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Effects of Ethanol Evaporative Cooling on Particulate Number Emissions in GDI Engines

Abstract

The spark ignition engine particulate number (PN) emissions have been correlated to a particulate matter index (PMI) in the literature. The PMI value addresses the fuel effect on PN emission through the individual fuel species reactivity and vapor pressure. The latter quantity is used to account for the propensity of the non-volatile fuel components to survive to the later part of the combustion event as wall liquid films, which serve as sources for particulate emission. The PMI, however, does not encompass the suppression of vaporization by the evaporative cooling of fuel components, such as ethanol, that have high latent heat of vaporization. This paper assesses this evaporative cooling effect on PN emissions by measurements in a GDI engine operating with a base gasoline which does not contain oxygenate, with a blend of the gasoline and ethanol, and with a blend of the gasoline, ethanol, and a hydrocarbon additive so that the blend has the same PMI as the original gasoline. As such, the dilution and the evaporative cooling effects of the ethanol could be separated. Measurements have also been done with methanol and MTBE. The results show that evaporative cooling effect can significantly change the PN emission. The extent of the change, however, depends on the details of the operating condition such as injection timing, engine coolant temperature, and load.

Introduction

Because of their adverse health impact [1-3], the fine particle emissions from spark ignition (SI) engines are of concern. Regulations have been established to constrain the particle number (PN) [4], which measures the non-volatile particles in the 23 to 2500 nm range according to the particle measurement protocol (PMP) [5]. These particles are mostly in the accumulation mode of the size spectrum [6]. A large body of study has been done on the particulate emissions from engines [6-10], and on identifying the emission sources [11, 12]. The fuel effects on the PN emissions have been addressed through a particulate matter index (PMI), which assesses the particle emission potential of the fuel through the reactivity and volatility of its components [13, 14]. Good correlations between the PN emissions in the Federal Test Procedure (FTP) and PMI have been reported [13-15]. The presence of ethanol in the fuel essentially dilutes the PMI value, and the PN emissions should lower accordingly. Depending on the vehicle being tested, however, mixed results with ethanol blends have been observed [16-18]. It has been suggested that the dilution effect of ethanol on the PMI is confounded by the suppression of fuel evaporation due to the high latent heat of vaporization of ethanol [18]. The purpose this paper is to assess the effect of ethanol on the PN emissions by separating the dilution and the evaporative cooling effects via using various blends of gasoline that does not contain oxygenate with ethanol and a PMI enhancing dopant. Then further studies of the evaporative cooling effect are done by replacing the ethanol with methanol (which has a significantly higher latent heat), and with MTBE (which has a latent heat comparable to the overall latent heat of the gasoline).

PMI

The particulate matter index [13] of a gasoline comprises the product of the index $I_i$ of the individual species, and the weight percentage point:

$$PMI = \sum I_i \times \text{(weight \% point)}_i$$

For the individual species, $I_i$ is defined by:

$$I_i = \frac{DBE_i+1}{VP_i(\text{kPa @ 443 K})}$$

where DBE is the species double-bond-equivalent, which is a measure of its reactivity, and $VP_i$ is its saturation vapor pressure at 443K. The DBE value of a hydrocarbon is related to the number of hydrogen and carbon atoms in the molecule:

$$DBE_i = (2C_i + 2 - H_i)/2$$

The numerator in the expression for $I_i$ in equation 2 is $DBE_i+1$ to account for the paraffin particulate forming potential since paraffin has DBE of 0. The vapor pressure term is to account for the propensity of the non-volatile fuel components to survive to the later part of the combustion event as wall liquid films which serve as sources of particulate emission. The reference temperature of 443K has been chosen to give the best correlation between vehicle PN emission and PMI. This temperature is consistent with the surface temperature of the engine combustion chamber.

Ethanol has DBE of zero and the vapor pressure at 443K is relatively high (1510 kPa). The value of $I_i$ for ethanol is correspondingly low, at 6.62x10^{-4} (For comparison, for toluene and iso-octane, their respective values are 1.22x10^{-2} and 1.85x10^{-3}). Thus the main effect of ethanol is to dilute the PMI value.
Use of the vapor pressure in the PMI definition accounts for the fuel species volatility effect. However, the evaporative cooling effects of the species are not included. For the species with a high heat of vaporization, evaporative cooling could substantially affects the vaporization of all the fuel species.

