

Unregulated Harmful Substances in Exhaust Gas from Diesel Engines

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ABSTRACT

The volatile organic compounds (VOC) from diesel engines, including formaldehyde and benzene, are concerned and remain as unregulated harmful substances. The substances are positively correlated with THC emissions, but the VOC and aldehyde compounds at light load or idling conditions are more significant than THC. When coolant temperatures are low at light loads, there are notable increases in formaldehyde and acetaldehyde, and with lower coolant temperatures the increase in aldehydes is more significant than the increase in THC. When using ultra high EGR so that the intake oxygen content decreases below 10%, formaldehyde, acetaldehyde, benzene, and 1,3-butadiene increase significantly while smokeless and ultra low NOx combustion is possible.

INTRODUCTION

The volatile organic compounds (VOC) from diesel engines, including aldehydes which also cause the sick-house syndrome and benzene which is a carcinogen, are concerned and remain as unregulated harmful substances [1-9]. Twelve substances including formaldehyde from diesel engines have been listed as unregulated harmful substances in Japan and emission characteristics of formaldehyde, 1,3 butadiene, benzene, and benzo[a]pyrene have been reported [3]. However, the characteristics of these substance emissions have not been sufficiently elucidated yet. As it is considered that these volatile organic substances often have positive correlations to THC, the characteristics of unregulated harmful exhaust gas emissions have to be

grasped under high THC emission including low coolant temperature conditions [4]. While the low temperature diesel combustion (LTC) and the premixed charge compression ignition combustion (PCCI) can simultaneously realize ultra low NOx and low particulate emissions, high levels of VOCs and PAHs (polycyclic aromatic hydrocarbons) as well as unburned HC and CO emissions are observed with these new combustion regimes [5-8].

In this research eleven of the twelve unregulated harmful substances (except for benzo[a]pyrene which is a non-volatile compound), were measured to clarify the characteristics of unregulated harmful exhaust gas emissions from a diesel engine under several operating conditions. First, the characteristics of these unregulated substance emissions under diesel eight-mode off-road diesel engine operation were investigated. Next, formaldehyde, acetaldehyde, 1,3-butadiene, benzene, and toluene under conditions with high THC emissions including low engine coolant temperatures and extremely high EGR rates were measured.

EXPERIMENTAL APPARATUS AND PROCEDURES

Experiments were conducted on a single cylinder, naturally aspirated, four-stroke cycle, 1.9 L DI diesel engine (Nissan Diesel, PR-6) with a common rail fuel injection system. Table 1 shows the engine specifications. The dynamic fuel injection timing is kept at 4°CA BTDC for all conditions except the experiment on the effect of EGR shown in Figs. 8, 9, and 10. In the experiment on the effect of EGR, the ignition timing was kept at the TDC determined by the fuel injection timing

Table 1 Specifications of the test engine

Bore x stroke	134 x 140 mm
Displacement	1950 cm ³
Compression ratio	18
Swirl ratio	2.2
Injection pressure	120 MPa
Nozzle	φ0.19 x 4
Combustion chamber	Toroidal
Fuel	Diesel fuel (JIS No.2)

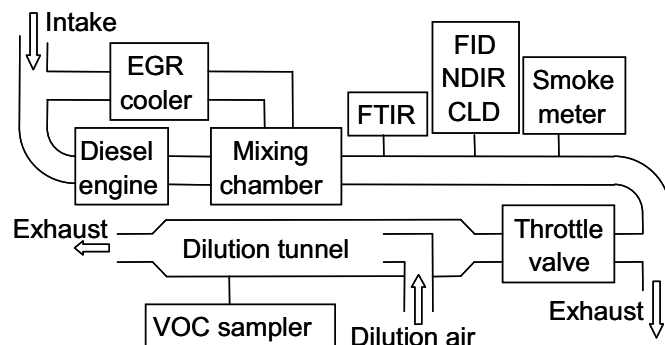


Fig. 1 Experimental apparatus

Table 2 Measured volatile unregulated exhaust gases

	Compound	Analyzer
Olefin	1,3-Butadien	GC/MS, FTIR
Aromatic	Benzene	GC/MS, FTIR
	Toluene	GC/MS, FTIR
	Ethylbenzene	GC/MS
	Xylene	GC/MS
	Styrene	GC/MS
	1,3,5-Trimethylbenzene	GC/MS
Aldehyde	Formaldehyde	HPLC, FTIR
	Acetaldehyde	HPLC, FTIR
	Acrolein	HPLC
	Benzaldehyde	HPLC

as the ignition delay changed significantly with the intake oxygen content.

