

Development of a Predictive Model for Gasoline Vehicle Particulate Matter Emissions

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ABSTRACT

The relationship between gasoline properties and vehicle particulate matter emissions was investigated, for the purpose of constructing a predictive model. Various chemical species were individually blended with an indolene base fuel, and the solid particulate number (PN) emissions from each blend were measured over the New European Driving Cycle (NEDC). The results indicated that aromatics with a high boiling point and a high double bond equivalent (DBE) value tended to produce more PN emissions. However, high boiling point components with low DBE values, such as paraffins, displayed only a minor effect on PN. Upon further analysis of the test results, it was also confirmed that low vapor pressure components correlated with high PN emissions, as might be expected based on their combustion behavior. A predictive model, termed the "PM Index," was constructed based on the weight fraction, vapor pressure, and DBE value of each component in the fuel. It was confirmed that the PM Index could accurately predict not only the total PN trend but also total particulate matter (PM) mass, regardless of engine type or test cycle.

A large number of gasoline samples were collected in various countries, and submitted for detailed hydrocarbon analysis (DHA). Using the resulting hydrocarbon speciation data, a PM Index distribution was calculated for each country from which fuel samples were acquired. Based on the range of PM Indices encountered, it was estimated that the highest PM Index fuel would produce 10 times the PM emissions of that of the lowest PM Index fuel. Therefore, it was concluded that worldwide PM emissions can be reduced not only through improvements in engine hardware, but also through improvements in fuel quality.

INTRODUCTION

Particulate matter (PM) emitted from gasoline engines consists of soot, ash, sulfates, a soluble organic fraction (SOF) containing unburned fuel and lube oil, and other components. Among those, soot and SOF are the primary components of PM. In particular, soot breaks down slowly and remains suspended in air for a long period of time, and thus presents a health risk [1]. Also, recent studies have shown that soot may contribute to global warming [2]. Among automobiles, vehicles equipped with a diesel engine have been considered a major source of PM emissions. However, recent studies report that a substantial amount of PM emissions are produced not only by diesel engines, but by gasoline engines as well [3]. Given this situation, Europe has already begun considering the regulation of solid PN emissions from gasoline engines under EUR06. Similar efforts are underway by the California Air Resources Board (CARB) regarding total PM mass limits for the upcoming LEV-III emission category. These examples show that the reduction of PM emissions emitted from gasoline engines is a very important challenge.

Diffusion combustion of fuel is suspected to be responsible for the generation of soot and other PM from gasoline engines. Here, "diffusion combustion" refers to the burning of fuel attached to the piston and cylinder walls as well as fuel residues, where they are not vaporized and are burned in liquid form. Low vapor pressure components of gasoline exhibit such behavior. Therefore, PM emissions are likely to be affected significantly by the vapor pressure of gasoline components. In addition to this vaporization factor, PM is also associated with aromatic substances that are well-known sources of PM emissions [4], and the molecular structures of

gasoline components are also considered an important factor of PM emissions.

When the mechanism of PM generation from a gasoline engine is considered, as explained above, it is clear that gasoline composition will likely have a significant impact on PM emissions. However, relatively few studies have been conducted to date regarding the relationship of gasoline composition to PM emissions [4-5]. Accordingly, this paper examines the effects of gasoline composition on PM emissions.

RELEVANCE OF PM EMISSIONS AND FUEL COMPOSITION

To study the effect of fuel composition on PM emissions, it is effective to vary the composition of components over a wide range and observe how the emissions change. Here, various hydrocarbons were mixed with a base fuel and the change in PM emissions was studied, in relation to the properties of hydrocarbons added.

Test Vehicle

A vehicle equipped with a 2.3-liter port fuel-injected (PFI) turbo-charged engine was used. The engine specifications of the vehicle used are shown in [Table 1](#).