The effects of ethanol on PN emissions can be attributed to the following aspects:

- Dilution effect
- Evaporative cooling effect
- Chemical effect
- Stoichiometric effect

Dilution effect – Ethanol displaces the soot forming gasoline components. Because PMI is proportional to DBE and inversely proportional to the vapor pressure, the zero DBE and the relatively high vapor pressure of ethanol result in a low PMI, hence reducing the PN emission.

Evaporative cooling effect – In contrast to hydrocarbon (HC) fuels, ethanol has much higher latent head of vaporization (HoV); see Table 1. The evaporative cooling suppresses the vaporization of gasoline components to form premixed charge and leads to more residual fuel film formation. The residual fuel film on the combustion chamber walls is a significant source of PN [11]. Therefore ethanol increases the PN emission from this perspective and confounds the dilution effect.

Chemical effect beyond what is ascribed in PMI – Due to the presence of oxygen in the ethanol molecule, the intermediate species from ethanol combustion are different from gasoline. This difference may affect the soot precursor chemistry.

Stoichiometric effect – Since ethanol is an oxygenate, less air is needed to constitute a stoichiometric mixture; see Table 1 for stoichiometric A/F. This difference suppresses the formation of fuel rich regions, hence lowers the PN emission.

The focus of this work is on separating the dilution effect and the evaporative cooling effect of ethanol. The chemical and stoichiometric effects are embedded in the results and they are not separated out.

**Methodology**

Dilution effect and evaporative cooling effect are studied by using a test procedure shown in Figure 1:

- At Step 1, the engine PN emission is measured using a base gasoline which does not contain oxygenate. The gasoline composition has been analyzed and the corresponding PMI is known.
- At Step 2, the gasoline is splash blended with ethanol. The dilution reduces the PMI. Simultaneously, the blending also increases the overall HoV and suppresses fuel vaporization through the evaporative cooling effect. The PN emission of the gasoline/ethanol blend at Step 2 is thus the combined result of PN reduction by dilution and PN enhancement by evaporative cooling. In Figure 1, for illustrative purpose, the dilution effect is arbitrarily assumed to be dominant, which leads to a net reduction of PN at Step 2.
- At Step 3, a HC dopant with high Ii is introduced. The new blend has the same PMI as the Step 1 base gasoline. It has the same volumetric percentage of ethanol as that of the blend in Step 2, and, assuming no non-linear blending effects, the overall HoV of the fuels are approximately the same in steps 2 and 3.

If the soot formation tendency of the dopant relative to the base gasoline species is indeed represented by the respective PMI values, fuels in steps 1 and 3, having the same PMI, should have the same soot formation tendency. The deviation would be due to the difference in ethanol content that is not accounted for by the PMI. This deviation could be attributed to evaporative effect of the ethanol. Fuels in steps 2 and 3 have the same ethanol content (and thus approximately the same HoV), but a different PMI, the difference in emission is attributed to dilution effect only. In this manner, the dilution and evaporative cooling effects are separated.

The same test is also conducted with methanol which has a substantially higher HoV than ethanol, and with MTBE, which has a HoV similar to that of the base gasoline overall value. If the fuel species chemical effects on PN emissions are indeed accounted for by the DBE values, the evaporative cooling effect could then be quantified.

![Figure 1. Schematic of the evaporative cooling effect test.](image)

**Fuels**

The base gasoline is US EPA Cert Fuel 96 RON from Gage Products. See Appendix for general fuel properties. Detailed hydrocarbon analysis of the batch (ASTM D-6733) using chromatography was performed by Saybolt Petroleum Services. The cumulative volume fraction and the cumulative PMI values of the individual species as a function of their normal boiling point (NBP) are shown as black curves in Figure 2 in the manner of Ref. [19]. Toluene and 1,2,4-trimethylbenzene (124tmb) are the two largest contributors to PMI. Because of its high Ii value, 124tmb is selected as the dopant for Step 3 in the tests.

