The influence of AdBlue dosage on the process of selective catalytic reduction of nitrogen oxides

This article presents test results obtained for nitrogen oxides emission reduction by the method of selective catalytic reduction in a diesel engine. A special steady-state test cycle was prepared in order to identify the most critical operating points of the SCR system. Areas of low system performance and the reasons for solid fractions formation and deposition were also investigated. The research examined the phenomenon of the occurrence of ammonia slip emissions into the environment.

Keywords: nitrogen oxide emissions, SCR catalytic converter, AdBlue, urea, ammonia slip

1. Introduction

New, more and more demanding legislation regulations concerning harmful exhaust emissions compounds necessitate the usage of additional exhaust aftertreatment systems, particularly in the case of Compression Ignition engines. Emission limits specified in the upcoming Euro 6 standard, which for passenger cars and heavy duty trucks for the first time introduced to the market will take effect from 31 December 2013, assumed mainly the need to further reduce the emission of nitrogen oxides. This is especially important with regards to the planned introduction of new common and global homologation cycles: the WHSC (World Harmonized Stationary Cycle) and WHTC (World Harmonized Transient Cycle) meant to reproduce the engine working conditions of Heavy Duty vehicles in Europe, USA, Australia and Japan. In addition, reports published by the European Commission show that such a method would also be suitable for certification of engines of smaller displacement, including those for vehicles weighing up to 3,500 kg. As it turns out, test results obtained using the previously used homologation cycles: (ESC and ETC) do not correspond well to real emission values, which are characteristic to the engines during operation in real traffic conditions.

Currently, the leading aftertreatment system technology to reduce emissions of toxic nitrogen compounds applied in the small-middle class passenger cars are catalytic converters base on the nitrogen oxide storage principle known as NSC (NOx Storage Catalysts) or LNT (Lean NOx Trap). This deNOx concept is of interests in applications with limited space or in which urea usage is difficult. The deNOx efficiency is nominally 70-80% and the PGM precious metal loading is high (10-12g for a 2 liter engine) [1]. However, a much more efficient is the next generation SCR system (Selective Catalytic Reduction) with deNOx efficiency of 95+. This method can be in principle successfully implemented in all types of engines, regardless of their purpose and size, but due to the SCR system’s complexity it is mostly applied in the range of vehicles from middle class passenger cars up to all heavy duty applications. The SCR system, seen as a primary method of reducing nitrogen oxides emissions, allows the new Euro 6 legislation requirements to be met and extensive research and development of this technology has been carried out over the past decade, providing the features of high efficiency and the required durability over the operating lifetime. However, due to complex multi-segment structure and operation of the whole system, many technical problems have been encountered in the field of research, design and performance requirements, which all have a significant impact on the expected exhaust treatment efficiency.

2. Operating conditions of a selective catalytic reduction system

Exhaust gas aftertreatment systems based on the selective catalytic reduction method feature a
number of constructional and operational problems, resolution of which is reflected in the increased complexity and costs of the entire system. The main issues in terms of system hardware design are related to the following: selection of special quality materials remaining in direct contact with the liquid reducing agent and other aggressive ammonia gases, ensuring AdBlue liquidity at low ambient temperature conditions, the need to drain liquid AdBlue back to the tank after engine shut down, or the decomposition and loss of AdBlue properties at high ambient temperature [3]. There are also significant problems with the urea dosing and mixing processes in the exhaust flow following chemical urea conversion into gaseous ammonia that determine the reduction efficiency of nitrogen oxides in the SCR converter. A very important issue for all SCR systems is the emission of gaseous ammonia at the outlet of SCR converter, known as ammonia slip. This phenomenon relies on the release of volatile ammonia previously accumulated in the SCR reactor. The ammonia storage capability inside the SCR reactor is strongly related to the temperature of the active area of the reactor. The lower the SCR converter temperature, the greater the storage capacity, while in the case of a sudden increase in exhaust gas temperature and thus an increase in SCR temperature, this ability decreases dramatically, leading to immediate release of ammonia (from the outlet the SCR) previously accumulated and stored under lower SCR temperature conditions. Maintaining the optimal level of ammonia saturation of SCR in a function of gas temperature has become one of biggest challenges in the SCR system modelling and development. The saturation level of ammonia storage has a significant effect on ammonia slip during transient processes. There is an corresponding amount of ammonia storage which can be defined as the “slip-preventing limit” that maximizes the NOx conversion efficiency while keeping ammonia slip as low as possible to comply with Euro 6 legislation for heavy-duty diesel engines [2]. The exhaust temperature is the key factor affecting the ammonia storage capacity of the catalyst, which sharply decreases with an increase of temperature. If the ammonia storage is not controlled properly, ammonia slip will occur under various transient conditions. Rapid heating of the catalyst at low temperature can cause serious ammonia slip. One of the methods to prevent excessive ammonia pollutions is the application of an additional catalytic converter known as a clean-up catalyst placed downstream of the SCR, whose task is to oxidize residual ammonia in exhaust gases. This solution, however, increases the costs of the entire system, making it more complex and also causes further expansion in the size of the exhaust aftertreatment system. Therefore, extended research is still needed to explain all the phenomena occurring during the process of selective catalytic reduction, which will aim to identify the appropriate methods for improving the reduction process of nitrogen oxides.