Test Method

PM can be measured in various ways. For example, the weight method traps PM by a filter and measures their weight, while the counting method measures the total particulate number (PN). In this study, the distance-averaged solid PN was measured in the NEDC mode, and also under a steady-state condition of 120 km/h. To eliminate the effects of ignition timing, fuel injection timing, etc., fixed engine calibration data were used in the measurement. PN was measured using the PMP method specified by ECE R83. Under the PMP method, SOFs and other volatile components are removed, and the remaining solid particles are measured. Before measuring in the NEDC mode, the vehicle was driven for NEDC preconditioning, and then soaked for at least 12 hours in a test chamber adjusted to 25°C, after which the test was conducted. The engine was fully warmed up before measuring at 120 km/h. [Figure 1](#) provides an overview of the PN measurement test, while [Table 2](#) lists the specifications of the PN measurement system.

Test Fuels

[Table 3](#) lists the test gasoline blends used in this study. The applicable fuels consist of eight types of test fuels (Nos. 2 to 10) prepared by adding various hydrocarbons or ethanol to a base fuel of Indolene (No. 1), which is an official emission test fuel in the US. The hydrocarbons were added at nominally 10 percent by weight in such a way that the overall

carbon number of the fuel remained constant. The ethanol was added 21 percent by weight. Each fuel was mixed by putting the base fuel and each reagent into a drum (120 liters) and mixing the ingredients using an agitator.

PN Measurement Results

[Figures 2](#) and [3](#) show the distance-averaged PN measured during the NEDC cycle and the 120 km/h steady-state cycle using the test fuels. As you can see, PN increased in a majority of gasoline blends to which hydrocarbons had been added. Partly because only hydrocarbons were added to the gasoline, and partly because SOFs and other volatile components are removed under the PMP method, all of the additional PN is considered a PAH (polycyclic aromatic hydrocarbon) with a high boiling point or soot. The higher the boiling point hydrocarbon added, the more the PN increases. This trend is particularly notable with aromatic substances. For example, while the PN of the ethyl benzene (409K boiling point) blend was approximately 1.3 times that of the base fuel, the PN of naphthalene (491K boiling point) blend was approximately 5.7 times, indicating a larger rate of increase relative to the boiling point. Among paraffins, on the other hand, the rate of increase in the PN was approximately 1.0 times in the case of the trimethyl pentane (372K boiling point) blend, but it was approximately 1.4 times with the dodecane blend; the boiling point of dodecane is 489K, similar to that of naphthalene. This indicates that the rate of increase in the PN is lower with paraffins than with aromatic hydrocarbons. Also, the PN of the indene (454K boiling point) blend was more than three times the PN of other hydrocarbons of a similar boiling point, which shows that indene has a significant impact on PN increase.

As far as hydrocarbons alone are concerned, generally there is a correlation between boiling point and vapor pressure; i.e., boiling point increases with lower vapor pressure. The lower vapor pressure component will evaporate slowly resulting in diffusion combustion instead of pre-mixed combustion. This is likely the reason why the PN increased more when a hydrocarbon with a high boiling point was added to the fuel. Also, the PN increased more relative to the boiling point of the added substance when aromatic hydrocarbons were added than when paraffins were added. This is likely due to the difference in molecular structure between paraffins and aromatic hydrocarbons. Ogawa et al. argue that among the PM emitted from diesel engines, generation of dichloromethane-insoluble soot and PAHs can be effectively explained by the amount of diesel oil components of high boiling points and DBE (double bond equivalent) [6, 7, 8]. The same applies to gasoline engines, where generation of soot and PAHs likely depends on the DBE of each substance. The DBEs of paraffins are 0, while DBEs of aromatic hydrocarbons are about 4 to 7, although the specific value varies depending on the structure. This is probably why aromatic hydrocarbons resulted in more PM emissions than

