

Research
Report

Effect of Hydrocarbon Molecular Structure on Diesel Exhaust Emissions

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燃料分子構造がディーゼル排気に及ぼす影響

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Abstract

In order to determine diesel fuel characteristics that might influence particulate matter (PM) emission, we have conducted a detailed investigation that combines combustion/exhaust emission measurements, in-cylinder observations, fuel analyses and chemical reactor experiments. A comparison between three representative diesel fuels, viz., “Base” (Japanese market fuel), “Improved”(lighter fuel with lower aromatics) and Swedish “Class-1” yielded the following results: (1) The amount of PM emission decreases in the order of “Base” > “Class-1” > “Improved”. Unexpectedly enough, “Class-1” produces more PM than “Improved” despite its significantly lower distillation temperature, and lower aromatics and sulfur content. (2) There is little difference in the combustion characteristics of the

three fuels. (3) Only “Class-1” contains significant quantities of iso and naphthenic structures. (4) Flow reactor pyrolysis shows that “Class-1” produces the largest amount of PM precursors, such as benzene and toluene. These results suggest that the presence of branched and ring structures can increase exhaust PM emissions. This finding was confirmed by flow-reactor and shock tube experiments using hexanes, which revealed that iso- and cyclo-paraffins produce more benzene and soot than n-paraffins do. The results obtained in this study indicate that the specific molecular structure of the paraffinic components needs to be considered as one of the diesel fuel properties closely related to PM formation.

Keywords

Diesel engine, Diesel fuel, Fuel properties, Hydrocarbon, Molecular structure, Emission, Particulate, Soot

要 旨

粒子状物質 (PM) 排出に関与する軽油性状因子を明らかにすることを目的に、エンジン排気・燃焼解析、筒内観察、軽油の精密分析および基礎反応実験による検討を行った。代表的3燃料 - Base (市販軽油)、Improved (若干の低沸点・低アロマ化)、Class-1 (大幅な低沸点・低アロマ・低硫黄化) - について比較検討した結果、一部で予想に反する興味深い事実を得た。(1)単筒ディーゼルからのPM排出量はBase > Class-1 > Improvedとなり、大幅な低沸点・低アロマ化を図ったClass-1の方がImprovedよりむしろPM排出量が多い。(2)燃料間で筒内燃焼特性にはほとんど差は無い。

(3) Class-1のみが多量のイソおよびナフテン構造を含む。(4)流動反応管による3軽油の熱分解の結果、Class-1が最も多くPM生成の前駆物質を生成する。これらの結果から、軽油中のイソおよびナフテン構造の増加がPMの増加を引き起こしたと推察した。また、ヘキサンを用いた基礎反応実験からも、イソおよびシクロ体がノルマル体に比べ、ベンゼンおよびすすを多く生成することが確かめられた。以上の事実から、PM低減のためには軽油中のパラフィン分子構造にも注意を払う必要があることを示した。

キーワード

ディーゼルエンジン，ディーゼル油，燃料性状，炭化水素，分子構造，排気，パーティキュレート，すす

1. Introduction

The reduction of diesel exhaust emissions, especially nitrogen oxides (NO_x) and particulate matter (PM), is an urgent problem to be tackled as the emission regulations become more and more stringent. Fuel sulfur levels have been lowered and the use of additives to maintain optimal engine performance has increased. There have been many studies of diesel fuel effects on exhaust emissions, especially on PM.¹⁾ The results suggest that reductions in sulfur, density, distillation temperatures and aromatic content (especially multi-ring aromatic content) lower PM emissions. However, fuel effects on the in-cylinder fuel-air mixture formation, combustion and chemical reaction processes remain largely unexamined. The ambiguity in previous studies makes it difficult to ascertain what fuel properties are the main, universal factors for PM reduction.

In this study, the fuel effects on not only exhaust emissions but also combustion characteristics and in-cylinder phenomena were carefully examined for three representative fuels. To account for the unexpected results obtained, the effect of the reactivity of chemical species in diesel fuel on PM formation was investigated.

