

Study on NO_x emissions from a national V heavy-duty diesel engine

Pi-qiang TAN & Huan ZENG & Zhi-yuan HU & Di-ming LOU

School of Automobile, Tongji University, Shanghai, China

KEYWORD: SCR; Diesel engine; pollution; Emissions; NO_x; Detail components

ABSTRACT: Detail components of nitrogen oxides (NO_x) emissions, which is including NO, NO₂, and N₂O, from a national V heavy-duty diesel engine with selective catalytic reduction (SCR) were studied under different operating conditions by using Fourier transform infrared spectrum (FTIR) technology. Results show that compared to the engine without SCR, descent of NO_x emissions from the engine with SCR on different load are different and the higher load, the more drop. NO and NO₂ emissions from the engine with SCR have an varying degrees of decline, N₂O emissions raise more than 50% as a result of SCR side reaction exists. N₂O emissions ascends with the increase of the load, and this is because increasing exhaust temperature leads to higher oxidation reaction rate of NH₃ to N₂O.

INTRODUCTION

Nitrogen oxide (NO_x) is important exhaust emissions of diesel engine, and its detailed components including NO, NO₂, and N₂O^[1-3]. High concentrations of NO can cause human neural disorder, NO will generate the nitrite in human body, and it would cause hypoxia by integrating with hemoglobin in the blood. NO will become NO₂ quickly in air, and NO₂ is one of the sources of acid rain and one of the important cause of photochemical smog, it also poisons the body's respiratory system^[4]. N₂O is an important greenhouse gas, its greenhouse effect as 300 times much as CO₂^[5-6].

The use of ammonia-based selective catalytic reduction is an important method for reducing heavy diesel engine NO_x to meet the national V diesel engine emissions standards^[7,8]. It may cause NH₃ leak in the process of using selective catalytic reduction (SCR). NH₃ will cause human ammonia poisoning and inhibit the central nervous system. Our country stipulates the average NH₃ emissions should not more than 25×10^{-6} in the transient ETC emissions test cycle of heavy duty diesel engine^[9].

Generally speaking, NO is main ingredients of NO_x, NO₂ is secondary components, and N₂O is very small amounts, and so on. Pi-qiang Tan studied the effects of engine load on emissions of NO₂ under different fuel injection advance angle and speed, he found that NO₂ /NO_x ratio has a significant reduction with the increase of engine load^[1]. Tang Tao studied N₂O formation characteristics under different diesel engine aftertreatment systems, he found that SCR which contained Cu zeolite catalyst and Cu/Fe composite catalysts, N₂O production showed a trend of decreases after increase and then increase with the rise of temperature^[10]. Klimczak found that redox reaction of NO can produce N₂O in the SCR^[11]. Pan Li studied redox reaction of NO in V₂O₅ SCR, he found that N₂O increases with the rise of temperature^[12].

From the above literature, we can see that the NO_x component have carried out some research in existing public literatures, but it is too few that the system research about the emissions characteristics of NO_x detailed components (NO, NO₂, N₂O) and NH₃ in diesel engine equipped with SCR.

Because of this reason, the paper carried out tests on a national V heavy-duty diesel engine, diesel engine exhaust NO_x detailed components NO, NO₂, N₂O and NH₃ were studied by using Fourier transform infrared spectrometer (FTIR), and emissions characteristics of NO_x detailed components of heavy-duty diesel engine with SCR and without SCR were explores.

Experimental Setup

Engine, SCR and FTIR

In this paper, the research object is a national V heavy-duty diesel engine with electronically controlled and high pressure common rail. The main specifications of the test engine were shown in table 1.

Table 1. Main Specifications of test engine

Items	Parameters
Displacement	8.82L
Cylinder type	6 cylinders line-engine, 4 valves
Type	Inter-cooling turbo
Bore/Stroke	114 mm/144 mm
Ratio	18:1
Rated power	184 kW (2200 r/min)
Max torque	1000N · m (1400 r/min)

In figures of this paper, the engine without SCR referred to as original, and the engine with SCR referred to as SCR. V-W/TiO₂ is main SCR catalyst of this experiment. Main Specifications of the SCR were shown in table 2.