The cumulative volume fraction and PMI for the individual species for the fuels used in Step 2 (E25) and Step 3 (E25 with 124tmb) are also shown in Figure 2 as curves in red and blue respectively.

Properties of the tested fuels are summarized in Table 1.
In the evaporative cooling effect test, 25% by volume of ethanol (E25), methanol (M25), and MTBE (MTBE25) were added to the gasoline at Step 2. The detailed fuel matrix of the evaporative cooling effect test is illustrated in Table 2. Note that while the oxygenates occupy a significant volume fraction of the fuel blends, their contributions to the fuel PMI are negligible; see Figure 2 for the case of the ethanol blends. Note also that the fuel in step 3 is formulated independent of the fuel in step 2 to have the correct composition.

Table 2. Fuel matrix of evaporative cooling effect test. Fuel components are in volume %. The HoV of the blends have been calculated from the contribution of each component by its mass fraction.

| Step 1 | Gasoline | EtOH | MeOH | MTBE | 124tmb | PMI | HoV (kJ/kg fuel) | Relative injection duration @ λ = 1 | Relative heat of vaporization per unit fuel energy |
|--------|----------|------|------|------|--------|-----|-----------------|----------------------------------------|---------------------------------------------|
|        |          |      |      |      |        |     |                 |                                        |                                             |
|        | 100      | -    | -    | -    | 1.49   | 305 | 1               | 1                                      |                                             |
| EtOH-Step 2 | 75 | 25   | -    | -    | 1.11   | 467 | 1.10            | 1.68                                    |                                             |
| EtOH-Step 3 | 65  | 25   | -    | -    | 1.51   | 471 | 1.09            | 1.69                                    |                                             |
| MeOH-Step 2 | 75  | -    | 25   | -    | 1.10   | 553 | 1.15            | 2.00                                    |                                             |
| MeOH-Step 3 | 65  | -    | 25   | -    | 1.50   | 536 | 1.14            | 2.01                                    |                                             |
| MTBE-Step 2 | 75  | -    | -    | 25   | 1.13   | 313 | 1.05            | 1.08                                    |                                             |
| MTBE-Step 3 | 66  | 25   | 9    | 1.49 | 320    | 1.04 | 1.10            |                                        |                                             |

The coolant temperature was at ambient (25 °C) for fast idle, and at maximum brake torque (MBT) spark timing. The intake air temperature was at approximately 25 °C for all the experiments.

Because the mass base energy content of the oxygenates are less than that of gasoline, more fuel mass and longer injection durations are required to have the same energy input as gasoline. The relative injection durations and the relative energy required to evaporate the fuel at the same fuel energy, for the different fuels are also shown in Table 2.

**Engine, instrumentation fuel and operating conditions**

Experiments were performed on a 2014 GM LTG engine (ECOTEC Gen III). The engine specification is summarized in Table 3.

Table 3. GM LTG engine specification.

| Configuration | Engine, instrumentation and operating conditions |
|---------------|-------------------------------------------------|
| 1998 cc       | Displaced volume: 1998 cc                       |
| 86 mm         | Stroke: 86 mm                                   |
| 86 mm         | Bore: 86 mm                                     |
| 145 mm        | Compression ratio: 9.5:1                       |
| 4             | Number of Valves                                |
| 52° BBDC @ 0.2 mm lift | Exhaust Valve Open                           |
| 10° BTDC @ 0.2 mm lift | Exhaust Valve Close                            |
| 11° ATDC @ 0.2 mm lift | Inlet Valve Open                              |
| 61° BBDC @ 0.2 mm lift | Inlet Valve Close                             |

The engine was modified to operate on one cylinder. The engine used a wall-guided direct injection. GM supplied the next-generation LTG engine injector which was designed to satisfy the Euro 6 emission standards. The fuel was supplied from an accumulator that was pressurized with compressed nitrogen. The firing cylinder had its own exhaust runner, from where the PN was measured by a Cambustion DMS500 MK II Fast Particle Analyzer.

