low load, and high load.
The general trend of the PN versus SOI is consistent with the discussions in section 3.6 and the results in literature [11]. The PN is high at the beginning. It drops rapidly afterwards and then stabilizes at the end. Reasons for such a trend can be found in section 3.6. The following discussions focus on accumulation mode versus nucleation mode, and different loading conditions.
In Figure 6.1 and 6.2, the nucleation mode PN and accumulation mode PN show almost the same trend. Though nucleation mode particles may come from lubricant, both nucleation mode and accumulation mode particles can originate from unburned HCs (section 2.4). Unburned HCs have to go through a series of processes, such as HACA, to form accumulation mode particles, while condensates of unburned HCs can form nucleation mode particles directly (section 2.2). The shared source of the accumulation mode and nucleation mode particles make the trends of the two modes scale coherently under common conditions.

It is worthwhile to divide the SOI into three regions, early SOI (20 – 40 °CA aTDC), transition SOI (60 – 100 °CA aTDC), and late SOI (120 – 160 °CA aTDC). For early SOI, the fast-idle and high load conditions tend to emit the largest amount of PN. Liquid fuel is the dominating source of PN for early SOI [11]. At the fast-idle condition, as the coolant temperature and fuel energy per cycle are low, the liquid fuel evaporation, which takes place mostly at the cylinder and piston surfaces whose temperature is close to the coolant temperature, is heavily impeded. More liquid fuel causes more PN. At the high load condition, the large amount of fuel injected and more fuel spray penetration cause more liquid fuel and PN.

For late SOI, the high load condition has the highest amount of PN, followed by low load and fast idle. When SOI is late, liquid fuel is greatly reduced and fuel is well evaporated and mixed with air [11]. PN is thus less sensitive to temperature, but is scaled with the amount of fuel injected. High load needs the highest amount of fuel per cycle, and thus emits the highest amount of PN. In addition, the higher in-cylinder temperature in the high load condition also promotes PM nucleation.
The transition region is a transition from early SOI to late SOI. From our experiment practice, this region is associated with the highest variability likely because of the fast instantaneous piston motion in this region. In addition, the low load case shows a marked trough, because the large charge motion induced by the piston motion helps fuel evaporate and mix with air so that liquid fuel is reduced and charge homogeneity is improved. The observation of the trough is consistent with [42].

Figure 6.3 and 6.4 show the number weighted median diameter in accumulation mode and nucleation mode respectively. The data have large variability due to instrument limitations.

![Figure 6.3. Number weighted median diameter in accumulation mode](image-url)
Particle diameter is correlated with particle mass, because the diameter (even mobility diameter) can imply the particle volume and thus mass. As discussed in section 2.3, PMM should scale with PN in general, so the trend of particle diameter should generally follow the trend of PN. In Figure 6.4, the median diameter in nucleation mode generally keeps constant or decreases with increasing SOI. This trend is weakly consistent with the decreasing trend of PN.

Particle size in nucleation mode is related to surface oxidation and growth as discussed in Section 2.3. The hypothesis is that particles originated from liquid fuel at early SOI is not well oxidized, because the particle formation from liquid fuel (by pool fires) happens mostly in the expansion stroke when oxygen concentration is low. On the other hand, at late SOI, piston is away from the fuel spray so there is not much liquid fuel on the piston head. The particles are generated mostly due to mixture inhomogeneity in the combustion phase where particles are better oxidized to smaller ones.
The weak decreasing trend of particle diameter in nucleation mode was also observed in the tests on other fuels. It is noted that the high load condition enhances the decreasing trend. As the in-cylinder temperature is higher due to higher coolant temperature and more fuel energy under the high load condition, oxidization, an Arrhenius process (section 2.2), is enhanced under the high load condition. Therefore, the decreasing trend is clearer.