Table 2. Main Specifications of SCR

Items	Parameters
Length of catalytic converter	660.4mm
Diameter of catalytic converter	152.4mm
Stable operation range	180~600 °C
Urea pump spray range	0~8000ml/h

The emissions of engine without SCR and engine with SCR were measured by AVL FTIR. FTIR is based on Raman Effect through the interferometer interference frequency modulation. To gain spectra, the interference figure is measured and interference figure Fourier transforms is carried out according to the corresponding relationship between interferogram and spectra. And the corresponding groups of atoms or groups of atoms combine information were gained by compared with standard atlas, then the concentration of the quantitative analyst is of the components can be done according to Bill Law^[13, 14].

Experiment Procedure

The heavy-duty diesel engine NO_x detailed component (NO, NO₂, N₂O) and NH₃ emissions characteristics were studied, test point is present as follows:

Two speeds were choose, respectively for the maximum torque speed 1400 r/min, the rated power speed 2200 r/min, those speed by 10%, 25%, 50%, 25% and 100% load, a total of 10 point.

The mass concentration of the tested urea solution wis 32.5%, which is the standard urea solution used by car. To provide enough ammonia, urea basic injection quantity will be set to 1.2 times as much as the amount of NO_x completely reaction in theory, namely the complete decomposition of urea solution produced by the molar ratio of NH₃ and NO_x is equal to 1.2:1.

RESULTS AND DISCUSSION

The average temperature and exhaust flow

NO_x production is related to average temperature and exhaust flow of catalytic converter, so it is necessary to studied them.

Figure 1 shows that the average temperature and exhaust flow. It can be seen that average temperature and exhaust flow of catalytic converter were significantly increased with the increase of load at 1400r/min and 2200r/min. And under the same load, average temperature of 1400 r/min significantly higher than that of 2200 r/min, but the exhaust flow rate of 1400 r/min is lower than 2200r/min.

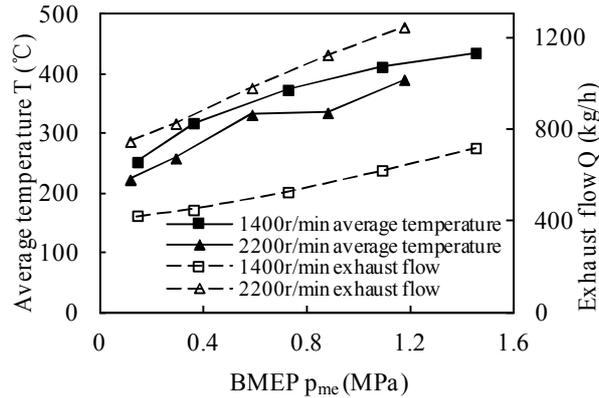


Figure 1. Average temperature and exhaust flow of SCR catalysts

Detail Components of NOx

Figure 2 shows that NOx emissions under different load. In original engine, NOx emissions were raising with the increase of load, and NOx emissions of 1400 r/min is higher than that of 2200 r/min. After adding SCR, compared with the original engine, NOx emissions has varying degrees of decline, but its rule of change is not obvious with the increase of load. After adding SCR, NOx emissions of 1400 r/min has an average decreased by 67.7% and biggest decreased by 92.9%, which appears in the region of the high load. At this load, exhaust temperature is high, SCR catalyst activity is strong, NOx emissions decline significantly. The smallest decline is 30.8% in small load area, where exhaust gas temperature is lower. After adding SCR, NOx emissions of 2200 r/min has an average decreased by 87.6% and biggest decreased by 97.1%, which appears in the region of the middle load. At this load, NOx emissions of the original engine were not very high, but its high exhaust temperature, SCR catalyst activity is strong, NOx emissions decline significantly. The smallest decline of 2200 r/min is 60.4% in the small load where exhaust gas temperature is low.