2. Exhaust emissions and combustion characteristics of the representative diesel fuels²⁾

2.1 Test engines and fuels

Two kinds of single-cylinder engines were used as shown in **Table 1**. Engine A was used for the evaluation of exhaust emissions and combustion characteristics based on pressure indicator analysis, and Engine B for in-cylinder observation.³⁾ Both engines were equipped with an electronically controlled, common-rail type, high-pressure injection system.

The properties of the fuels are listed in **Table 2** and the distillation curves are shown in **Fig. 1**. Test fuel “Base” corresponds to the average market fuel in Japan. Test fuel “Improved” is the best fuel among those evaluated in a previous study.⁴⁾ “Class-1” is a sample of Swedish class-1 fuel used in Europe.

Table 1 Engine specifications.

	Engine A	Engine B
Type	Single-Cylinder DI Diesel NA	Single-Cylinder DI Diesel SC, Optical Accessible
Bore × Stroke	φ 94 × 100 mm	φ 102 × 110 mm
Displacement	694 cc	899 cc
Comp. Ratio	18.6	17.0
Valve System	In.: 2, Ex.: 2	In.: Liner Ports Ex.: Side Valve
Inj. System	Common-Rail System	
Inj. Nozzle	φ 0.15 mm × 6, VCO	φ 0.18 mm × 5, Mini Sac

Table 2 Fuel properties.

		Base	Improved	Class-1
Density g/cc @15 °C		0.838	0.821	0.815
Cetane Number		53.0	53.1	51.6
Cetane Index (IIS)		58	59	54
Viscosity cst @30 °C		3.546	2.989	2.390
Aromatics (HPLC) vol.%	Total	21.9	13.9	3.9
	Mono-	18.8	9.8	3.6
	Di-	1.9	3.4	0.3
	Tri-	1.2	0.7	ND
Sulphur mass %		0.05	0.06	0.00045
H / C		1.87	1.93	1.97
QL kJ/kg		42,890	43,079	43,167

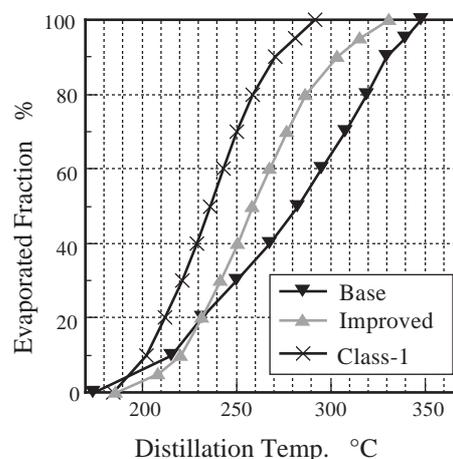


Fig. 1 Distillation curves.

2.2 Exhaust emissions

Figure 2 shows the exhaust emissions and the injection and combustion characteristics for the three

