High NO$_2$/NO$_x$ emissions downstream of the catalytic diesel particulate filter: An influencing factor study

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ABSTRACT

Diesel vehicles are responsible for most of the traffic-related nitrogen oxide (NO$_x$) emissions, including nitric oxide (NO) and nitrogen dioxide (NO$_2$). The use of after-treatment devices increases the risk of high NO$_2$/NO$_x$ emissions from diesel engines. In order to investigate the factors influencing NO$_2$/NO$_x$ emissions, an emission experiment was carried out on a high pressure common-rail, turbocharged diesel engine with a catalytic diesel particulate filter (CDPF). NO$_2$ was measured by a non-dispersive ultraviolet analyzer with raw exhaust sampling. The experimental results show that the NO$_2$/NO$_x$ ratios downstream of the CDPF range around 20%–83%, which are significantly higher than those upstream of the CDPF. The exhaust temperature is a decisive factor influencing the NO$_2$/NO$_x$ emissions. The maximum NO$_2$/NO$_x$ emission appears at the exhaust temperature of 350°C. The space velocity, engine-out PM/NO$_x$ ratio (mass based) and CO conversion ratio are secondary factors. At a constant exhaust temperature, the NO$_2$/NO$_x$ emissions decreased with increasing space velocity and engine-out PM/NO$_x$ ratio. When the CO conversion ratios range from 80% to 90%, the NO$_2$/NO$_x$ emissions remain at a high level.

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Introduction

Nitrogen dioxide (NO$_2$) represents an important urban pollutant in most countries. Epidemiologic studies show strong evidence for an association between NO$_2$ exposure and adverse human health effects, especially respiratory morbidity (Wolfe and Patz, 2002; EPA US, 2008). Besides its toxicity to humans, NO$_2$ can also lead to increasing photochemical ozone production, which then impacts the air environment (Zielinska, 2005; Ma et al., 2013). Concerns over the health impacts of NO$_2$ have prompted legislation at a national and international level (EPA US, 2010). In Europe, the EU First Daughter Directive (99/30/EC) sets an annual mean limit of 40 µg/m$^3$ and an hourly limit of 200 µg/m$^3$ not to be exceeded on more than 18 occasions each year (Council Directive, 1999/30/EC, 1999).

With the enforcement of stringent emission standards, the nitrogen oxide (NO$_x$) concentration in ambient air showed a decreasing trend, however, the NO$_2$ emission was not alleviated, and even rose in some cities, which has led to the NO$_2$ fraction in NO$_x$ (NO$_2$/NO$_x$) spiraling recently (Minoura and Ito, 2010; Mavroidis and Chaloulakou, 2011; Tian et al., 2011). Carslaw (2005) and Carslaw et al. (2007) undertook statistical analysis of roadside concentrations of NO$_2$ in London and indicated that the increased use of diesel particulate filters (DPFs) fitted to buses made an important contribution to the...
increasing trends in NO$_2$/NOx emissions. A study reported that the NO$_2$/NOx road traffic emission ratio had increased from 14% in 1992 to 23% in 2004 in Switzerland, and this trend had been caused by increasing primary NO$_2$ road traffic emissions (Hueglin et al., 2006). The primary NO$_2$ emissions from road traffic were assessed for ten case study locations across the European Union, and the primary NO$_2$ was predicted to increase further to an average of 32.0% in 2020 (Grice et al., 2009). The long-term trend in emission ratio of NO$_2$ to NO was analyzed in relation to traffic activities using ambient monitoring data in Seoul, and the authors suggested that the diesel particulate filter (DPF) or diesel oxidation catalyst (DOC) had direct influences on the primary NO$_2$ values at urban roadside sites (Shon et al., 2011).