The engine coolant temperature was kept constant at 80°C except the experiment on the influence of the engine coolant temperature. The coolant was circulated between the engine and a tank (20 l) with a water pump, and the temperature was maintained with addition of cold water into the tank.

The exhaust gas recirculation (EGR) was realized by diverting a part of the exhaust gas cooled by an EGR cooler into the intake port, and the intake gas temperature was kept below 30°C. The EGR rate was defined as the volume fraction of the EGR gas to the total intake gas.

The Measured volatile unregulated exhaust gases in the experiments are listed in Table 2 and an outline of experimental setup is shown in Fig. 1. For the analysis of the eight-mode test, the exhaust gas, diluted with ten times the volume of air via a dilution tunnel was sampled in an air-evacuated stainless steel canister. Aromatic hydrocarbons and 1,3-butadiene were quantified with GC-MASS spectroscopy (GC/MS), and aldehydes were quantified with high performance liquid chromatography

Table 3 Details of GC-MASS

Column	HP-1 φ0.32mm x 60 m
Column temp.	35°C (7min) ↓ 5°C/min 100°C ↓ 15°C/min 220°C (6 min)
Ionization	EI
Interface temp.	250°C
Injection temp.	220°C
Carrier gas	He 1.0 mL/min
Detection	SIM

Table 4 Details of HPLC

Column	Waters Nova-Pak C18 3.9 x 150 mm
Column temp.	40°C
Mobile phase	A: H ₂ O/CH ₃ CN/THF (70/20/5) B: H ₂ O/CH ₃ CN (40/60) 100%A (3 min) ⇒ 3~30 min ⇒ 100%B (12min) ⇒ 42~50 min ⇒ 100%A (10 min) Flow rate: 1.5 mL/min
Injection quantity	20 μL

(HPLC). The details of GC/MS and HPLC are listed in Tables 3 and 4. An FTIR engine exhaust gas analyzer (Horiba, MEXA-4000FT) was also used to measure formaldehyde, acetaldehyde, 1,3-butadiene, benzene, and toluene under low coolant temperature and extremely high EGR rate conditions. The total hydrocarbon (THC) was analyzed with an automotive exhaust gas analyzer (Horiba, MEXA-8120) and a high-pressure flame ionization detector).

EXPERIMENTAL RESULTS AND DISCUSSION

CHARACTERISTICS OF ELEVEN VOLATILE UNREGULATED HARMFUL SUBSTANCES IN EXHAUST GAS DURING DIESEL EIGHT-MODE OPERATION – The volatile unregulated harmful substances in exhaust gas at each BMEP condition in the diesel eight-mode operation are shown in Fig. 2 (1,3-butadiene and aldehydes) and in Fig. 3 (Aromatic hydrocarbons). Here, aldehydes are analyzed with HPLC, and 1,3-butadiene and aromatic hydrocarbons are analyzed with GC/MS. The engine speeds were set at 1600 rpm for the rated engine speed, at 1200 rpm for the medium engine speed, and at 800 rpm for the idling. The dynamic injection timing is kept at 4°CA BTDC for all conditions. All the volatile unregulated harmful substances increase at low BMEP, and especially at 10% load (BMEP = 0.05 MPa, 1600 rpm), they show very high concentrations. At idling (800 rpm), the concentrations of formaldehyde and acetaldehyde are relatively high around 40 ppm, and other emissions are also high. All emissions at idling are

