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Particulate matter indices using fuel smoke point for vehicle emissions with gasoline, ethanol blends, and butanol blends

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ABSTRACT

Recent studies have led to significant improvements in the prediction of particulate matter (PM) emissions from gasoline vehicles based on differences in fuel composition. This is an issue that has taken on increased importance recently given the introduction of gasoline direct injection (GDI) technology to improve fuel economy and the challenges it has meeting new stringent PM emissions standards. One productive effort in this area is the PM Index (PMI) developed by Aikawa and collaborators. This approach relates the effects of fuel composition on its PM forming potential. The present work explores the use of experimental smoke point measurements and various fuel volatility metrics to better characterize these effects. Smoke point (SP) values as scaled by the Oxygen Extended Sooting Index (OESI) incorporate all fuel molecular structural effects known to have an impact on soot formation, including branching, degree of saturation, carbon chain length, and oxygenate functional group effects. A strong correlation is found for vehicle-level particle number (PN) and PM emissions with SP, OESI and PMI. Fuel volatility effects are considered, including characteristics derived from molecular weight, distillation, vapor pressure, and heat of vaporization. For hydrocarbon blends, no volatility factor significantly improved the correlation as compared to PMI, SP, or OESI alone. However, inclusion of a heat of vaporization term with OESI better matched the emissions trend for ethanol–gasoline blends. Sooting tendencies for *n*-butanol- and isobutanol-gasoline blends exhibited trends similar to those with ethanol.

1. Introduction

The past decade has seen a myriad of developments in vehicle technologies and fuel formulation. These have been driven by recent worldwide legislation and concerted efforts to reduce reliance on oil imports and to reduce greenhouse gas (GHG) emissions, while at the same time reducing pollutant emissions. These goals can often conflict. An important current example is gasoline direct injection (GDI) technology. Combined with turbocharging and lightweighting this technology provides a cost effective means to improve fuel consumption and reduce carbon dioxide (CO_2) emissions [1–3]. Compared to port fuel injection (PFI) engines, GDI engines to date have exhibited higher particulate matter (PM) emissions [4]. GDI involves the direct spray of gasoline into the combustion chamber, which poses challenges to meet new particulate matter (PM) emissions standards. Incompletely evaporated fuel droplets and droplet impingement onto piston and cylinder walls, especially during cold start, lead to locally rich, diffusion-governed liquid fuel combustion or pyrolysis that is prone to PM formation [5,6]. Thus, more care is needed in GDI combustion system design and calibration to maintain low PM emissions and to meet stringent future PM emissions requirements. Changes in fuel composition, such as blending ethanol with gasoline (to reduce petroleum consumption and fossil-based CO_2 emissions) can potentially have an adverse influence on the spray and evaporation characteristics of the fuel and exacerbate PM emissions [5,7,8]. Conversely, ethanol addition and other fuel modifications such as reduction in the aromatic hydrocarbon content can also reduce PM emissions [7] and therefore potentially serve as enablers for GDI technology, especially at the European EU6b standard of 6×10^{11} solid particles/km and 2025 California LEV III standard of 1 mg/mi. Such fuel changes also have been shown to have positive or negative PM emissions effects in port fuel injected (PFI) engines [5,9–12].

In the current climate of rapid regulatory changes and proposals of new fuel formulations, it becomes important to have a rapid means to assess potential impacts on emissions performance. Aikawa et al. [9] introduced a PM Index (PMI), an empirical parameter intended to characterize the propensity of gasoline

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formulations to produce PM in spark ignition (SI) engines. The PMI combines effects of fuel molecular compositional information and the volatility of individual compounds contained in a gasoline. The PMI has provided a strong correlation with engine data [5,9,10,12] and appears to be a useful means to predict PM trends (mass and number) for SI engines associated with fuel composition and properties. However, there remain aspects of this index that can potentially be improved, including a very limited representation of chemical structure effects on soot formation. An additional practical limitation for some users is that the fuel must be speciated to the individual compound level (e.g., by high-resolution gas chromatography) to perform the model calculations.

The present work provides a detailed analysis of the primary fuel factors (i.e., molecular structure and volatility) that influence PM emissions in SI engines and investigates various fuel-PM correlations. The fuel smoke point (SP), an experimentally-determined parameter, is widely used in the literature to characterize the sooting tendency of a given fuel and is also used in aviation fuel specifications [13]. Indices based on smoke point have been developed to harmonize sooting tendencies related to fuel composition, but have not been related directly to PM emissions from SI engines. Here, the smoke point is evaluated as an alternative predictor for use in PM indices. Various volatility measures are discussed and potential alternative, complementary correlations for prediction of PM emissions from SI engines are presented. PM analysis of two sets of fuels is performed. The first set simulates the gasoline blends initially studied by Aikawa et al. [9] while the second consists of a series of gasoline blends with ethanol, *n*-butanol, and isobutanol. The smoke point data and resulting correlations are compared with the PMI correlation and available vehicle PM emissions data.