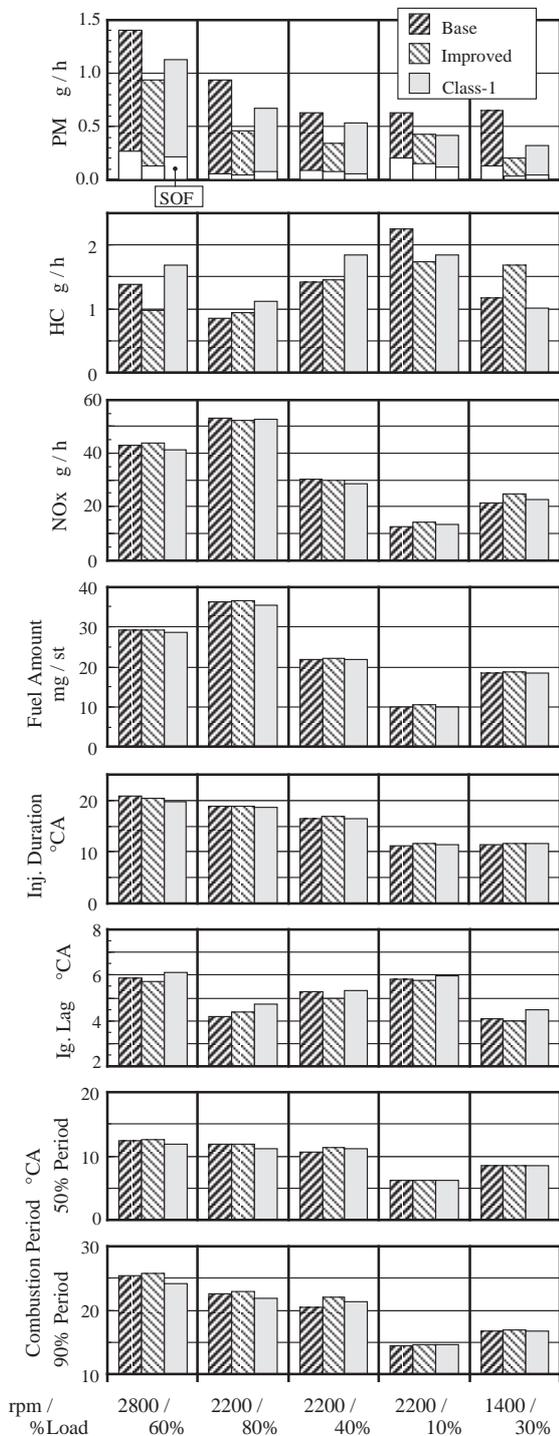


Fig. 2 Comparison of exhaust emissions and combustion characteristics (Engine A).

test fuels obtained under the five representative operating conditions.²⁾ The amount of PM from “Improved” and “Class-1” was significantly lower than that from “Base”, as to be expected. However, the order of exhaust PM quantity was “Base” > “Class-1” > “Improved” under virtually all operating conditions. Surprisingly, “Class-1” generated more PM than “Improved” despite its lower distillation temperature, aromatics and sulfur content, and density compared with “Improved”.

Both the mass-based fuel amounts and injection duration were virtually the same for the three fuels under all operating conditions. Ignition lag differences were very small as the cetane number of “Class-1” differs from those of the other two fuels by only about 1.5. In addition, the 50% and 90% combustion periods are almost the same.

From Fig. 2, it is clear that the three fuels do not differ much with respect to injection and macroscopic combustion characteristics. Thus, the differences in PM amount are considered to be attributable to differences in local in-cylinder phenomena and/or chemical reactions. To elucidate the causes, the in-cylinder mixture formation and combustion processes were investigated.

2.3 Mixture formation and combustion processes

Figure 3 shows the fuel-air mixture formation and flame development processes for the three fuels. “Improved” and “Class-1” exhibit the same in-cylinder trends. Thus, it is suspected that the difference in PM amount observed between the “Improved” and “Class-1” in the present study is mainly due to the difference in the chemical reactions that occur, which in turn is induced by the compositional difference between the two fuels.

3. Analysis of fuel composition²⁾

3.1 Fuel composition

Using a combination of Supercritical Fluid Chromatography, Mass Spectrometry and Gas Chromatography/Mass Spectrometry, the aromatic, naphthenic, and paraffinic contents of three fuels were determined. The results are shown in Fig. 4. The naphthene content in “Class-1” was found to be a minimum of 50 wt%, i.e., about twice the amount as in the other two fuels.