The analyzer uses a log normal distribution to fit respectively and to separate the nucleation and the accumulation modes in the size distribution, which was measured in the bin size range of 5-1000 nm [20]. The PN value reported here is the total number in the accumulation mode. Since there are comparatively few particles above 1000 nm, and that the number of nucleation mode particles above 23 nm is relatively small (compared to the total number of accumulation mode particles), the accumulation mode PN is a good measure of the total number density of the 23-2500 nm particles called out in PMP. Further details of the engine setup and instrumentation can be found in [12].

The experiments were performed at three engine operation conditions: fast idle, low load, and high load. These conditions are representative of those in the FTP. They are summarized in Table 4. The coolant temperature was at ambient (25 °C) for fast idle, and at fully warmed up condition (80 °C) for the low and high load operating points. For each condition, the engine was operated at λ = 1, and at maximum brake torque (MBT) spark timing. The intake air temperature was at approximately 25 °C for all the experiments.

For the next-generation injector supplied by GM, the nominal injection pressure of the system was specified to be at 200 bar. In the preliminary run of the experiment at this injection pressure, the PN emissions at some of the operating conditions were as low as 1x10^4 /cc. These values were close to the ambient air value (at 6x10^4 /cc) measured in the test cell. To obtain adequate signal to noise ratio, the
injector was de-rated by lowering the injection pressure to 125 bar. Then all the PN values were above $1 \times 10^5$ /cc.

Since a major source of the PN emission is the residual fuel film created by the injection process, derating the injection pressure would significantly change the PN emission. The PN emission levels with the derated next-generation injector, however, were on par with those of the previous-generation LTG engine injector which operated under a lower pressure [12]. Therefore, the amount of the residual fuel film should be similar, and should be representative of those in GDI engines with substantial fuel film. Hence the data from the current study would serve as a valid reference set to assess the impact of the fuel evaporative cooling effect on PN emission.

Table 4. Engine operation conditions. The spark timings at maximum NIMEP were the same for all the fuels.

|                     | Fast idle | Low load | High load |
|---------------------|-----------|----------|-----------|
| Engine speed (RPM)  | 1200      | 1500     | 1500      |
| NIMEP (bar)         | 2         | 4        | 8         |
| Spark timing (°ATDC)| -35       | -25      | -18       |
| Engine coolant temp. | 25        | 80       | 80        |
| Gasoline inj. dur.  | 780       | 1280     | 2120      |
| (°)                 | 5.6°      | 11.5°    | 19.1°     |

The gasoline injection duration at each condition is given Table 4. The injection duration for the different tested fuels may be calculated by scaling the gasoline injection duration with the relative values that have been summarized in Table 2.

To minimize the effect of day-to-day measurement variations, all steps for a test for the three loads were performed in the same day. Additionally, at least four repeats per test were performed on different days. To avoid fuel residual effect, the fuel system was flushed with the new fuel between each step and the engine was fired for 10 minutes before recording data.

Results

Base gasoline

Figure 3 shows the PN emissions using the base gasoline as a function of the start-of-injection (SOI) in the 20° to 160° ATDC-intake range (open-valve injection) for the three engine operating conditions. The general trend indicates high PN emissions with early SOI. With retard of SOI, PN emissions decreased rapidly (by approximately two orders of magnitude) when injection was at where the fastest instantaneous piston velocity occurred (at approximately 70° ATDC-intake); then the PN increased somewhat and eventually stabilized at later SOI. This trend had been observed not only in tests with the base gasoline, but also with all the other fuels. Similar behaviors have been observed in another GDI engine [11].

From the observed trend of PN emission as a function of SOI, emission data are separated into three regions per injection timing as shown in Figure 3:

- Early region – data from SOI at 20° and 40° ATDC of intake stroke.
- Transition region – data from SOI at 60° and 80° ATDC of intake stroke.
- Late region – data from SOI from 100° to 160° ATDC of intake stroke.