In Figure 6.3, the particle diameter in accumulation mode also has a very weak decreasing trend, since particle diameter should roughly follow the decreasing trend of PN. However, if Figure 6.3 is compared to Figure 6.1, it is found that a local decrease in PN corresponds to a local increase in particle diameter. Surface reactions, such as oxidization, that affect particle diameters in nucleation mode do not strongly affect the mobility diameters of the fractal-shape particles in accumulation mode (section 2.4 and 2.3). Instead, the main reason for the locally opposite trends in accumulation mode is likely the available time for agglomeration. High level of PN largely comes from pool fires that occur late in the combustion phase and in the expansion stroke. There is not much time for PN to coagulate to form large accumulation mode particles before they are displaced out of the cylinder, so the diameters are small. Low level of PN usually indicates that there is minimal amount of liquid fuel to cause pool fires. PN is thus formed mostly during the combustion phase in the locally rich regions, so there is more time for the particles to accumulate to generate large particles.

The locally opposite trends between PN and particle diameter were observed in the tests on other fuels. The general decreasing trend of particle diameter was also observed for other fuels. Figure 6.5 shows the number weighted median diameter in accumulation mode for different fuels under
the high load condition. Figure 6.5 can be compared to Figure 6.1 (gasoline), 6.8 and 6.11 (other fuels) to observe the locally opposite trends.

From our data, it is found that there are no consistent changes in particle diameters between different fuels. In addition, nucleation mode PN generally follows accumulation mode PN. Therefore, the rest of the discussions will focus on accumulation mode PN only.

Figure 6.5. Number weighted median diameter in accumulation mode for different fuels at high load

6.2 OXYGEN EFFECT

The results of the MTBE fuel are shown in Figure 6.6, 6.7, and 6.8, which correspond to fast-idle, low load, and high load conditions respectively. MTBE has a similar HOV as the HOV of gasoline. Therefore, the difference in PN between gasoline and MTBE25 should come from the displacement effect, and the oxygen effect if there is any. The difference in PN between gasoline and MTBE25+124TB should come from the oxygen effect only (if there is any).
At all the three conditions, the points of MTBE25+124TB more or less overlap on the gasoline points. This observation indicates that the oxygen effect (and any potential unidentified effects) should be negligible. In addition, the PN from MTBE 25 is always lower than the PN from gasoline because of the displacement effect.

Figure 6.6. PN in accumulation mode from MTBE 25 and MTBE 25 with dopant (124 – trimethylbenzene) at fast idle

Figure 6.7. PN in accumulation mode from MTBE 25 and MTBE 25 with dopant (124 – trimethylbenzene) at low load
Figure 6.8. PN in accumulation mode from MTBE 25 and MTBE 25 with dopant (124 – trimethylbenzene) at high load. The gasoline point in this figure are the average of the gasoline data collected within the period when MTBE tests were performed.

6.3 EVAPORATIVE COOLING EFFECT

The experiment results of the ethanol-gasoline and methanol-gasoline blends are shown in Figure 6.9, 6.10, and 6.11, which correspond to fast idle, low load, high load conditions respectively.
Figure 6.9. PN in accumulation mode from (a) ethanol and (b) methanol fuels at fast idle

Figure 6.10. PN in accumulation mode from (a) ethanol and (b) methanol fuels at low load
Figure 6.11. PN in accumulation mode from (a) ethanol and (b) methanol fuels at high load. The gasoline points in figure (b) are the average of the gasoline data collected within the period when methanol tests were performed.

As discussed in Section 5.1, if the effect of oxygen content is negligible, the difference between the PN from gasoline and E25/M25 + 124TB only originates from the evaporative cooling effect. On the other hand, the difference between the PN from E25/M25 and E25/M25 + 124TB only originates from the displacement effect. The difference between the PN from gasoline and E25/M25 represents the net effect of both evaporative cooling and dilution.
Ethanol-gasoline blends: The PN from E25+124TB is almost always higher than the PN from gasoline (Figures 6.9, 6.10, and 6.11) under all the three loading conditions. This clearly indicates the existence of the evaporative cooling effect. The magnitude of the effect (i.e. the magnitude of the difference in PN) changes for different SOI timings and different loading conditions. Such changes are expected because loading conditions and SOI timings can affect the geometry of liquid fuel films, heat transfer, and other fuel evaporation conditions. In addition, HOV depends on temperature, so the temperature differences in different loading conditions can affect the evaporative cooling effect.