In order to decrease the levels of harmful pollutants, after-treatment systems are widely used in diesel engines. Wall-flow DPFs are considered to be the key technology to detoxify diesel exhaust (Mayer et al., 2000; Johnson, 2009). To avoid an increase of the exhaust back pressure and realize the regeneration of DPF, a catalyst is usually employed to convert nitric oxide (NO) to NO$_2$, which is a powerful oxidizing agent supporting the oxidation of soot (Kim et al., 2010; Shrivastava et al., 2010). The catalytic DPF (CDPF) increases the risk of high NO$_2$/NOx emissions of diesel engines. The real-world NO and NO$_2$ emissions of modern vehicles were studied and the results indicated that the NO$_2$/NOx emissions of Euro III cars or Euro IV vehicles without DPF were lower than those of Euro IV vehicles with DPF, reaching the maximum proportions of 35%–70% (Alvarez et al., 2008). The research of Heeb et al. (2010) showed that the DPFs with high oxidation potential induced NO$_2$ formation up to 3.3 ± 0.7 g/kWh, whereas low oxidation potential DPFs reduced the NO$_2$ emissions. The after-treatments did not exhibit significant impacts on the conversion of NO$_2$, however, the emission ratios of NO$_2$/NOx were significantly increased for an engine equipped with two CDPFs and one particle oxidation catalyst (POC) (Liu et al., 2012). Furthermore, NO$_2$/NOx ratio variation affects the conversion efficiency and the catalyst chosen in the selective catalytic reduction (SCR) system that follows the filter to meet the Euro IV diesel engine emission standard (Liu et al., 2010; Colombo et al., 2012).

Although many researchers have reported the phenomenon of high NO$_2$/NOx emissions by CDPFs, the formation mechanism is seldom studied. The origins of NO$_2$-production were investigated by the after-treatment industry (Spruk et al., 2010; Czerwinski et al., 2013), who paid attention to the parameters of CDPF. High content of Pt in the coating and low space velocity were identified as the reason for NO$_2$ increase. However, the role of engine-out parameters in the increase of NO$_2$/NOx emissions has barely been considered.

In this paper, an experiment on a diesel engine with CDPF was carried out and the influencing factors on NO$_2$/NOx emissions were investigated, such as exhaust temperatures, space velocity, carbon monoxide (CO) conversion ratio, and engine-out particulate matter (PM) emissions. The work should be beneficial to the further optimization potential of diesel engine–CDPF system developments to reduce NO$_2$/NOx emissions.

### 1. Materials and methods

#### 1.1. Experimental setup

The test engine is a direct injection, high pressure common-rail, turbocharged diesel engine (6DF3, FAW-WDEW, Wuxi, China), whose characteristics are shown in Table 1. The specifications of the CDPF are shown in Table 2. The engine with CDPF was tested on an engine test bench based on an AC dynamometer (HT350, Schenck, Darmstadt, Hessen, Germany) with emission measurement system (Fig. 1). A gas analyzer (SEMTECH-DS, Sensor, Saline, Michigan, USA) equipped with a non-dispersive ultraviolet (NDUV) analyzer was used to measure NO and NO$_2$, as well as carbon monoxide (CO) and hydrocarbons (HC). An electrical low pressure impactor (ELPI, Dekati, Kangasala, Finland) was used for the investigation of particulate matter (PM). To prevent particle condensation and nucleation, two stages of ejector diluter (ED) upstream ELPI were used for sampling from the raw exhaust stack (Burtscher, 2005). The fuel used in this study was locally available commercial low sulfur (50 ppm) diesel.

#### 1.2. Test methods

Because bag sampling has the potential to convert NO to NO$_2$, the direct sampling of raw exhaust was employed to measure NO$_2$ (Gense et al., 2006). The exhaust pollutant, temperature and pressure measurements were performed upstream and downstream of the after-treatment device. The results of emissions, fuel consumption and relevant engine parameters were recorded by the dynamometer control system. The stationary operation points (OPs), so called step-tests, were

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**Table 1 – Specifications of the test engine.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Feature/size</th>
</tr>
</thead>
<tbody>
<tr>
<td>Engine type</td>
<td>4-stroke, 6-cylinder, in-line</td>
</tr>
<tr>
<td>Bore (mm) × stroke (mm)</td>
<td>107 × 125</td>
</tr>
<tr>
<td>Displacement (L)</td>
<td>6.7</td>
</tr>
<tr>
<td>Compression ratio</td>
<td>16.8</td>
</tr>
<tr>
<td>Fuel system</td>
<td>High pressure common rail (BOSCH)</td>
</tr>
<tr>
<td>Max. power (kW at 2300 r/min)</td>
<td>147</td>
</tr>
<tr>
<td>Max. torque (N-m at 1400 r/min)</td>
<td>760</td>
</tr>
</tbody>
</table>

