Nanoparticle characteristics with the latest after-treatment systems on the market
-Urea SCR systems and DPNR-

Sousuke Sasaki, Yoshio Tonegawa, Toru Nakajima
(Japan Automobile Research Institute)

1. INTRODUCTION
Recent stringent regulation for automobile exhaust brings us many kinds of after-treatment systems on the market. Particle size is one of the important factors for evaluating the health effects of its new technologies. In this report, nanoparticle emissions from a heavy duty diesel truck equipped with an urea SCR system (SCR-HDV, complied with 2005 exhaust regulation) and a light duty diesel engine equipped with DPNR system (DPNR-LDE, Complied with 2003 exhaust regulation) which technologies will be expected to glow its demand in the future were investigated.

2. EXPERIMENTAL METHODS
Particle size distributions from urea SCR system and DPNR system were measured with the partial flow dilution system (PPFDII) which was designed to reproduce dilution process in the atmosphere. Temperature and relative humidity of dilution air were controlled at 25 degree C and 50 % respectively. Double dilution system was employed and dilution ratio was fixed by 200 (15 x 13.4). Particle size distributions were measured by DMS500. SCR-HDV (25t, 9.2L with SCR system, complied with 2005 exhaust regulation), HDE (as a reference engine, same type of 9.2L engine without after-treatment system, complied with 1999 exhaust regulation) and DPNR-LDE (4L,complied with 2003 exhaust regulation) were investigated. Test fuel was commercial diesel fuel which sulfur content was 6 ppm by weight. These engines and vehicle were derived under the Japanese transient test mode i.e. JE05. Cold start and hot start test were conducted to observe the particle behavior under these conditions. Nano particle characteristic of SCR-HDV was observed with the thermo denuder. Effect of urea water on particle size was also investigated under the artificial condition in which urea water was injected outside of the SCR system without changing ECU control. Particle emissions of forced regeneration period were observed after low load and middle speed driving by DPNR-LDE.

3. RESULTS AND DISCUSSION
3.1 SCR system
Particle size distribution of SCR-HDV were compared with HDE complied with 1999 regulation. Nuclei mode particles which were usually observed with HDE at the deceleration period were reduced well by the effect of two oxidation catalysts located in both side of SCR and whole particles were decreased in SCR-HDV. Mean diameter of average size distribution for SCR-HDV was smaller than that for HDE. There were no differences between cold start and hot start driving on it particle size distributions. Injection of urea water for the reduction of nitrogen oxides did not affect on the size distributions. Thermo-denuder test for volatility of particles at the temperature of 300 degrees and changes of relative humidity for dilution air from 20% to 80% did not show the significant change of size distribution. Therefore these particles from SCR-HDV can be solid and non-hygroscopic particle. The condition of cold start did not change the size distribution.

3.2 DPNR system
Particle number concentration of DPNR system was very low and close to noise level of DMS measurement. Forced regeneration period of DPNR, concentration of particles is increased temporarily, and then it reduces at the level of before regeneration in next fifteen minutes. Frequency of forced regeneration was estimated by the literature data as once par 220 km diving under the condition that did not allow continuous PM oxidation.

4. CONCLUSION
Nanoparticle emissions from the latest after-treatment systems i.e. SCR-HDV and DPNR-LDE on the market were investigated. Average size distribution of SCR-HDV under the transient test cycle showed that these particles were mainly accumulation mode particle and nuclei mode particles were not observed. Influential factors on size distribution for the SCR-HDV, i.e. warm-up condition (cold and hot start), relative humidity of dilution air and injection of urea water hardly affect particle size distributions. Particle number concentration of DPNR-LDE was very low. Forced regeneration period of DPNR, concentration of particles was increased temporarily, and then reduced at the level of before regeneration in next fifteen minutes.
Nanoparticle Characteristics with the Latest After-Treatment Systems on the Market

Japan Automobile Research Institute
Sousuke Sasaki
Yoshio Tonegawa
Toru Nakajima
Introduction

● Feature of Selective catalytic reduction system (SCR)
  ● PM and fuel consumption can be reduced by improving of combustion with engine modifications. NOx is reduced by SCR system separately.