With early injection (e.g. at 20° ATDC-intake), the piston is very close to the injector so that the spray has not adequately spread when it hits the piston surface. The foot print on the piston is small and a deep puddle is formed (See Ref. [11] for a scale drawing of the injection geometry). The thick liquid fuel film contributes to the high PN emission. As the piston descends, the foot print on the piston becomes larger, resulting in a thinner fuel film which facilitates evaporation. The PN emission decreases correspondingly. In the late SOI region, the piston has sufficiently descended so that the injection foot print is almost entirely on the cylinder wall. Then the piston position has little effect on the fuel film. Hence the PN emission is less sensitive to the injection timing. The fuel evaporation and mixing process is assisted by the charge motion, which is most intense at when the piston is moving fastest (at approximately 70° ATDC-intake). Therefore, there is a dip in PN emission when the fuel is injected around that time.

It is noted that since the energy for evaporating the fuel film comes predominantly from the solid/liquid interface, evaporative cooling effect on evaporation, which takes place at the free surface, would be more prominent with a thicker film.

Ethanol blends

Results of ethanol test at fast idle, low load, and high load are shown in Figure 4, 5, and 6, respectively. For the transition and late SOI timing regions in all three operating conditions, the PN was lower when gasoline (Step 1) was replaced by E25 (Step 2). When the fuel was reconstituted (Step 3) with the 124tmb addition so that it was an
E25 fuel with the same PMI as the original gasoline, the PN was higher than the original gasoline. This behavior has been schematically illustrated in Figure 1. Referring to that figure, the evaporative effect (at the same PMI) in enhancing the PN emission is the difference between the E25+124tmb fuel (Step 3 fuel) and the gasoline (Step 1 fuel). The dilution effect is the difference between the Step 3 fuel and the Step 2 fuel (E25). That the PN emissions from Step 3 is always higher than that from Step 1 illustrates the evaporative cooling effect on enhancing PN emissions.

The dilution effect of the ethanol addition on PN emission has been substantially reduced by the evaporative cooling effect and the net PN emission is the Step 1-to-Step 2 difference, which is significantly smaller than the Step 3-to-Step 2 difference if dilution were the only effect. The interplay between the evaporative effect and the dilution effect, however, is not uniform. It is different for different operating condition, and for different injection timing. Since the evaporative cooling effect on vaporization depends on the details of the fuel film geometry, and the heat and mass transfer processes, the amount of residual fuel, and thus the amount of PN emission depends very much on the operating condition.

Figure 4. PN emissions of ethanol evaporative cooling effect test at fast idle. Gasoline (Step 1), E25 (Step 2), and E25+124tmb (Step 3) results are colored by black, red, and blue respectively. Symbols denote the day-to-day results and lines connect the corresponding means.

Figure 5. PN emissions of ethanol evaporative cooling effect test at low load. See Figure 4 caption for definition of symbols.

Figure 6. PN emissions of ethanol evaporative cooling effect test at high load. See Figure 4 caption for definition of symbols.

Figure 7. PN emissions of methanol evaporative cooling effect test at fast idle. Gasoline (Step 1), M25 (Step 2), and M25+124tmb (Step 3) results are colored by black, red, and blue respectively. Symbols denote the day-to-day results and lines connect the corresponding means.

Figure 8. PN emissions of methanol evaporative cooling effect test at low load. See Figure 7 caption for definition of symbols.
For the early SOI region under the three operating conditions, PN from the Step 3 fuel (E25+124tmb) was always the highest compared to those from gasoline and from E25. This observation confirms the enhancement of PN by evaporative cooling. However, the emission with E25 could be comparable or higher than the gasoline as the evaporative cooling effect compensates for or overpowers the dilution effect. It is noted in the preceding section that at the early SOI, the liquid fuel film is thicker. Therefore evaporative cooling effect is more dominant in this SOI region than that in the other two regions, and so it could negate the dilution effect to a larger extent.

**Methanol blends**

The experiments were repeated with methanol replacing the ethanol in the blends. Methanol has a higher HoV than ethanol. If the other factors (chemical and stoichiometric effects) have already been accounted for by the PMI, the PN results using methanol would accentuate the evaporative effect.

Results of methanol test at fast idle, low load, and high load are shown in Figure 7, 8, and 9, respectively.