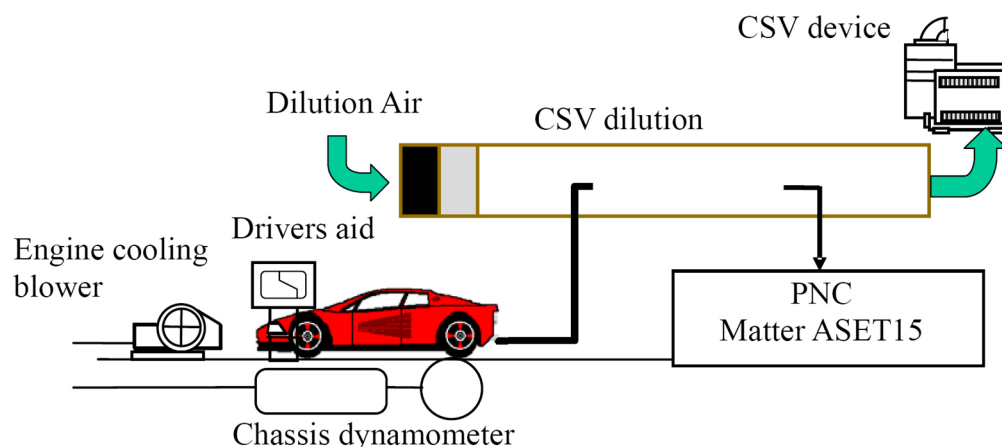


Fig. 1. PN measurement system

paraffins. Also, it is very interesting that indene, whose DBE of 6 is the same as that of divinylbenzene and whose boiling point is lower than that of divinylbenzene, resulted in a higher PN than divinylbenzene. This is likely because indene not only has a benzene ring but is also highly reactive and thus promoted growth of PAHs into soot.

Based on those results, PN is likely determined by the vapor pressure, DBE and reactivity of each gasoline component.

Table 1. Test engine specifications

	Test vehicle
Cylinder configuration	In-line 4-cylinder
Bore × Stroke [mm]	86 × 99
Displacement [cm ³]	2321
Compression ratio	8.8 : 1
Valve train	DOHC
Number of valves	4 valves / cyl
Fuel injection system	MPI
Turbocharger	Equipped

Table 2. Particulate counter specification

Model	MD19-2E + ASET15-1
Dilutor	Adjustable range 1:10 – 1:2000
PM counter	CPC 3010D
Maker	Matter Engineering

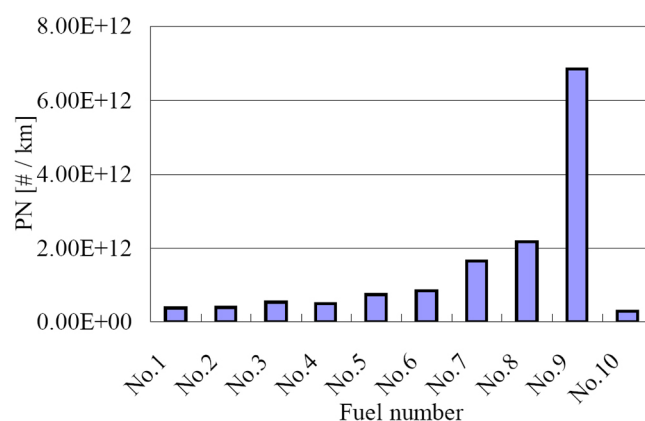


Fig. 2. PN of test fuels on NEDC

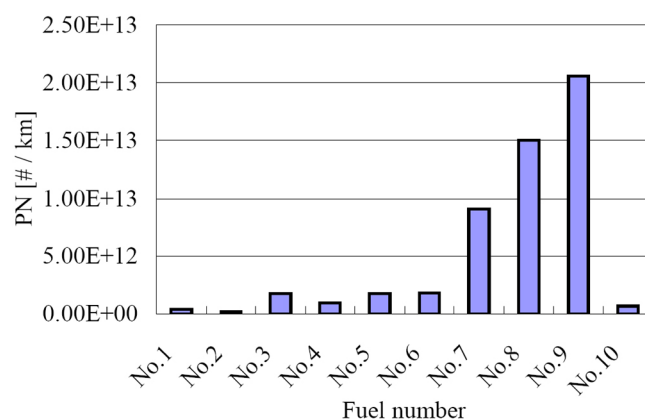


Fig. 3. PN of test fuels on 120km/h

NUMERICAL CONVERSION OF THE PN INCREMENT

The previous section predicted that the molecular structure that determines the vapor pressure, DBE, reactivity, etc., of each substance constituting the gasoline would have a great