The PN from E25+124TB is almost always higher than the PN from E25 under all the three loading conditions. This indicates the existence of the displacement effect. As discussed in section 4.1, PN should scale linearly with PMI. In addition, PMI incorporates vapor pressure and DBE, whose effects on PM emissions are independent of SOI, so the difference in the PN between E25+124TB and E25 should be uniform for different SOI timings. Under the low load and high load conditions (Figure 6.10 and 6.11), the difference does manifest some uniformity as the log scale is taken into consideration. However, in the fast-idle condition (Figure 6.9), the PN difference is not uniform across the SOI. The reason is possibly the measurement uncertainty. The fast-idle condition is intrinsically unstable because only a small amount of fuel is injected in a cold environment (coolant temperature 25 °C) and combustion is thus not robust. The uncertainty can be observed by comparing the error bars at late SOI (80 – 160 °CA aTDC) in Figures 6.9, 6.10, and 6.11.
The net effect of both evaporative cooling and displacement is seen from the difference in PN between E25 and gasoline. In the transition and late SOI regions (60 – 160 °CA aTDC), E25 produces lower or comparable amount of PN than gasoline. In the early SOI region (20 – 40 °CA aTDC), E25 produces higher or comparable amount of PN than gasoline. This behavior suggests that evaporative cooling outpowers displacement at early SOI, while displacement outweighs evaporative cooling at transition and late SOI. At early SOI, thick liquid fuel films on the piston head are the main PM source. The evaporation of such liquid films occurs at the interface between the film and the gaseous air-fuel mixture, while the energy for the evaporation mainly comes from the interface between the piston head and the liquid films. Therefore, the evaporative cooling is stronger when the films are thicker, which explains why the evaporative cooling effect outruns the displacement effect at early SOI.

Methanol-gasoline blends: The PN from M25+124TB is higher than or comparable to the PN from gasoline in all the cases. This result again indicates the existence of evaporative cooling effect. Its magnitude again depends on SOI and loading conditions. The PN from M25+124TB is always higher than the PN from M25, indicating the displacement effect.

The net effect of evaporative cooling and displacement can be seen from the difference in PN between M25 and gasoline. The difference shows a similar trend as the E25 cases. However, methanol has a higher HOV and thus stronger evaporative cooling than ethanol. As a result of the stronger evaporative cooling, the evaporative cooling effect of methanol almost always overwhelms its displacement effect in the fast-idle condition, where liquid fuel is more difficult to evaporate due to the low coolant temperature. In addition, under the low load and high load
conditions, the displacement effect starts to overpower the evaporative cooling effect later at 80 °CA aTDC SOI in contrast to 60 °CA aTDC as in the ethanol cases.

Under the low load condition, the methanol blends do not show a trough at 60 °CA aTDC (Figure 6.10). This behavior currently does not have a sound explanation and it needs further investigations.
Chapter 7: CONCLUSIONS

This thesis is an effort to study how the addition of ethanol to gasoline changes the PM emissions from a DI engine. The main contributions of this thesis are a thorough literature review regarding PM and experimental work to measure ethanol effects directly.

The take-aways from the literature review are the followings:

- PM formation depends on three key processes, HACA, agglomeration, and oxidation. HACA is generally responsible for the formation and growth of particles. Agglomeration is important for the formation of large fractal-shape particles in the accumulation mode. Oxidation competes with the nucleation and growth of particles (section 2.2).

- High level of PM in a DI engine comes from pyrolysis of fuel vapor from the liquid fuel films on the combustion chamber walls. This part of PM is rarely oxidized because the process occurs in the expansion stroke when oxygen concentration is low. In addition, PM may form during the main combustion phase in locally rich regions. However, this part of PM is easily oxidized by the oxygen in the nearby lean regions (section 2.5).

- Many parameters and hardware designs can affect PM emissions. Some parameters are speeds, loads, equivalence ratios, residuals (or valve timings), engine coolant temperature (ECT), spark timings, start of injection timings (SOI), multiple injections, and fuel pressure. Hardware effects include spray-guided versus wall-guided DI, injectors, and catalyst converters (chapter 3).
- Widely accepted ethanol effects are replacement effect (PMI), evaporative cooling effect (HOV), heating value effect, distillation characteristics, and oxygen content effect. The heating value effect is considered negligible through calculations and our experiment practice. The effect of distillation characteristics can be treated together with the evaporative cooling effect because they are based on similar physics principals (chapter 4 and section 5.1).