For fast idle (Figure 7), the M25 (Step 2) PN emissions were higher or comparable to the corresponding gasoline (Step 1) values. This observation contrasts with what was observed with ethanol (Figure 4), for which the E25 PN were consistently lower than the gasoline values. Thus for methanol, because of the higher HoV, the evaporative effect overpowered the dilution effect at fast idle for which the ECT was low (25 °C).

At the low and high load conditions where the ECT was at the fully warmed up temperature (80 °C), the evaporative effect should be less, and the dilution effect should be more prominent. The M25 PN emissions were lower in the late SOI region, showing the dominance of the dilution effect. However, they were higher than or comparable with the gasoline values in the early and transition SOI regions. The extent of the evaporative effect was thus not uniform. The behavior is consistent with the previous discussion that at early SOI, the fuel film is thicker; so evaporative effect is relatively more prominent, and compensates or over-compensates the dilution effect.

It is noted that in Figure 8, the PN emissions for M25 and M25+124tmb blends did not exhibit a “dip” at SOI=60° ATDC-intake as in the gasoline PN emission. We do not have an explanation for this behavior.

**MTBE blends**

MTBE has HoV comparable to that of gasoline. So the evaporative effect should be minimized. So the effect of blending MTBE in gasoline is essentially in dilution. If the chemistry effect and stoichiometric effects are already encompassed in the PMI value, PN emissions from Step 1 (gasoline) and Step 3 (MTBE25+124tmb so that blend has the same PMI as the gasoline) should be the same. PN from Step 2 (MTBE25) should be lower because of dilution.

The PN emissions are shown in Figures 10 to 12 respectively for the three operating conditions. For all loads and the range of SOI, the gasoline (Step 1) and MTBE25 + 124tmb (Step 3) emissions were approximately the same. Thus for MTBE, the evaporative cooling effect was small.
The MTBE25 PN emissions were generally lower than the gasoline values, showing the dilution effect. The effect, however, was again not uniform across the range of SOI and it was different for each of the three loads. At low load in the late and transition SOI regions (Figure 11), the MTBE25 PN was approximately a factor of 1.46 lower than those of gasoline. This factor is in line with the dilution of the PMI (1.49/1.13=1.32; see Table 2). This factor was not observed in the early SOI region. At fast idle and at high load (Figures 10 and 12), the dilution factor was not consistent. Sometimes dilution was not observed; e.g. in the late SOI region at fast idle and in the transition region at high load.

**Summary/Conclusions**

Presence of ethanol as a gasoline component has two confounding effects on the PN emissions. It has low particulate formation potential chemically and lowers PN by diluting the particulate forming species. It has high latent heat of vaporization, and suppresses fuel vaporization through evaporative cooling thereby enhances formation of residual liquid fuel films which are sources of particulates. In this study, these effects are separated by comparing the PN emissions from gasoline (Step1) to a gasoline blended with 25% by volume of ethanol (Step 2), and a gasoline blended with 25% ethanol and a dopant (124tmb) with a high particulate forming potential so that the PMI is the same as that of the original gasoline (Step 3). If the PMI encompasses the dilution and volatility effects, the difference between Step 3 and Step 1 would be due to the evaporative cooling effect only; and the difference between Step 2 and Step 1 would be due to the combined cooling and dilution effects.

The experimental matrix includes SOI sweep at cold-fast-idle (1200 rpm; 2 bar NIMEP; 25 °C ECT), and at warmed up condition (80 °C ECT) low and high loads (at 1500 rpm and respectively at 4 and 8 bar NIMEP). Methanol and MTBE have also been used in place of the gasoline in these experiments to confirm the role of evaporative cooling.

The following conclusions are drawn from this work:

(a) In all cases, the evaporative cooling effect of ethanol and methanol enhances PN emissions when the dilution effect has been taken out by the dopant addition.

(b) The above evaporative cooling effect is further confirmed when ethanol is replaced by MTBE which has approximately the same HoV as the gasoline. Then the PN emissions from Step 3 and Step 1 are almost identical, since the HoV are approximately the same.

(c) The combined effect on PN emissions (suppression by dilution and enhancement by evaporative cooling) is not uniform. Since the details of the fuel vaporization depends on the fuel film geometry and the heat and mass transfer processes, the evaporative cooling effect on PN formation depends on the operating condition and injection timing.