3. Methodology and testing description of the Selective Catalytic Reduction process

Research on the SCR system was carried out on a development test bed with a Schenck eddy-current dynamometer, Horiba Stars automatic control and data storage systems. A Diesel engine was used, with a direct fuel injection system and swept volume of 3 liter. The test bed was equipped with an AVL AMA i60 exhaust gas analyser, which supports two independent sampling lines for online conversion efficiency measurements and a stand-alone LDD AVL gas analyser for continuous ammonia emissions measurement downstream of the SCR converter. Moreover, the test bed was enhanced with a fully controlled and automatic development urea dosing system. Similar systems are currently in use in vehicles equipped with SCR systems designed to meet the Euro 5 and Euro 6 emission standards.
The test bed dosing system gave the possibility to freely model the urea injection strategy by working in either an open or closed loop mode. The open loop permitted the injection of a fixed set amount (mass) of urea regardless the exhaust mass flow and current NOx concentration. The closed-loop mode was commanded by feedback signals from an on-board NOx sensor and the ECU unit and permitted the amount of AdBlue dosed to be precisely controlled as a function of the current exhaust gas mass flow, NOx concentration and the exhaust gas temperature upstream of the SCR converter.

In order to study and analyse the impact of urea dosing quantity on the operation and conversion efficiency of the SCR converter, a special test cycle was developed which consisted of six 20-minute steady-state engine running points. The exhaust temperature was controlled at the inlet SCR converter and covered the range from 160°C to 400°C with around 40°C step between subsequent operating points. The test was performed three times, each time for a different amount of AdBlue dosing, defined by means of the α (alpha) factor. The test temperature window chosen was selected on a basis of analysis made of the SCR converter’s working condition over the World Harmonized Transient Cycle test (Figure 4). The WHTC is foreseen as the first common and worldwide certification test for heavy duty vehicles to meet the requirements of Euro 6 legislation.

The amount of AdBlue reducing agent was described by the stoichiometric coefficient defined as α, which describes the ratio of the amount of ammonia molecules in the reducing agent over the amount of nitrogen oxides molecules present in the exhaust gas mass flow.

\[ \alpha = \frac{NH_3_{IN}}{NOx_{IN}} \]

In principle, a α coefficient equal to one (α=1) means the introduction into the exhaust flow of the minimum amount of reducing agent that permits complete removal (reduction) of nitrogen oxides, without causing any excessive ammonia storage or emission downstream SCR (ammonia slip). The test cycle was run for three different amounts of AdBlue dosing with an α factor equal to 0.6, 0.8 and 1.0 respectively. The desired mass of AdBlue liquid injected, corresponding to the set α ratio was expressed in mg /s and was calculated online by the urea dosing system as a function of NOx concentration and exhaust gas mass flow signal. Then desired amount of AdBlue was injected into the gas stream at a pressure of about 5 bar by the multi-hole AdBlue injector placed upstream of the SCR reactor. During the test run, continuous measurements of the concentration of toxic compounds in the exhaust gas were simultaneously performed at two locations: at the engine outlet for raw exhaust emission and downstream the SCR converter with
the additional NH3 concentration measurement. Furthermore, exhaust gas temperature at the inlet of the SCR and the AdBlue mass flow were also measured.

Before each test cycle, the SCR converter and the entire exhaust system underwent a specific conditioning cycle in order to clean out any residual ammonia deposits stored or left inside the SCR substrate. The conditioning was executed by exposing the exhaust system to an engine operating point of high exhaust gas temperature measured at the SCR inlet. The above method aimed to ensure the repeatability of the initial testing conditions and to eliminate any possible SCR initial saturation with ammonia through the SCR cleanup.

The total test cycle duration time for each α coefficient value chosen was 120 min, split into six 20-minute steady-state engine operating points. A constant engine speed for all test points was selected and set at 1900 1/min, while the engine load was gradually increased in the range between 60 to 400 Nm, so that in each successive test step the exhaust temperature measured upstream of the SCR converter increased by approximately 40°C in the range 160°C to 400°C. The corresponding exhaust mass flow rate varied from about 230 kg/h to 390 kg/h.