● Feature of Diesel Particulate –NOx Reduction system (DPNR)
  ● Simultaneous reduction of NOx and Particulate

→ More detail analysis is required on number concentration
Objective

- Investigation of nanoparticle characteristics from the SCR system and DPNR system under transient test cycles
  - Size distribution, Average diameter, Particle number concentration
  - Cold start, Hot start
  - Specification of nanoparticles
  - Effect of urea water on nanoparticles (SCR)
Test procedure

- Test vehicle and engine
  - **SCR**: Heavy duty diesel truck (25t, 9.2L, 2005)
    - Ref: Heavy duty diesel engine (9.2L, 1999)
  - **DPNR**: Medium duty diesel engine (4.0L, 2003)
- Fuel: market diesel fuel (**Sulfur 6 wt ppm**)
- Test mode: Transient mode (**JE05**)
  - trial of cold start test
  - applied for C/D test
Experimental setup (PPFDII)

After treatment

1st dilution

2nd dilution
dilution ratio: 200 (15x13.3)
25°C, 50%RH
View of experiment

Without urea injection
Result SCR

- Nanoparticulate behavior
  - Size distribution, Average diameter, number concentration
- Average size distribution
  - Cold start, Hot start
- Specification of nanoparticle
  - Effect of humidity on size distribution
  - Evaporative specification by thermo denuder
- Effect of urea water on nanoparticle
Urea SCR System

\[
\begin{align*}
CO(NH_2)_2 + H_2O & \rightarrow 2NH_3 + CO_2 \\
4NO + 4NH_3 + O_2 & \rightarrow 4N_2 + 6H_2O \\
6NO_2 + 8NH_3 & \rightarrow 7N_2 + 12H_2O \\
NO + NO_2 + 2NH_3 & \rightarrow 2N_2 + 3H_2O
\end{align*}
\]

Source: Hirata et al. SAE 2005011860
Nanoparticle behavior
Detail analysis
Size distribution

Nuclei mode particles are not observed
Nanoparticle behavior

Detail analysis 1  Number and Mean diameter

Comparison with 1999 engine, # is reduced and particle size is smaller
Result Urea-SCR

- Nanoparticle behavior
  - Size distribution, Average diameter, # concentration
- Average size distribution
  - Cold start, Hot start
- Specification of nanoparticle
  - Effect of humidity on size distribution
  - Evaporative specification by thermo denuder
- Effect of urea water on nanoparticle
JE05  Average size distribution under the transient test cycle

Nuclei mode particles disappear and accumulation mode particles are reduced

![Graph showing average size distribution under the transient test cycle. The graph compares the number of particles per log diameter (dN/dlogDp) across different engine types and compliance years. The x-axis represents mobility diameter in nm, while the y-axis shows the number of particles per log diameter. The graph indicates a decrease in nuclei mode particles and a reduction in accumulation mode particles for SCR-HDDV (complied with 2005) compared to the same type of engine (complied with 1999).]
Comparison of cold start and hot start

Differences are negligible
Result Urea-SCR

- Nanoparticle behavior
  - Size distribution, Average diameter, # concentration
- Average size distribution
  - Cold start, Hot start
- Specification of nanoparticle
  - Effect of humidity on size distribution
  - Evaporative specification by thermo denuder
- Effect of urea water on nanoparticle
Volatile specification by thermo denuder

Main components are solid or higher volatile particles
Effect of relative humidity on size distribution

Relative humidity does not affect size distribution (RH 30% to 80%)
⇒These particles are not hygroscopic particles
Result Urea-SCR

- Nanoparticle behavior
  - Size distribution, Average diameter, # concentration
- Average size distribution
  - Cold start, Hot start
- Specification of nanoparticle
  - Effect of humidity on size distribution
  - Evaporative specification by thermo denuder
- Effect of urea water on nanoparticle
Effect of urea water on nanoparticles

no effects on size distribution

Idling

Acceleration

Deceleration

Others

with Urea injection

without Urea injection
Conclusion - Urea SCR system

- Accumulation mode are main particles from Urea-SCR system.
- Nuclei mode particles are not observed even the deceleration period. (Oxidation catalysts work effectively).
- Injection of Urea water does not affect size distribution.
Result-DPNR

- Average size distribution
  - Cold start, Hot start
- Regeneration
DPNR System

Source: SAE2004-01-0579, Shoji et al.
Average size distribution

JE05 test cycle

![Graph showing average size distribution with Cold start, Hot start, and Noise level curves.]
Result-DPNR

- Average size distribution
  - Cold start, Hot start
- Regeneration
Nanoparticle behavior during and after regeneration

Low load driving for 2hrs causes automatic regeneration (forced regeneration by fuel injection)

Regeneration 170s

Temporally, particles are emitted but reduced to the initial level in a short time

Engine out level: OEM data
Estimation for the frequency of regeneration w/o continuous PM oxidation

Figure 9. Pressure Loss Transition of DPNR
Created running pattern at an average vehicle speed of 12 km/h to simulate driving on a congested urban road. The temperature of the DPNR catalyst during the driving in the range from approximately 100 degrees C to 150 degrees C under the condition that did not allow continuous PM oxidation. Source: A. Shoji et al. (Toyota). SAE2004-01-0579

45 times regeneration during 10000 km driving
= about one regeneration / 220km
Conclusion- DPNR

- Concentration of particles are very low
- Forced Regeneration after low load driving,
  - Particles emit for some period during regeneration and just after regeneration
  - Frequency of forced regeneration is low and average particle number per km is negligible
Thank you for your kind attention
## Fuel specification