Table 3. Test fuel characteristics

Fuel number	Designation	Weight fraction of additive (Wt %)	Boiling point of additives (K)	DBE of additives	PM Index of fuel
No.1	Base gasoline (Indolene)	-		-	1.36
No.2	BASE + 2,2,4 - Trimethylpentane	10.000	372	0	1.26
No.3	BASE + Dodecane	9.947	489	0	1.54
No.4	BASE + Ethylbenzene	9.364	409	4	1.44
No.5	BASE + Alpha Methylstyrene	9.275	436	5	1.62
No.6	BASE + 1,2,4 - Trimethylbenzene	9.417	442	4	1.69
No.7	BASE + Divinylbenzene	9.204	468	6	2.43
No.8	BASE + Naphthalene	9.075	491	7	3.74
No.9	BASE + Indene	9.132	455	6	(2.09)
No.10	BASE + Ethanol	21.070	351	0	1.09
No.11	Commercially available fuel in Japan	-	-	-	1.01
No.12	Commercially available fuel in Japan	-	-	-	2.94
No.13	Commercially available fuel in US	-	-	-	1.41
No.14	Commercially available fuel in Japan				1.99
No.15	Commercially available fuel in Japan	-	-	-	2.45
No.16	Commercially available fuel in Japan	-	-	-	2.78
No.17	Commercially available fuel in Japan	-	-	-	3.86
No.18	Euro 5 certification fuel	-	-	-	1.63

bearing on the effect the gasoline has on the PN. This section presents the results of analyzing such relationships.

As evident from the test results in the previous section, the PN increases significantly when the gasoline contains indene or other highly reactive substances. From the viewpoints of oxidation stability and reactivity, however, it is unlikely that highly reactive substances exist in large volumes in gasoline under normal circumstances. Accordingly, the results of indene are excluded in this analysis. The amount of the hydrocarbon added to each test gasoline was approximately 10 percent by weight relative to the base fuel, and thus the change in PN is nearly all attributable to the added substance. Regarding the generation of soot, which can be considered the bulk of the PM emission increment measured in the test, it generally increases as DBE increases. Also taken into consideration is the fact that the lower the boiling point of the substance, the higher its vapor pressure and the greater its chances of evaporating into the gas phase, thereby mitigating the formation of soot. Accordingly, the increment of PN, or ΔPN , in the test can be expressed in relation to the DBE and VP of the substance added, as follows:

$$\Delta PMN \propto \frac{f_{DBE}(DBE)}{f_{V.P}(V.P)} \times Wt \quad (1)$$

Here, Wt indicates the weight fraction of the added substance. The weight fraction factor reflects the fact that a component's concentration is proportional to the effect it will have upon PN emissions. The functions f_{DBE} and $f_{V.P}$ can take various forms and cannot be defined based on this experiment alone. Here, verification was attempted by assuming that both functions are simply proportional, directly or inversely, to ΔPN . To be specific, a new variable I which can consider the added substance effect in the test was defined, where this variable is calculated as follows:

$$I(V.P, DBE) = \frac{f_{DBE}(DBE)}{f_{V.P}(V.P)} \times Wt = \frac{DBE + 1}{V.P} \times Wt \quad (2)$$

Here, f_{DBE} is given as $DBE+1$ because paraffins, whose DBE is 0, are assumed to form no PM but still must be accounted for. That is, to allow the values of paraffins to be used as the reference, 1 was added to their DBE in the evaluation. Figure 4 shows the relationship of I calculated from the vapor pressure in units of kPa at 443K, and ΔPN . Fig. 5 shows the determination coefficients of the relationship of I and ΔPN at various temperatures, where the determination coefficient $R^2 = 0.9889$ at 443K best explains the relationship with ΔPN . In other words, ΔPN can be explained by the added substance's