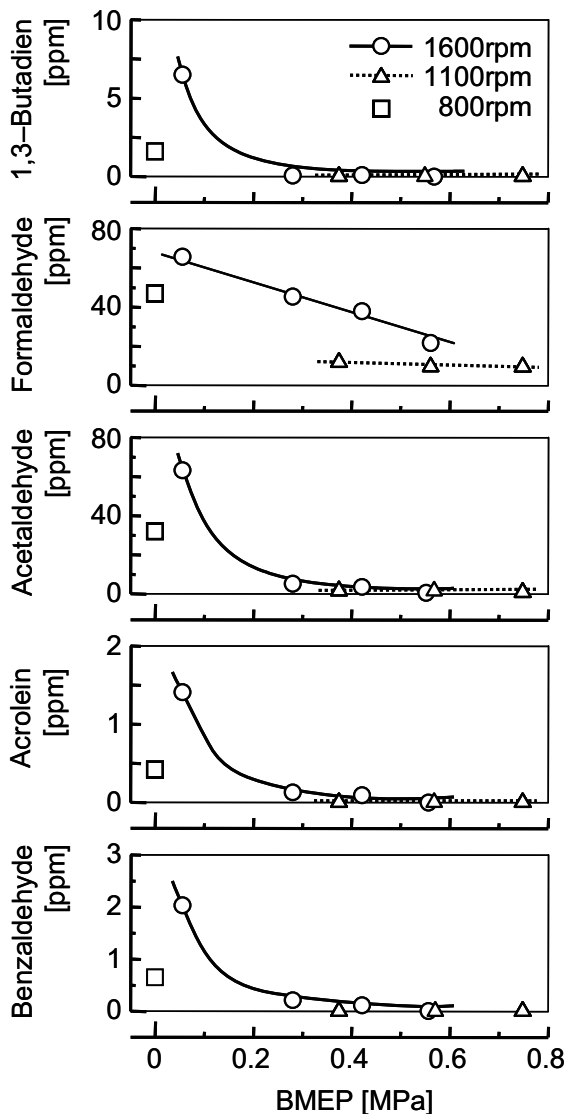


Fig. 2 1,3-butadiene and aldehyde emissions at each BMEP in the diesel eight-mode

lower than at 10% load (BMEP = 0.05 MPa, 1600 rpm), but higher than at medium and high BMEP conditions. At both 1200 rpm and 1600 rpm, most of the concentrations are low at medium and high BMEP conditions while formaldehyde at the medium BMEP at 1600 rpm is relatively high.

Fig. 4 shows the total quantities emitted per unit work (1 kW·h) of unregulated harmful substances in exhaust gas during diesel eight-mode operation. While the formaldehyde and acetaldehyde quantities are relatively high, the other substances are very low.

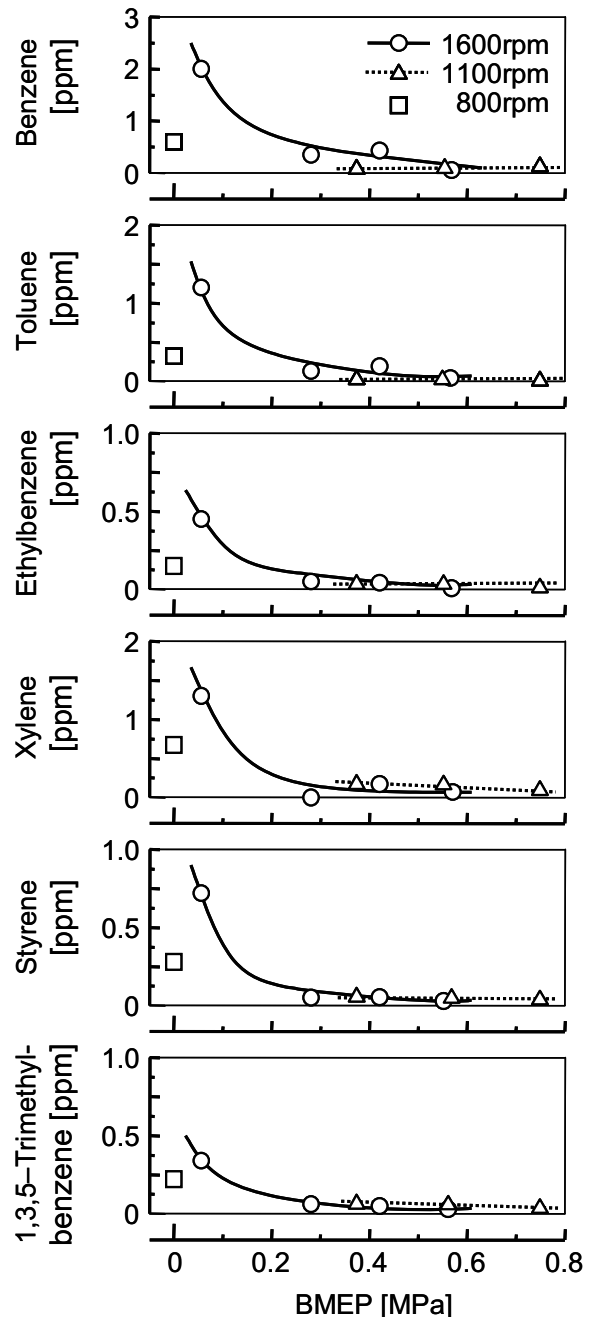


Fig. 3 Aromatic hydrocarbon emissions at each BMEP in the diesel eight-mode