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit(s)</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>15°C g/cm³</td>
<td>0.8279</td>
</tr>
<tr>
<td>Flash Point</td>
<td>PM°C</td>
<td>71.0</td>
</tr>
<tr>
<td>Kinetic Viscosity</td>
<td>mm²/s@30°C</td>
<td>3.734</td>
</tr>
<tr>
<td>Pour Point</td>
<td>°C</td>
<td>-15.0</td>
</tr>
<tr>
<td>Sulfur</td>
<td>Mass %</td>
<td>0.0006</td>
</tr>
<tr>
<td>Distillation Properties</td>
<td>°C 90 %</td>
<td>339.5</td>
</tr>
<tr>
<td>Cetane Index</td>
<td></td>
<td>57.3</td>
</tr>
<tr>
<td>Total Calorimetric Value</td>
<td>J/g</td>
<td>45890</td>
</tr>
<tr>
<td>C.F.P.P</td>
<td>°C</td>
<td>-8</td>
</tr>
</tbody>
</table>
# Specification of test engines and vehicle

<table>
<thead>
<tr>
<th></th>
<th>HDDE</th>
<th>HDDV</th>
<th>HDDE</th>
</tr>
</thead>
<tbody>
<tr>
<td>After treatments</td>
<td>DPNR</td>
<td>Urea SCR</td>
<td>non</td>
</tr>
<tr>
<td>Exhaust gas regulation</td>
<td>2003</td>
<td>2005</td>
<td>1999</td>
</tr>
<tr>
<td>Gross vehicle weight</td>
<td>—</td>
<td>24840 kg</td>
<td>—</td>
</tr>
<tr>
<td>Engine displacement</td>
<td>4.0L</td>
<td>9.2L</td>
<td>←</td>
</tr>
<tr>
<td>Fuel injection</td>
<td>Common rail DI</td>
<td>Common rail DI</td>
<td>←</td>
</tr>
<tr>
<td>EGR system</td>
<td>Cooled EGR</td>
<td>Cooled EGR</td>
<td>←</td>
</tr>
</tbody>
</table>
DMS: Differential Mobility Spectrometer

Sample Aerosol → Aerosol Charger → Sheath air flow → Charged Particle → Grounded Electrode → Sheath air flow → Charged Particle → High voltage electrode
Urea water

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Urea</td>
<td>32.5 mass%</td>
</tr>
<tr>
<td>Water</td>
<td>67.5 mass%</td>
</tr>
<tr>
<td>Standardized</td>
<td>JIS K2247-1</td>
</tr>
</tbody>
</table>
# Measuring condition

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dilution ratio (DR1xDR2)</td>
<td>200 (15 x 13.3)</td>
</tr>
<tr>
<td>Temperature of dilution air</td>
<td>25 °C</td>
</tr>
<tr>
<td>Relative humidity of dilution air</td>
<td>50 %RH</td>
</tr>
<tr>
<td>DMS sampling rate</td>
<td>10 Hz</td>
</tr>
</tbody>
</table>
Calculation of emission ratio

dN/d\log Dp \ [/s]

= \frac{dN}{d\log Dp} \ [m^{-3}] \times \text{Exhaust flow rate} \ [m^3/s] \times \text{Dilution ratio}
### Time schedule of preconditioning

<table>
<thead>
<tr>
<th>Test mode</th>
<th>DPNR engine</th>
<th>Urea-SCR Vehicle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test mode</td>
<td>JE05 (min)</td>
<td></td>
</tr>
<tr>
<td>Start</td>
<td>Hot</td>
<td>Hot</td>
</tr>
<tr>
<td>Warming up</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Full load/speed</td>
<td>20</td>
<td>10</td>
</tr>
<tr>
<td>Engine stop</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Dummy mode</td>
<td>30.5</td>
<td>30.5</td>
</tr>
<tr>
<td>Engine stop</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Measurement</td>
<td>30.5</td>
<td>30.5</td>
</tr>
</tbody>
</table>

JE05 mode is applied for a vehicle test
Preconditioning is partly changed, Trial of cold start test
Differences between cold and hot start

**Graph:**
- X-axis: Time [s]
- Y-axis (left): Exhaust Temperature
- Y-axis (right): Normalized Cumulative Particle Number

**Legend:**
- Green: ΔExhaust Temp. (hot-cold)
- Blue: Cold start
- Red: Hot start
- Purple: ΔNumber (Cold-Hot)
- Pink: Engine speed pattern

**Engine speed pattern:**
- High
- Low

**Notes:**
- ΔNumber (Cold-Hot) represents the difference in particle number between cold and hot starts.
- Engine speed pattern indicates the variation in engine speed during the start-up process.
Differences between cold and hot start SCR

![Graph showing differences between cold and hot start SCR](image-url)