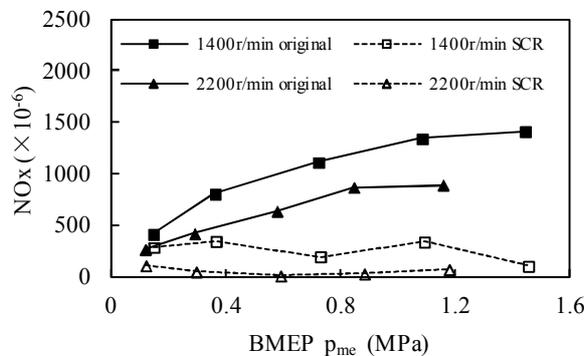


Figure 2. NOx emissions

NO Emissions

Figure 3 shows that NO emissions under different load. In original engine, NO emissions is rising with the increase of load, and NO emissions of 1400 r/min is higher than that of 2200 r/min. This is mainly due to temperature in cylinder of 1400 r/min is higher than that of 2200 r/min. After adding SCR, NO emissions has decrease sharply compared with the original engine, but its rule of change is not obvious with the increase of load. NO emissions of 1400 r/min has an average decreased by 68.2% and biggest decreased by 94.1%. NO emissions of 2200 r/min has an average decreased by 87.4% and biggest decreased by 97.7%.

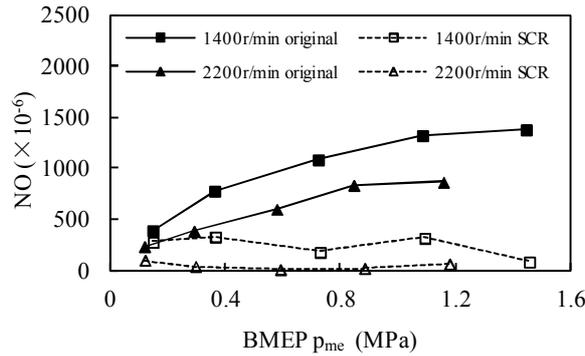


Figure 3. NO emissions

NO₂ Emissions

Figure 4 shows that NO₂ emissions under different load. In original engine, NO₂ emissions of 1400 r/min ascends firstly and then decline with the improvement of mean effective pressure, and then increase around 1 MPa. NO₂ emissions of 2200 r/min ascends firstly and then decline with the increase of the mean effective pressure.

After adding SCR, NO₂ emissions has fallen sharply compared with the original engine. NO₂ emissions of 1400 r/min is on the rise roughly with the increase of the mean effective pressure, NO₂ emissions of 2200 r/min change smaller with the increase of the mean effective pressure, emissions are mostly around 3×10^{-6} .

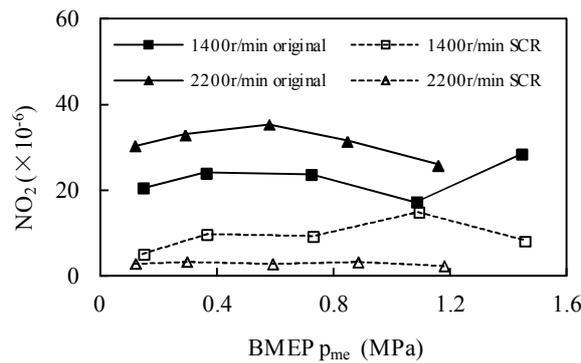


Figure 4. NO₂ emissions

It is important to note that NO₂ emissions of 2200 r/min more than 1400 r/min in the original engine, but after adding SCR, NO₂ emissions of 2200 r/min less than 1400 r/min. After adding SCR, NO₂ emissions of 1400 r/min has an average decreased by 56.6% and biggest decreased by 75.6% compared to the original engine. NO₂ emissions of 2200 r/min has an average decreased by 90.9% and biggest decreased by 92.3%. The main reason is that NH₃-based SCR have different reaction under different conditions^[15-17]: standard SCR reaction and rapid SCR reaction.