**Table 2 – Specification of catalytic diesel particulate filter (CDPF).**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Feature/size</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOC substrate</td>
<td>Cordierite</td>
</tr>
<tr>
<td>DOC cell density (cells/in$^2$)</td>
<td>40</td>
</tr>
<tr>
<td>DOC Pt content (g/ft$^3$)</td>
<td>50</td>
</tr>
<tr>
<td>DOC diameter (mm) × length (mm)</td>
<td>215.9 × 88.9</td>
</tr>
<tr>
<td>DPF substrate</td>
<td>Cordierite</td>
</tr>
<tr>
<td>DPF cell density (cells/in$^2$)</td>
<td>200</td>
</tr>
<tr>
<td>DPF Pt content (g/ft$^3$)</td>
<td>35</td>
</tr>
<tr>
<td>DPF diameter (mm) × length (mm)</td>
<td>215.9 × 355.6</td>
</tr>
</tbody>
</table>

DOC: diesel oxidation catalyst.
performed, as shown in Fig. 2 (Hsieh and Wang, 2011). The engine was operated at 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90% and 100% of full load at seven engine speeds (1030, 1200, 1400, 1600, 1800, 2000 and 2300 r/min). In order to investigate the effect of exhaust temperature (ET) upstream of the CDPF, 15 operation points were tested additionally at three constant exhaust temperatures (ET = 250, 300 and 350°C respectively), with five OPs for each constant ET. In a similar way, another 15 OPs were added for constant space velocities (SV = 7, 11, and 16 sec\(^{-1}\) respectively). All operation points were performed with a warm engine and for each research task always in the same sequence. Before the experiment, the gas analyzer, SEMTECH-DS, was warmed about half an hour and calibrated by zero gas and span gases of NO, NO\(_2\), CO and HC. After warm-up, the engine was allowed to run for 2 min until the engine operating condition became steady and then the data were measured. Every mode was measured three times and the average values are reported in the results.

2. Results and discussions

2.1. \(\text{NO}_2/\text{NO}_x\) emission characteristics

The \(\text{NO}_2/\text{NO}_x\) emissions upstream and downstream of the CDPF are shown in Fig. 3. It can be seen that the \(\text{NO}_2/\text{NO}_x\) emissions downstream of the CDPF are obviously higher than those upstream of the CDPF. Without the CDPF, the \(\text{NO}_2/\text{NO}_x\)
ratio in the exhaust of the diesel engine was about 2%–20% and usually decreased with engine load. It is generally considered that NO$_2$ is generated by the reaction of NO and HO$_2$ in the flame zone and survives with the cold flow inside the engine cylinder (Schejbal et al., 2010). At low engine loads, the combustion temperatures were lower, so the engine-out NO$_2$ emissions in NO$_x$ were comparatively higher. Downstream of the CDPF, the NO$_2$/NO$_x$ ratio in the emissions was about 20%–60% and could reach as high as 83%, and showed no obvious trend with changes in the engine load or engine speed. This will make it more difficult for engineers calibrating the diesel-CDPF system to control NO$_2$/NO$_x$ emissions. In order to remove PM and realize the regeneration of the DPF, an oxidation catalyst is employed by the CDPF to oxidize CO and HC emissions, but it is also able to convert NO to NO$_2$. The NO$_2$ is then used to assist in the oxidation of trapped particles. However, if the generated NO$_2$ is more than what is needed to react with PM, it will be emitted from the tailpipe and increase the NO$_2$/NO$_x$ emissions. According to the operation principle of the CDPF, the NO$_x$ emissions upstream and downstream of the CDPF will be basically the same, which was also verified by this experiment. Since the NO$_2$/NO$_x$ ratios downstream of the CDPF are higher, the NO$_2$ emissions downstream of the CDPF are higher too.

### 2.2. Effect of the exhaust temperature

Fig. 4 gives the relationship between the engine-out exhaust temperatures and NO$_2$/NO$_x$ emissions downstream of the CDPF for different engine modes. It can be seen that when the temperatures ranged from 240 to 410°C, the NO$_2$/NO$_x$ emissions downstream CDPF were over 40%. When the exhaust temperatures were lower than 200°C or higher than 400°C, the NO$_2$/NO$_x$ emissions remained at a low level. The reaction of NO to NO$_2$ in the DOC is controlled by kinetics and thermodynamics. When Pt is used as catalyst in the DOC, the maximum generated NO$_2$ appears at the temperature of 300–350°C (Benajes et al., 2014). In spite of the variation of other influencing factors with operation points, the NO$_2$/NO$_x$ emission showed a noticeable trend with the change of exhaust temperature. The relationship between the engine-out exhaust temperatures and NO$_2$/NO$_x$ emissions was modeled by extreme value distribution fitting, as seen in Fig. 4. According to the distribution, the peak of NO$_2$/NO$_x$ emission was 60.3%, which appeared at 311°C. This indicated that the NO$_2$/NO$_x$ emission was higher when NO$_2$ generated from the DOC was higher.