As seen from the literature review, PM formation and emission in a DI engine involve complex processes and are affected by many parameters. This partially explains why the results regarding ethanol effects on PM in literature are diverse, because different researchers conducted experiments under different conditions and even the slightest difference might have strong influence on the PM emissions. Therefore, in our experiment work, all these parameters were carefully controlled and PM emissions were measured in such controlled settings.

Displacement effect (or dilution effect), evaporative cooling effect, and oxygen content effect were studied in the experiment work. The basic principal was to compare PN from three blends, gasoline alone (step 1), gasoline with alcohol (step 2), and gasoline with alcohol plus a dopant (step 3). The dopant was used to cancel the displacement effect of the alcohol so that the difference in PN between step 1 and step 3 can represent either oxygen content effect or evaporative cooling effect depending on the choice of alcohol.
The key findings in the experiment work are the followings:

- Through the use of MTBE, which has a similar HOV as gasoline, only oxygen content effect would affect the PN from the step 3 blend. It was found that the difference between step 1 and 3 was negligible and thus the oxygen content effect was negligible.

- Through the ethanol and methanol tests, replacement effect was confirmed by observing that the step 3 blend always had higher PN than the step 2 blend. Evaporative cooling effect was also confirmed by noticing that the step 3 blend always had higher PN than step 1 gasoline.

- The displacement effect as a function of SOI (20 – 160 °CA aTDC) was roughly uniform between two fuels, because PN should scale linearly with PMI. However, the evaporative cooling effect was not uniform across the SOI sweep. At early SOI, thicker liquid films aggregate the evaporative cooling, so it overpowered the displacement effect. At late SOI, displacement effect dominated. As methanol has a higher HOV than ethanol and thus a stronger evaporative cooling effect, the swap of the dominating effect was delayed to a later SOI timing. In addition, the net effect of both displacement and evaporative cooling also depended on the loading conditions.

The experiment observations further explain the diverse literature results regarding ethanol effects on PM emissions, because the interplays between the displacement and evaporative cooling effects can easily cause different results. The practical implication of this thesis is that PM emissions from gasohol fuels depend on operating conditions so there are potentials to tune
a DI engine that is run on gasohol fuels to optimize the emissions. SOI is a major calibration parameter to consider.
REFERENCES


APPENDIX I

The gasoline (US EPA Cert. Fuel 96 Ron) composition was identified via chromatography by Saybolt Petroleum Services. The cumulative PMI and volume fraction versus normal boiling point (at 1 atm.) are shown in Figure A1 in the same manner as [46].

Figure A1. Gasoline cumulative PMI and volume fraction versus normal boiling point
APPENDIX II

The calculations below show how to obtain the numbers at step 2 in Table 5.2 for MTBE25. The calculations make use of the property values in Table 5.1.

1. Calculate weight fraction based on volume fraction.

Assume 75 m\(^3\) gasoline and 25 m\(^3\) MTBE.

\[
\begin{align*}
\text{mass gasoline} & = 75 \text{ m}^3 \times 0.717 \text{ kg/m}^3 = 53.775 \text{ kg} \\
\text{mass MTBE} & = 25 \text{ m}^3 \times 0.74 \text{ kg/m}^3 = 18.5 \text{ kg}
\end{align*}
\]

\[
\begin{align*}
\text{wt}\% \text{ gasoline} & = \frac{53.775}{53.775 + 18.5} = 74.4\% \\
\text{wt}\% \text{ MTBE} & = \frac{18.5}{53.775 + 18.5} = 25.6\%
\end{align*}
\]

2. Calculate quantities based on weight fraction.

\[
\begin{align*}
\text{PMI} & = 74.4\% \times 1.49 + 25.6\% \times 0.0714 = 1.13 \\
\text{HOV} & = 74.4\% \times 350 + 25.6\% \times 338 = 346.928 \text{ kJ/kg} \\
\text{LHV} & = 74.4\% \times 43.7 + 25.6\% \times 35.2 = 41.524 \text{ kJ/kg}
\end{align*}
\]

3. Calculate relative injection duration.

Assume constant injection mass flow rate, so injection duration is proportional to the mass injected. The total energy released by the injected fuel is kept constant.