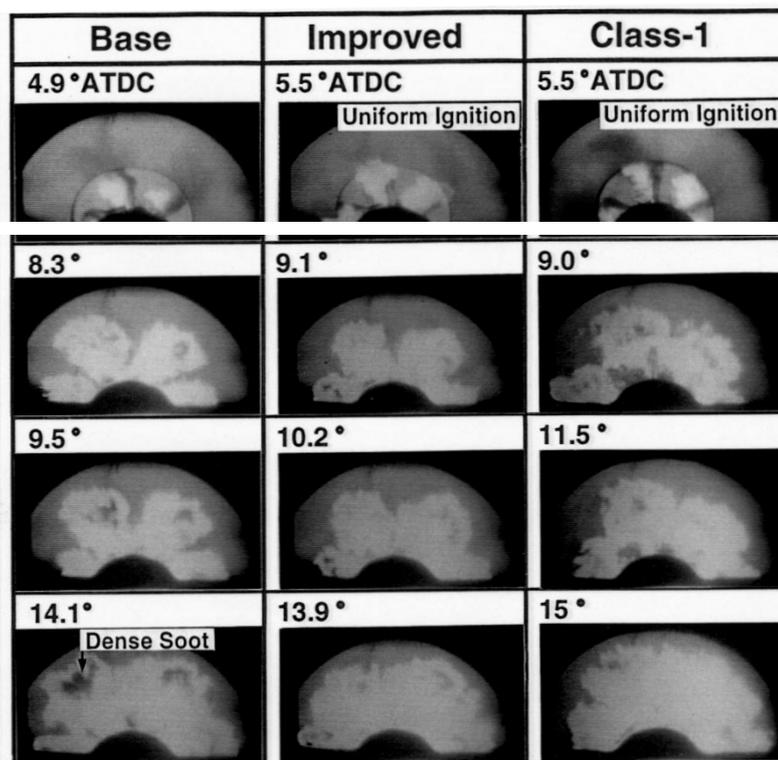
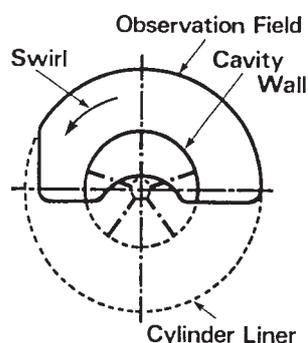


Fig. 3 Mixture formation and flame development processes for each fuel. (Engine B, 1800rpm, $\phi = 0.29$, $P_{inj} = 40\text{MPa}$, $IT = 0^\circ$ BTDC)

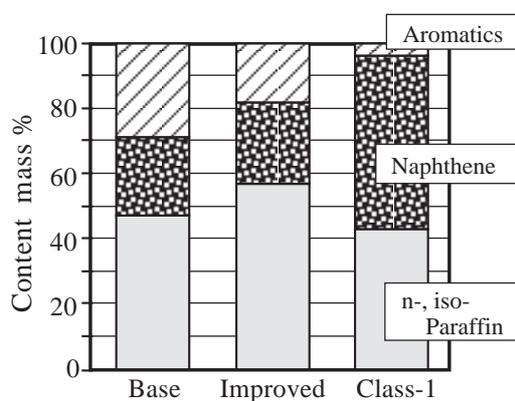


Fig. 4 Contents of representative components.

3.2 Branched structures in the saturated hydrocarbon portions

Table 3 tabulates the major peaks in the ^{13}C -NMR spectrum²⁾. The letters “a”, “b”, “c” and “d” correspond to the straight-chain hydrocarbon portions of the fuel, while “e” denotes the branched structure number in the saturated hydrocarbon portions of the fuel. The percentage of the peak area of “e” for “Class-1” is greater than 30%, i.e., indicating a higher iso-paraffin, iso-alkyl and branched structure content within the saturated hydrocarbon portions as compared to “Base” and “Improved”.

4. Effect of branched and ring paraffin structures on benzene and soot formation⁵⁾

The results in **Section 3** suggest that the PM emissions of the three fuels are probably influenced

maximum soot production near 2000°C. The maximum soot yields in bell shape are compared in Fig. 7. It is found that, compared with n-hexane, 2-methylpentane produces ca. 1.9 times as much soot, 2, 2-dimethylbutane ca. 3.9 times, and cyclohexane ca. 4.2 times. The soot formation in the high temperature range can be affected by paraffin molecular structure in the same manner as PM precursor formation at medium temperatures: in both cases, the formation yield increases in the order of normal paraffin, 1-branched iso-paraffin, 2-branched iso-paraffin and cycloparaffin.

5. Conclusion

In this study, we combine the research using chemical reactors with engine emission tests, exploring diesel fuel chemical characteristics that

might influence PM emissions. The combustion and exhaust emission characteristics of three representative diesel fuels were compared using single cylinder D.I. diesel engines, and the chemical components of the fuels were analyzed. It was found that: (1) PM emissions decreased in the order of “Base” > “Class-1” > “Improved”, suggesting that “Class-1” tested in this study unexpectedly produced more PM than “Improved” despite its significantly lower distillation temperature, and aromatics and sulfur content, (2) there was little difference in the combustion characteristics of the three fuels, and (3) only “Class-1” contained significant quantities of branched structures and naphthenes in the saturated hydrocarbon portion.

