Results of on-line measurement of organic compounds adsorbed on diesel exhaust particles by PTR-TOFMS

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Abstract

Organic compounds in particle-phase of diesel emission are of interest in view of particle nature and origin. In this work, particle-phase organic compounds from a modern diesel engine were analyzed using on-line PTR-TOFMS (Proton Transfer Reaction – Time of Flight Mass Spectrometer). To analyze particle-phase organic compounds, sampled exhaust was passed through a heating tube upstream of PTR-TOFMS. The results show that higher molecular weight compounds had higher portion in particle-phase and concentration changes corresponded to operating condition change of the engine.

Introduction

Diesel exhaust is composed of a large number of gaseous and particle-phase compounds. Diesel exhaust particles are known to be toxic, so it is important to analyze chemical composition of particles as well as gaseous compounds. Size distributions of diesel particles are shown in Fig.1. Diesel particle filter (DPF) reduces particles in entire size range.

In this work PTR-TOFMS was used to analyze exhaust emissions from a modern diesel engine. Transient behavior of gaseous organic compounds (i.e. volatile organic compounds VOCs), such as benzene, toluene, and acetaldehyde were detected at as low as 1ppb level (Fig.2). In order to analyze particle-phase compounds by PTR-TOFMS, a heating tube was installed upstream of PTR-TOFMS. This paper shows results of analysis of particle-phase volatile compounds of engine out emission measured by PTR-TOFMS.

Experimental Methods (Continued)

The diluted exhaust for PTR-TOFMS was passed through a heating tube which enables particle-phase compounds to evaporate. Thus PTR-TOFMS is capable of analysis of particle-phase compounds in addition to gaseous compounds. Additional measurements were conducted by exhaust gas analyzers (THC, NOx etc.) and particle sizing instrument (EEPS).

Results and Discussion (Continued)

To investigate particle-phase organic compounds, 2 experiments were conducted. First, the heating tube was kept at lower temperature (100 degC) to analyze gaseous organic compounds. Second, the heating tube was kept at higher temperature (300 degC) to analyze gaseous and particle-phase organic compounds. The 2 TOF mass spectra are shown in Fig.6. The difference between 2 mass spectra corresponds to particle-phase compounds.

Table 1 Measurement conditions of PTR-TOFMS

<table>
<thead>
<tr>
<th>Measurement conditions</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emission method</td>
<td>Proton Transfer Reaction by H_3O^+</td>
</tr>
<tr>
<td>Mass spectrometer</td>
<td>High resolution Time of Flight type</td>
</tr>
<tr>
<td>Mass range &amp; resolution</td>
<td>1 to 600, Ca. 3500</td>
</tr>
<tr>
<td>Averaging time</td>
<td>1 sec</td>
</tr>
</tbody>
</table>

Fig. 1 Size distributions of diesel particles with and without DPF

Fig. 2 Concentration change of gaseous compounds from diesel engine measured by PTR-TOFMS.

Experimental Methods

A LD diesel engine (displacement 3L with turbo-intercooler) was used to analyze diesel particles by PTR-TOFMS. Experimental setup is shown Fig.3. To measure engine out emission, DPF was not installed the engine. Exhaust was sampled from an exhaust pipe to a partial flow dilution system. In the dilution system the sampled exhaust was mixed with dilution air and the dilution ratio (DR) was kept constant (15:1). The diluted exhaust was then split into 2 flows, one for PTR-TOFMS and the other for particle filter.

Results and Discussion

The engine operations condition (speed and torque) and THC and particle number concentrations are shown in Fig.4. The engine was operated in a stepwise operation test cycle (World Harmonized Stationary Cycle - WHSC). THC and particle concentrations raised sharply around 200s, and THC concentration was higher at lower torque.

The diluted exhaust was measured using PTR-TOFMS with the heating tube upstream. The exhaust was sampled into the partial dilution system. The diluted exhaust was cooled to lower temperature than 52 degC. Averaged size distribution of particles of WHSC is shown in Fig.5.

Fig.3 Experimental setup of diesel exhaust measurement by PTR-TOFMS.

Fig. 4 THC and particle number concentrations during WHSC test.

Fig. 5 Size distribution of particles of WHSC.

Reference


Fig. 6 Averaged TOF mass spectra of gaseous compounds and compounds evaporated from particles of WHSC.

Concentration change of selected hydrocarbon compounds are shown in Fig.7. Higher molecular weight compounds had higher portion in particle-phase and concentration changes corresponded to operating condition change of the engine.