\[
\begin{align*}
\text{fuel mass required} & = \frac{1 \text{ kJ}}{\text{LHV}} \\
\text{mass required for gasoline} & = \frac{1 \text{ kJ}}{43.7 \text{ kJ/kg}} = 0.02288 \text{ kg} \\
\text{mass required for MTBE25} & = \frac{1 \text{ kJ}}{41.524 \text{ kJ/kg}} = 0.02408 \text{ kg} \\
\text{relative injection duration} & = \frac{0.02408 \text{ kg}}{0.02288 \text{ kg}} = 1.05
\end{align*}
\]
4. Calculate relative HOV per unit fuel energy.

\[ HOV \text{ for gasoline per unit fuel energy} = 0.02288 \times 305 = 8.0092 \text{ kJ} \]
\[ HOV \text{ for MTBE25 per unit fuel energy} = 0.02408 \times 346.928 = 8.3546 \text{ kJ} \]
\[ \text{relative HOV per unit fuel energy} = \frac{7.5478 \text{ kJ}}{6.9784 \text{ kJ}} = 1.04 \]
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>aTDC</td>
<td>After-top-dead-center</td>
</tr>
<tr>
<td>CA</td>
<td>Crank angle</td>
</tr>
<tr>
<td>COV</td>
<td>Coefficient of variation</td>
</tr>
<tr>
<td>DBE&lt;sub&gt;i&lt;/sub&gt;</td>
<td>Double bond equivalent of the i&lt;sup&gt;th&lt;/sup&gt; species</td>
</tr>
<tr>
<td>DI</td>
<td>Direct injection</td>
</tr>
<tr>
<td>ECT</td>
<td>Engine coolant temperature</td>
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<td>EtOH</td>
<td>Ethanol</td>
</tr>
<tr>
<td>FTP</td>
<td>Federal test procedure</td>
</tr>
<tr>
<td>GDI</td>
<td>Gasoline direct injection</td>
</tr>
<tr>
<td>GIMEP</td>
<td>Gross indicated mean effective pressure</td>
</tr>
<tr>
<td>HACA</td>
<td>Hydrogen-abstraction-acetylene-addition</td>
</tr>
<tr>
<td>HC</td>
<td>Hydrocarbon</td>
</tr>
<tr>
<td>HOV</td>
<td>Latent heat of vaporization</td>
</tr>
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<td>LHV</td>
<td>Lower heating value</td>
</tr>
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<td>Manifold air pressure</td>
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<td>Methanol</td>
</tr>
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<td>MBT</td>
<td>Maximum brake torque</td>
</tr>
<tr>
<td>MTBE</td>
<td>Methyl tertiary butyl ether</td>
</tr>
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<td>NBP</td>
<td>Normal boiling point</td>
</tr>
<tr>
<td>NIMEP</td>
<td>Net indicated mean effective pressure</td>
</tr>
<tr>
<td>PAH</td>
<td>Polycyclic aromatic hydrocarbons</td>
</tr>
<tr>
<td>PFI</td>
<td>Port fuel injection</td>
</tr>
<tr>
<td>PM</td>
<td>Particulate matter</td>
</tr>
<tr>
<td>PMEP</td>
<td>Pumping mean effective pressure</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
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<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>PMI</td>
<td>Particulate matter index</td>
</tr>
<tr>
<td>PMI&lt;sub&gt;i&lt;/sub&gt;</td>
<td>Particulate index for i&lt;sup&gt;th&lt;/sup&gt; species</td>
</tr>
<tr>
<td>PMM</td>
<td>Particulate mass emission</td>
</tr>
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<td>PMP</td>
<td>Particle measurement protocol</td>
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<td>Particulate number emission</td>
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<td>RON</td>
<td>Research octane number</td>
</tr>
<tr>
<td>SI</td>
<td>Spark ignition</td>
</tr>
<tr>
<td>SOI</td>
<td>Start of injection</td>
</tr>
<tr>
<td>VP&lt;sub&gt;i&lt;/sub&gt;</td>
<td>Saturation vapor pressure of i&lt;sup&gt;th&lt;/sup&gt; species</td>
</tr>
<tr>
<td>λ&lt;sub&gt;S&lt;/sub&gt;</td>
<td>Air-fuel equivalence ratio</td>
</tr>
<tr>
<td>124TB</td>
<td>1,2,4-Trimethylbenzene</td>
</tr>
</tbody>
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