Because of (c), a quantitative assessment of the evaporative cooling effect on PN emission is difficult. The practical implication is that in standard tests such as the FTP which encompasses different operating conditions, the PN emissions obtained with ethanol/gasoline blends very much depends on the vehicle and the calibration. As such, different results have been obtained [16-18].

**References**

1. Murphy, D. M., “Something in the air,” Science, 307 (5717): 1888–1890, 2005.
2. Kaiser, J., “Mounting Evidence Indicts Fine-Particle Pollution,” Science, 307 (5717): 1858–1861, 2005.
3. Gunter, O., “Toxicology of Ultrafine Particles: In vivo Studies,” Phil. Trans. of the Royal Soc. of London, Series A, Math. Phys. and Eng. Sc., 358 (1775): 2719–2740, 2000.
4. Commission Regulation (EU) No 459/2012.
5. Giechaskiel, B., Mamakos, A., Andersson, A.D., et al, “Measurement of Automotive Nonvolatile Particle Number Emissions within the European Legislative Framework: A Review,” Aerosol Sc. and Tech., 46(7): 719–749, 2012.
6. Kittelson, D. B., “Engines and Nanoparticles, a Review,” Journal of Aerosol Science, 29(5): 575–588, 1998.
7. Whitaker, P., Kapus, P., Ogris, M., and Hollerer, P., “Measures to Reduce Particulate Emissions from Gasoline DI engines,” SAE Int. J. Engines 4(1): 1498-1512, 2011, doi: 10.4271/2011-01-1219.
8. Sabathil, D., Koenigstein, A., Schaffner, P., Fritzsche, J. et al., “The Influence of DISI Engine Operating Parameters on Particle Number Emissions,” SAE Technical Paper 2011-01-0143, 2011, doi: 10.4271/2011-01-0143.
9. Piock, W., Hoffmann, G., Berndorfer, A., Salemi, P. et al., “Strategies Towards Meeting Future Particulate Matter Emission Requirements in Homogeneous Gasoline Direct Injection Engines,” SAE Int. J. Engines 4(1): 1455-1468, 2011, doi: 10.4271/2011-01-1212.
10. Peckham, M., Finch, A., Campbell, B., Price, P. et al., “Study of Particle Number Emissions from a Turbocharged Gasoline Direct Injection (GDI) Engine Including Data from a Fast-Response Particle Size Spectrometer,” SAE Technical Paper 2011-01-1224, 2011, doi: 10.4271/2011-01-1224.
11. Ketterer, J. and Cheng, W., "On the Nature of Particulate Emissions from DISI Engines at Cold-Fast-IDle," SAE Int. J. Engines 7(2): 986-994, 2014, doi: 10.4271/2014-01-1368.
12. Oh, C., and Cheng, W., “Assessment of Gasoline Direct Injection Engine Cold Start Particulate Emission Sources,” SAE Int. J. Engines 10(4): 1556-1565, 2017, doi: 10.4271/2017-01-0795.
13. Aikawa, K., Sakurai, T., and Jetter, J., "Development of a Predictive Model for Gasoline Vehicle Particulate Matter Emissions," SAE Int. J. Fuels Lubr. 3(2): 610-622, 2010, doi: 10.4271/2010-01-2115.
14. Aikawa, K., and Jetter, J., “Impact of Gasoline Composition on Particulate Matter Emissions from a Direct-injection Gasoline Engine: Applicability of the Particulate Matter Index,” Int. J. of Eng. Research, Vol. 15(3), pp 2998-306, 2014.
15. Khalek, I., Bougher, T., and Jetter, J., "Particle Emissions from a 2009 Gasoline Direct Injection Engine Using Different Commercially Available Fuels," SAE Int. J. Fuels Lubr. 3(2): 623-637, 2010, doi: 10.4271/2010-01-2117.
16. Vuk, C., “Fuel Property Effects on Particulates in Spark Ignition Engines,” SAE Paper 2013-01-1124, doi: 10.4271/2013-01-1124.
17. Butler, A., Sobotowski, R., Hoffman, G., Machiele, P., “Influence of Fuel PM Index and Ethanol Content on Particulate Emissions from Light-Duty Gasoline Vehicles,” SAE Paper 2015-01-1072, doi: 10.4271/2015-01-1072
18. Sobotowski, R., Butler, A., Guerra, Z., “A Pilot Study of Fuel Impacts on PM Emissions from Light-Duty Gasoline Vehicles,” SAE Paper 2015-01-9071, doi: 10.4271/2015-01-9071
19. Barrientos, E., Anderson, J., Maricq, M. Boehman, A., supplementary materials to paper “Particulate Matter Indices Using Fuel Smoke Point for Vehicle Emissions with Gasoline, Ethanol Blends, and Butanol Blends,” Comb. & Flame, 167, 2016, pp 308-319.
20. Cambustion Limited, “Fast-response Particle Size Analyzer,” http://www.cambustion.com/products/dms500/engine.