The NO$_2$/NO$_x$ emissions at constant engine-out exhaust temperatures are shown in Fig. 5. When the exhaust temperature increased from 250 to 300°C, the NO$_2$/NO$_x$ emissions increased by 50.8%–113.3%. When the exhaust temperature increased from 300 to 350°C, the NO$_2$/NO$_x$ emissions increased by 9.8%–35.3%. No matter how other factors varied, the exhaust temperature of 350°C resulted in the highest NO$_2$/NO$_x$ emissions, which was consistent with the results of Fig. 4. It was found that the engine-out exhaust temperature is a very important factor influencing the NO$_2$/NO$_x$ emissions.

### 2.3. Effect of the space velocity

Space velocity (SV) is the ratio of the volumetric exhaust gas flow to the reference volume of the after-treatment device. For the step-tests, unlike the exhaust temperature, the effect trend of space velocity on the NO$_2$/NO$_x$ emissions is not significant. In step-tests, the space velocity changed with the engine speed and load, and other factors influencing the NO$_2$/NO$_x$ emission varied, so its effect cannot be separated. This means that the effect of space velocity is not as significant as that of exhaust temperature.

A trial was performed for different operation points of the engine, but with constant space velocities, that is 7, 11, 16 sec$^{-1}$, as shown in Fig. 6. It can be seen that most of the NO$_2$/NO$_x$ emissions at low space velocity are higher than those at high space velocity. When the space velocity was 7 sec$^{-1}$, the maximum NO$_2$/NO$_x$ ratio reached 69.0%; while for 11 sec$^{-1}$, the maximum was 60.4%, and it was 51.6% for 16 sec$^{-1}$. This trial also confirmed that the maximum intensity of NO$_2$/NO$_x$ in the exhaust temperature occurred around 350°C.
The relationship between the space velocities and NO\textsubscript{2}/NO\textsubscript{x} emissions downstream of the CDPF at constant exhaust temperature is shown in Fig. 7. When the exhaust temperature is constant, the effect trend of space velocity is obvious, that is, the NO\textsubscript{2}/NO\textsubscript{x} emissions decreased with increasing space velocities. Higher space velocity means shorter residence time for gas in the CDPF, which significantly lowers the potential for the oxidation of NO to form NO\textsubscript{2}, so the NO\textsubscript{2}/NO\textsubscript{x} emission is lower. This suggests that NO\textsubscript{2}/NO\textsubscript{x} emission can be reduced by using a small after-treatment device, which increases the space velocity for a specific engine.

### 2.4. Effect of CO conversion ratio

The up- and down-stream CO emission concentrations and CO conversion ratios in step-tests are shown in Fig. 8. The CO conversion ratios were mostly over 85%, which means that CDPF can reduce CO emissions effectively. The relationship between the CO conversion ratios and NO\textsubscript{2}/NO\textsubscript{x} emissions downstream of the CDPF for different engine modes is shown in Fig. 9. When the CO conversion ratios were more than 90% or less than 80%, the NO\textsubscript{2}/NO\textsubscript{x} emissions maintained a low level, below 40%. When the CO conversion ratios were in the range 80%–90%, most of the NO\textsubscript{2}/NO\textsubscript{x} emission ratios were higher than 40%. In the DOC, NO\textsubscript{2} is more reactive for the oxidation of CO than oxygen, thus, the generated NO\textsubscript{2} will also be used by the system as an oxidizing reactant for CO (Spruk et al., 2010; Al-Harbi et al., 2012). When the CO conversion ratio is low, it means that oxygen or NO\textsubscript{2} in the exhaust is insufficient, so that most CO is not oxidized. Thus, less NO\textsubscript{2} is formed by NO oxidation and the NO\textsubscript{2}/NO\textsubscript{x} emissions are low. When the CO conversion ratio increases, it means that the DOC is capable of oxidizing NO. In addition, the oxidation of CO can release heat and raise the exhaust temperature, which favors NO\textsubscript{2} formation (Desprès et al., 2004; Minoura and Ito, 2010). When the CO conversion ratio is over 90%, the engine-out CO concentration is usually high and most NO\textsubscript{2} is used for the oxidation of CO, so the NO\textsubscript{2}/NO\textsubscript{x} emission ratio is low.
2.5. Effect of engine-out PM/NO\textsubscript{x} ratio