As a next step, the effect of the chemical reactivity of diesel fuel on PM formation was investigated.

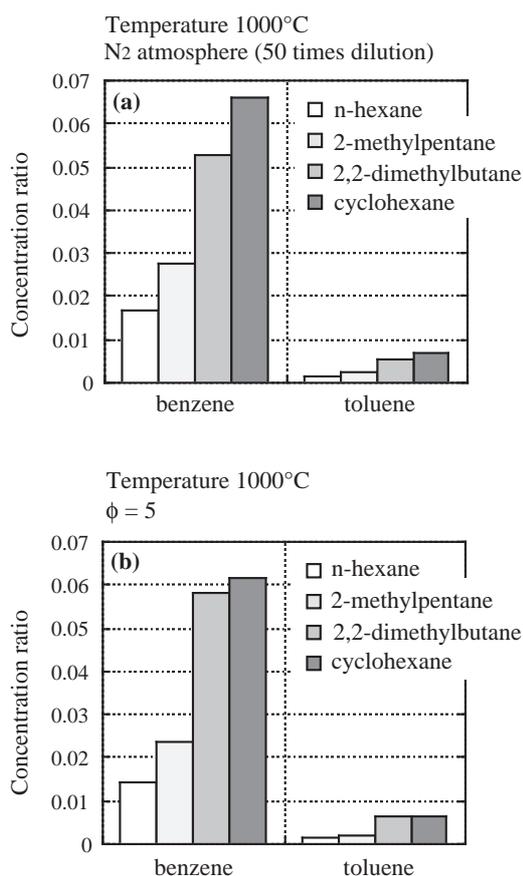


Fig. 6 Concentration of aromatic products.
(a) Pyrolysis of hexanes
(b) Oxidation of hexanes

Sample composition	Fuel	2.0 %
	O ₂	1.9 % (n-, iso-) 1.8 % (cyclo-)
	Ar	96.1 % (n-, iso-) 96.2 % (cyclo-)
Equivalence ratio		10
Pressure		1.0 - 1.4 atm
[C] ₀		2.8×10^{17} atoms/cc

[C]₀: Initial carbon atom concentration in reflected shock zone

$$\text{Soot yield} = \frac{\text{Total carbon number accumulated in soot}}{\text{Initial total carbon number in fuel in reflected shock zone}}$$

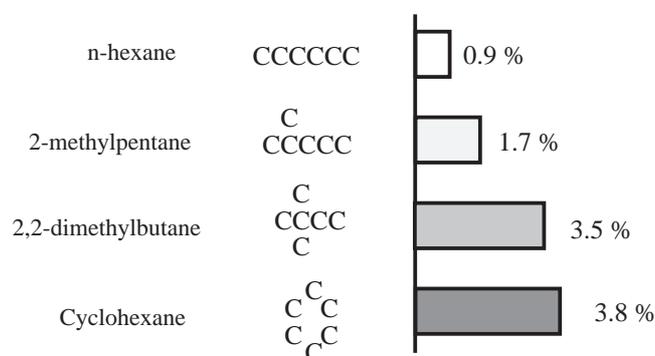


Fig. 7 Comparison of soot yield at bell peak for various hexanes.

The flow-reactor results showed that “Class-1” produced the largest amount of PM precursors, such as benzene and toluene, among the three fuels, despite its very low aromatics content. These results suggest that the presence of branched and ring structures can increase exhaust PM emissions. This finding was confirmed by flow reactor experiments with hexane isomers, which revealed that iso- and cycloparaffins produce more benzene than n-paraffins. With branched hexane isomers, the benzene amount increased with the number of branches. The shock tube measurements of fuel-rich oxidation near 2000°C showed that the soot formation yield increases in the order of n-hexane, 2-methylpentane, 2, 2-dimethylbutane and cyclohexane.

The results obtained in this study indicate that the specific molecular structure of the paraffinic components should be considered as one of the diesel fuel properties closely related to PM formation.

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