Contact Information
Yu Chen: yuc@mit.edu
Yihao Zhang: yihaozh@mit.edu
Wai Cheng: wkcheng@mit.edu.

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Definitions/Abbreviations
A/F Air fuel ratio
ATDC After-top-dead-center
DBE_i Double bond equivalent of i^th species
ECT Engine coolant temperature
EtOH Ethanol
FTP Federal test procedure
GDI Gasoline direct injection
HoV Latent heat of vaporization
I_i Particulate index for i^th species
MeOH Methanol
MBT Maximum brake torque
MTBE Methyl tertiary butyl ether
NBP Normal boiling point
NIMEP Net indicated mean effective pressure
PM Particulate mass emission
PMI Particulate matter index
PMP Particle measurement protocol
PN Particulate number emission
RON Research octane number
SOI Start of injection
VP_i Saturation vapor pressure of i^th species
## Appendix

### General properties of the base gasoline

| Property                      | Test Method   | Unit      | Value  |
|-------------------------------|---------------|-----------|--------|
| Specific gravity @ 60.0°F     | ASTM D4052    |           | 0.7    |
| API gravity @ 60°F            | ASTM D4052    |           | 60.2   |
| Distillation, IBP             | ASTM D86      | DEG F (DEG C) | 88.1 (31.2) |
| Distillation, 10%             | ASTM D86      | DEG F (DEG C) | 125.5 (51.9) |
| Distillation, 50%             | ASTM D86      | DEG F (DEG C) | 218.3 (103.5) |
| Distillation, 90%             | ASTM D86      | DEG F (DEG C) | 317.3 (158.5) |
| Distillation, dry point       | ASTM D86      | DEG F (DEG C) | 357.6 (180.9) |
| RVP @ 100°F                   | ASTM 5191     | PSI (KPA) | 8.93 (61.53) |
| Research octane number        | ASTM D2699    | RON       | 97.8   |
| Motor octane number           | ASTM D2700    | MON       | 89.1   |
| Octane rating                 | GAGE-CALCULATED | R+M/2    | 93.4   |
| Octane sensitivity            | GAGE-CALCULATED | R-M     | 8.7    |
| Aromatic content              | ASTM D1319    | VOL. %    | 29.4   |
| Olefin content                | ASTM D1319    | VOL. %    | 0.5    |
| Saturate content              | ASTM D1319    | VOL. %    | 71.3   |
| Sulfur content                | ASTM D5453    | PPM       | 29.0   |
| Lead content                  | ASTM D3237    | G/GAL     | 0.0    |
| Phosphorous content           | ASTM D3231    | G/GAL     | 0.0    |
| Carbon content                | ASTM D5291    | WT. %     | 86.3   |
| Hydrogen content              | ASTM D5291    | WT. %     | 13.7   |
| C/H ratio                     | CALCULATED    | WT/WT     | 6.3    |
| H/C ratio                     | CALCULATED    | MOLE/MOLE | 1.9    |
| Net heat of combustion        | ASTM D240     | BTU/LB (MJ/KG) | 18750.4 (43.7) |
| Carbon density                | CALCULATED    |           | 2403.0 |
| Oxygenates                    | ASTM D4815    | VOL.%     | NONE   |