Standard SCR reaction is mainly catalytic reduction reaction between NH₃ and NO_x, it has higher rate of reaction at 300 °C ~ 400 °C, reaction rate will lower when the temperature is lower, the reaction is as follows:



The rate of reaction (1) is slow relatively, when the ratio of NO/NO₂ rising, NO₂/NO ratio to 1 at someplace, there is a more ideal reaction process, namely rapid SCR reaction, it can be working under the low temperature. The reaction is as follows:

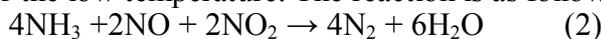


Figure 5 shows that NO₂/NO ratio of original engine under different load. NO₂/NO ratio of 1400 r/min has fallen with the increase of load, it means that rapid SCR reaction reduces, standard SCR reaction increases, the reduction of NO₂ decreases, and NO₂ emissions of original engine don't change much, so the range of NO₂ emissions decline isn't big after adding SCR.

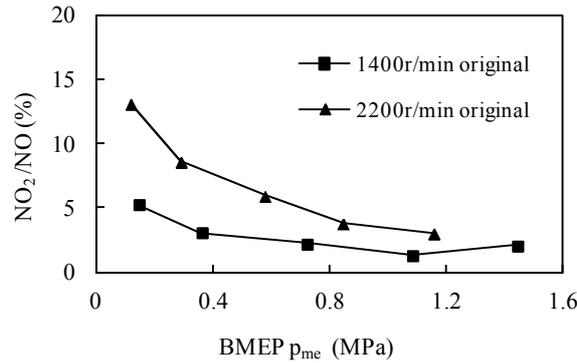
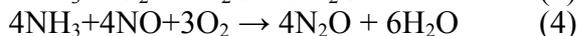
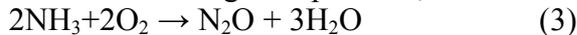


Figure 5. NO₂/NO ratio without SCR at different load

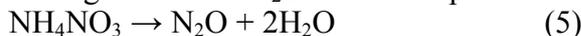
N₂O Emissions

Figure 6 shows that N₂O emissions under different load. With the improvement of mean effective pressure, the original engine N₂O emissions don't change much. N₂O emissions of 1400 r/min is mainly about 2.0×10^{-6} , while it is mainly about 2.5×10^{-6} of 2200 r/min. After adding SCR, N₂O emissions has raised sharply compared with the original engine. With the increase of mean effective pressure, N₂O emissions of 1400 r/min and 2200 r/min were on the rise. Considering that the greenhouse effect of N₂O is about 300 times of carbon dioxide, N₂O emissions should bring to the forefront after adding SCR.

After adding SCR, N₂O emissions is increased sharply compared to the original engine, this is mainly due to the reaction of SCR in addition to the normal reaction (1) and (2), there are side effects occur under high temperature, those reactions will produce N₂O [18, 19]:



At the same time, because of using urea as a reducing agent of SCR reactions, there is side effects might generate NH₄NO₃, if it is attached in the surface of the SCR, part of NH₄NO₃ occur decomposition to generate the N₂O at low temperature [19, 20]:



It is important to note that N₂O emissions of 1400 r/min is less than that of 2200 r/min in original engine, but after adding SCR, N₂O emissions of 1400 r/min is more than that of 2200 r/min. After adding SCR, N₂O emissions of 2200 r/min has an average increase by 61.9% and biggest increase by 83.1% compared with original engine, N₂O emissions of 1400 r/min has an average increase by 2.23 times and biggest increase by 3.29 times.