The up- and down-stream PM emission concentrations and PM conversion ratios in step-tests are shown in Fig. 10. The PM conversion ratios were mostly over 85%, which means that the CDPF can reduce the PM emission effectively. In the CDPF, the generated NO\textsubscript{2} oxidizes the trapped PM to realize the regeneration of the CDPF. The engine-out PM mass will influence the participation of NO\textsubscript{2}, which determines the NO\textsubscript{2}/NO\textsubscript{x} emissions, so the engine-out PM/NO\textsubscript{x} ratio (mass based) should be considered as a factor.

The relationship between the engine-out PM/NO\textsubscript{x} ratio and NO\textsubscript{2}/NO\textsubscript{x} emissions downstream of the CDPF for different engine modes is shown in Fig. 11a. When PM/NO\textsubscript{x} ratios are greater than 0.1, the NO\textsubscript{2}/NO\textsubscript{x} emission ratios downstream of the CDPF are lower than 40%. The reason is that more NO\textsubscript{2} is needed to react with PM. While the PM/NO\textsubscript{x} ratios are less than 0.1, the NO\textsubscript{2}/NO\textsubscript{x} ratios are mostly higher, over 40%; however, there are many operation points where the NO\textsubscript{2}/NO\textsubscript{x} emissions are lower than 40%. This means that the PM/NO\textsubscript{x} ratio is not a decisive factor, and should be considered in combination with other factors. According to the modeling study of Kandylas and Koltsakis (2002), when the NO\textsubscript{2}/soot ratio is 7.2 (that is, soot/NO\textsubscript{x} = 0.14), NO\textsubscript{2} is generated in the CDPF and the loaded PM will be completely reacted. This experimental study is consistent with the simulation, but the equilibrium PM/NO\textsubscript{x} value is different due to the variation of other factors in the experiment, such as exhaust temperatures.

Furthermore, Fig. 11b gives the NO\textsubscript{2}/NO\textsubscript{x} ratio dependence on PM/NO\textsubscript{x} ratio and exhaust temperature. At a constant exhaust temperature, the NO\textsubscript{2}/NO\textsubscript{x} emissions decreased with increasing PM/NO\textsubscript{x} ratios. At 300°C, a drastic drop of NO\textsubscript{2}/NO\textsubscript{x} emissions can be found when the PM/NO\textsubscript{x} ratio increased from 0.01 to 0.05. However, the drop at 250 or 350°C is not so significant. For a diesel engine compliant with Euro III, given that without after-treatment, the exhaust PM/NO\textsubscript{x} ratio is about 0.02, which favors a high NO\textsubscript{2}/NO\textsubscript{x} ratio in the CDPF. When calibrating a Euro III engine with a CDPF for the more stringent emission standard, the engine-out PM emission should be modestly enlarged, so as to increase the PM/NO\textsubscript{x} ratio to more than 0.1 and reduce the NO\textsubscript{2}/NO\textsubscript{x} ratio to a tolerable level. The excess PM can be trapped by the DPF and the final PM emission will be able to meet the requirements.

3. Conclusions

In order to study the engine-out influencing factors for NO\textsubscript{2}/NO\textsubscript{x} emissions, emission experiments were carried out on a high pressure common-rail, turbocharged diesel engine with CDPF. NO\textsubscript{2} was measured by a NDUV analyzer with raw exhaust sampling. The test cycle included the step-tests and additional operational points with constant exhaust temperature.

The catalytic diesel particle filter results in significant augmentation of the NO\textsubscript{2}/NO\textsubscript{x} emissions of diesel engines. The NO\textsubscript{2}/NO\textsubscript{x} ratios downstream of CDPF range around 20%–83%. The engine-out exhaust temperature is a decisive factor.
on the NO$_2$/NO$_x$ emissions. The maximum NO$_2$/NO$_x$ emission ratio appears in the exhaust temperature range around 350°C. The effect of space velocity and engine-out PM/NO$_x$ ratio is not as significant as that of exhaust temperature. At a constant exhaust temperature, the NO$_2$/NO$_x$ emissions decreased with increasing space velocity and PM/NO$_x$ ratio. The CO conversion ratio is also a factor influencing the NO$_2$/NO$_x$ emissions. When the CO conversion ratios were more than 80% or less than 90%, the NO$_2$/NO$_x$ emissions remained at a low level.

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