2. A review of PM indices

2.1. PM emissions indices for SI engines

As a means to predict how fuel changes might affect PM emissions in SI engines, Aikawa et al. recently proposed an empirical PM index based on fuel composition and properties, originally developed using emissions data from a PFI vehicle and later demonstrated with GDI vehicle data [9,10]. Two main fuel factors that influence PM emissions in SI engines were included: fuel molecular structure, which accounts for the fuel's chemical propensity to produce soot, and volatility, a physical property that relates to the fuel's ability to evaporate and mix with air to avoid fuel-rich combustion conditions. Eight different hydrocarbons and ethanol were individually blended into United States (U.S.) certification gasoline (indolene) and the solid particulate number (PN) emissions from each blend were measured over the New European Driving Cycle (NEDC). An empirical correlation, termed the "PM Index" (PMI),

$$\mathrm{PMI} = \sum_{i=1}^{n} \left(\frac{\mathrm{DBE}_i + 1}{\mathrm{VP(443\ K)}_i} \times \mathrm{Wt}_i \right) \tag{1}$$

was introduced based on the weight percentage (Wt) of each component *i* in the fuel, using the double-bond equivalent (DBE) to represent fuel molecular structure effects and vapor pressure (VP) at 443 K (170 °C) to represent the volatility effect of each component.

DBE is a measure of the degree of unsaturation of each gasoline component, calculated as:

$$\mathrm{DBE} = \left(\frac{2n + 2 - m + N}{2} \right) \tag{2}$$

where n, m, and N are the number of carbon, hydrogen, and nitrogen atoms respectively present in an organic compound ($C_nH_mN_N$). In hydrocarbons, unsaturation derives from both double bonds and ring structures and is closely linked to the carbon to hydrogen ratio (n/m). However, there is no direct physical basis for chemical structure effects adhering to a DBE + 1 relationship. Furthermore, the DBE model does not distinguish straight chain from branched hydrocarbons, or olefins from naphthenes, though these are known to affect the chemical sooting tendency [14–19]. Likewise, the DBE model and PMI correlation do not explicitly account for oxygen in fuel molecules and its potential effects on soot formation [20–22]. Therefore, aspects of this index that can potentially be improved are investigated.

Subsequently, Leach et al. [23] investigated PN emissions in GDI engines and proposed a modification of the PMI denoted as PN Index (PNI), defined as follows:

$$\mathrm{PNI} = \frac{1}{\mathrm{DVPE\ (kPa)}} \sum_{i=1}^{n} \ (\mathrm{DBE}_i + 1)\ \times V_i \tag{3}$$

where DVPE is the dry vapor pressure equivalent of the entire fuel and V_i is the volume fraction of each component *i* in the mixture. Dry Vapor Pressure Equivalent (DVPE) is measured at a temperature of 37.8 °C in accordance with EN 13016-1 [24] or ASTM D4953 [25] and is intended to be an equivalent measure of the Reid Vapor Pressure (RVP), but for gasoline with oxygenates. Calculated PNI values were compared with engine PN emissions using both simple fuel blends and commercially available fuels [23]. The blends were prepared using varying ratios of a medium and heavy hydrocarbon fraction having matched DBE values, for which PM emissions differences were ascribed to differences in bulk fuel DVPE.

This seemingly minor difference in how volatility is included in the two correlations has a profound impact, however. In the PMI approach, the contribution of each component is scaled by its DBE + 1 value and vapor pressure such that compounds with low volatility are more highly weighted. A mechanistic explanation is that low volatility compounds evaporate more slowly from the fuel spray and are more likely to be present in fuel that adheres to injector deposits or that contacts metal surfaces. These areas see poor air–fuel mixing which leads to locally fuel-rich combustion and higher PM emissions. In contrast, the PNI approach scales the contribution of each component only by its DBE + 1 value. Fuel volatility effects are included through the DVPE of the entire ("bulk") fuel mixture, which is primarily determined by the amounts of high volatility compounds and is relatively unaffected by low volatility compounds. Leach et al. [23] note that lower fuel DVPE hinders fuel spray breakup and evaporation and thus provides poorer air–fuel mixing which increases PM emissions.

2.2. Smoke point measurements and sooting tendency indices

Since as early as 1927 [26], the smoke point parameter has been used to characterize the sooting tendency of fuels. The SP is measured as the height in millimeters of the highest diffusion-controlled flame produced without smoke when the fuel is burned in a specific test lamp [27]. Smoke point tests were initially conducted using a liquid fuel pool fire [15,17,18] and more recently with the current wick-fed approach [27]. It has been well documented that a fuel's sooting tendency is inversely proportional to its smoke point [14–19]. A large amount of smoke point data is available in the literature showing strong correlations to fuel molecular structure.

At first glance, sooting tendency measurements and indices based on diffusion flames might seem inappropriate for SI engines where extensive efforts are made to maintain stoichiometric combustion to help the three-way catalyst meet carbon monoxide (CO), nitrogen oxide (NO_x) and hydrocarbon emissions standards. Diffusion flames are typically associated with combustion in compression ignition (CI) engines, which generate orders of magnitude