It is result of comprehensive action among the reaction (3), (4) and (5). After adding SCR, N₂O emissions of 2200 r/min ascends firstly and then decline with the improvement of mean effective pressure, this is due to the exhaust temperature of 2200 r/min is lower than 1400 r/min, the N₂O under low load is mainly generated by the decomposition of NH₄NO₃, which mainly comes from the reaction (5). NH₄NO₃ decomposition will increase with temperature increasing properly, and when the exhaust temperature increased to a certain temperature, the generation of NH₄NO₃ decrease, N₂O emissions becomes down. And when the exhaust temperature continues to raise, reaction (3) and (4) increase, so the N₂O emissions continue to rise again. N₂O emissions of 1400 r/min rise with the increase of the load, this is mainly due to the average effective pressure increase, the exhaust temperature increased, NH₄NO₃ generation decreases, reaction (5) decreases, but it is increased that NH₃ is oxidized into N₂O by NO₂ or O₂, the reaction (3) and (4) increase significantly, so the N₂O emissions rise gradually, and because exhaust gas temperature of 1400 r/min is higher than 2200 r/min, N₂O emissions is generated more than 2200 r/min by reaction (3) and (4).

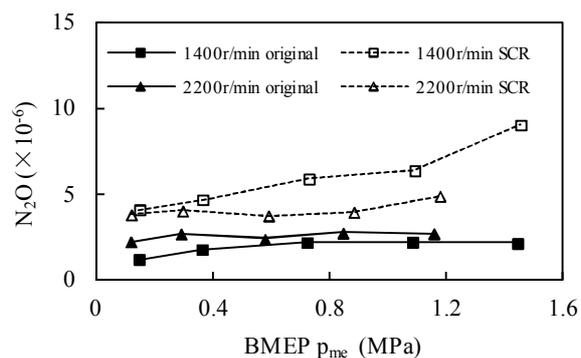


Figure 6. N₂O emissions

Conclusions

Detail components of NO_x emissions including NO, NO₂, and N₂O from a national V heavy-duty diesel engine with SCR were studied by using FTIR technology. Main conclusions are as follows:

(1) In original engine, with the increase of the load, NO emissions continues to raise, NO₂ emissions ascends firstly and then decline, N₂O emissions is rare.

(2) Compared with the original engine, NO_x emissions of diesel engine with SCR have varying degrees of decline, the drop of high load is more ideal.

(3) After adding SCR, NO and NO₂ emissions were lower significantly, NO₂ emissions decreases significantly under the rated speed. It is due to the slightly higher NO₂/NO ratio cause of SCR reaction more quickly.

(4) The N₂O emissions from the engine with SCR is more than 50% the emissions from the engine without SCR, particularly higher under the maximum torque speed at full load, and this is because the SCR side reaction exists. N₂O emissions is rising with the increase of the load, the main reason is high temperature lead N₂O generation rate increases by NH₃ oxidation reaction.

REFERENCES

- [1] Piqiang TAN, Jiayang LU, Kangyao DENG, et al. 2003. Emission characteristic of nitrogen oxides from a direct injection diesel engine. *Transactions of CSICE* 21(6): 435—439
- [2] Yue Peng, Junhua Li, Wenzhe Si. 2015. Deactivation and regeneration of a commercial SCR catalyst: comparison with alkali metals and arsenic. *Applied Catalysis B: Environmental* 168: 195-202
- [3] Jun Yu, Zhichun Si, Lei Chen, et al. 2015. Selective catalytic reduction of NO_x by ammonia over phosphate-containing Ce_{0.75}Zr_{0.25}O₂ solids. *Applied Catalysis B: Environmental*, 163: 223-232
- [4] Fredrik R Westlye., Anders Ivarsson, Jesper Schramm. 2014. Experimental investigation of nitrogen based emissions from an ammonia fueled SI-engine. *Fuel* 111: 239-247
- [5] Choong-Kil Seo, Hwanam Kim, Byungchul Choi, et al. 2011. De-NO_x characteristics of a combined system of LNT and SCR catalysts according to hydrothermal aging and sulfur poisoning. *Catalysis Today* 164: 507—514
- [6] Cristina Campa Maria, Daniela Pietrogiaconia, Manlio Occhiuzzia. 2015. The simultaneous selective catalytic reduction of N₂O and NO_x with CH₄ on Co- and Ni-exchanged mordenite. *Applied Catalysis B: Environmental* 168:293-302
- [7] Lei Ma, Yisun Cheng, Giovanni Cavataio, et al. 2014. In situ DRIFTS and temperature-programmed technology study on NH₃-SCR of NO_x over Cu-SSZ-13 and Cu-SAPO-34 catalysts. *Applied Catalysis B: Environmental* 156-157: 428-437
- [8] Sebastian Fogel, Pär Gabrielsson. 2014. H₂-assisted NH₃-SCR over Ag/Al₂O₃: An engine-bench study. *Applied Catalysis B: Environmental* 158-159: 1-10
- [9] Ministry of Environmental Protection of the People's Republic of China. HJ437-2008.2008. Technical specification for on-board diagnostic (OBD) system of compression ignition and gas fuelled positive ignition engines of vehicles.
- [10] Tao Tang, Jun Zhang, Shijin Shuai, et al. 2014. An experimental study on the N₂O emission characteristics of diesel engine aftertreatment system. *Automotive Engineering* 36(10): 1193-1196
- [11] M Klimczak, P Kern, T Heinzelmann, et al. 2010. High-throughput study of the effects of inorganic additives and poisons on NH₃-SCR catalysts-Part I: V₂O₅-WO₃/TiO₂ catalysts. *Applied Catalysis B: Environmental* 95: 39-47
- [12] Pan Li, Qingya Liu, Zhenyu Liu. 2011. N₂O and CO₂ formation during selective catalytic reduc-

- tion of NO with NH₃ over V₂O₅/AC catalyst. *Industrial & Engineering Chemistry Research* 50: 1906-1910
- [13] Luis F Bobadilla, Olivier Marie, Philippe Bazin, et al. 2013. Effect of Pd addition on the efficiency of a NO_x-trap catalyst: A FTIR operando study. *Catalysis Today* 205:24-33
- [14] Piqiang Tan, Zhiyuan Hu, Diming Lou. 2012. FTIR detection of unregulated emission from a diesel engine with biodiesel fuel. *Spectroscopy and Spectral Analysis* 32(2): 360- 363
- [15] Kurnia Wijayantia, Stanislava Andonova, Ashok Kumar. 2015. Impact of sulfur oxide on NH₃-SCR over Cu-SAPO-34. *Applied Catalysis B: Environmental* 167:568-579
- [16] Jin Wang, Yaying Ji, Zhengwang He, et al. 2012. A non-NH₃ pathway for NO_x conversion in coupled LNT-SCR systems. *Applied Catalysis B: Environmental* 111: 562– 570
- [17] Hui Zhang, Junmin Wang, Yue-Yun Wang. 2015. Removal of NO_x sensor ammonia cross sensitivity from contaminated measurements in diesel-engine selective catalytic reduction systems. *Fuel* 150: 448-456
- [18] Shijian Yang, Shangchao Xiong, Yong Liao, et al. 2014. Mechanism of N₂O formation during the low-temperature selective catalytic reduction of NO with NH₃ over Mn-Fe Spinel. *Environmental Science & Technology* 48(17): 10354-10362
- [19] Sachi Shrestha, Michael P Harolda, Krishna Kamasamudram, et al. 2014. Selective oxidation of ammonia on mixed and dual-layer Fe-ZSM-5+Pt/Al₂O₃ monolithic catalysts. *Catalysis Today* 231: 105-115
- [20] Lei Chen, Zhichun Si, Xiaodong Wu, et al. 2015. Effect of water vapor on NH₃-NO/NO₂ SCR performance of fresh and aged MnO_x-NbO_x-CeO₂ catalysts. *Journal of environmental sciences* 31:240-247