4. Test Results and Discussion

The test results obtained are presented and compared graphically for three different urea dosing values defined by factors of α equal to 0.6, 0.8 and 1.0 respectively. For test result comparison purposes the following parameters were selected and analysed:

- the total NOx conversion rate of the exhaust aftertreatment system calculated by the following equation:
  \[
  \text{NOx conversion} [\%] = \frac{\text{NOx in DOC} - \text{NOx out SCR}}{\text{NOx in DOC}} \times 100\%
  \]
- ammonia emissions at the outlet of the SCR converter (ammonia slip)
- exhaust gas temperature at the inlet of the SCR
- quantity of AdBlue dosing

Fig. 5. Comparison of AdBlue dosing quantity on the SCR operation over the test cycle

In the first step of the test cycle, under conditions of the lowest exhaust gas temperature range between 160°C to 180°C, the nitrogen oxide conversion rate was decidedly the lowest, but with a trend steadily increasing as a function of time, starting from values of just a few percent. The repeatability of this phenomenon was observed in all three cases of the α factors studied. Such low nitrogen oxide reduction during the initial phase was justified by the fact of SCR preconditioning and cleaning out from any residual urea solution prior to the test so no ammonia saturation. At low exhaust gas temperature conditions and thus low temperatures of the SCR system’s active surface, the urea evaporation and mixing processes in the exhaust stream are significantly slowed down and then as a consequence, the following urea thermolysis and hydrolysis reactions are sluggish and reduced - in some cases even being impossible to occur. As a matter of fact, in this case, the degree of AdBlue conversion ratio and the actual release of volatile ammonia, which is an elementary reducing agent for nitrogen oxides, is very low and insufficient. In addition, another side effect of dosing AdBlue in cold and warming up engine conditions is the formation of solid fractions originating from unreacted urea and leading to a dangerous accumulation of solid deposits inside the exhaust aftertreatment system, significantly impairing its functionality.

In the subsequent steps of the test cycle, the conversion rate of nitrogen oxides strongly increased, mainly due to higher gas temperatures and the greater degree of SCR converter saturation with the reducing agent.
The most critical issue and test parameter witnessed during the test cycle was the emission of gaseous ammonia at the outlet of the SCR converter, known as ammonia slip. This phenomenon was measured as a sudden emission of volatile ammonia previously stored in the SCR converter at lower temperature range, due to an increase of the exhaust gas temperature. The ammonia storage capacity inside the SCR converter is strongly related to gas temperature. The lower the gas temperature, the greater the storage capacity - and vice-versa.

It was noticed that the NOx conversion efficiency strongly depends on the amount of ammonia storage when the temperature is lower than around 260°C, and it is nearly linear with the amount of ammonia storage at low gas temperatures near to release of the urea injection. In the case of a sudden increase of exhaust gas temperature, and thus the temperature of the system, the ammonia storage capacity reduces dramatically, resulting in considerable ammonia emission downstream of the SCR converter. This phenomenon is well documented in studies and Figure 5 presented here.

5. Conclusions

The nitrogen oxide reduction process by means of selective catalytic reduction is technically complex, but also highly effective method of reducing that toxic compounds in Diesel engine exhaust gases. However, it requires further refinement, especially for certain operating conditions, such as the warm-up phase of the engine and the entire exhaust system and a sudden increase in engine load and exhaust gas temperature causing ammonia slip. During engine warm-up, especially under low load conditions, a significant obstacle for proper system functionality is the limited capability for evaporation of liquid AdBlue in the insufficiently warm exhaust gas stream. Furthermore, cold running conditions enhance the formation and accumulation of unreacted urea solid deposits, significantly reducing the efficiency of the SCR system. In this case, further optimization in the reducing agent dosing strategy and the temperature threshold for AdBlue injection release can be considered, as well as the possibility of AdBlue pre-treatment to enhance the thermal decomposition and hydrolysis phenomena occurring during normal operation of the system. The last (but not least) critical operation issue of the SCR system occurs in the case of a sudden increase in the gas temperature and the release of ammonia stored inside the converter causing massive, uncontrolled ammonia emission into the environment. This phenomenon can be significantly reduced through the introduction of an AMOX converter (clean-up catalyst) and further developing the ammonia saturation storage model inside the SCR converter.

**Nomenclature/Skróty i oznaczenia**

- **SCR** Selective Catalytic Reduction/selektywna redukcja katalityczna
- **DOC** Diesel Oxidation Catalyst/utleniający reaktor katalityczny
- **DPF** Diesel Particulate Filter/filtr cząstek stałych
- **NSC** NOx Storage Catalyst/reaktor katalityczny adsorbujący NOx
- **AMOX** Ammonia oxidation catalyst/reaktor utleniający amoniak
- **PGM** Platinum group metal

**Bibliography/Literatura**


and Automobile Sources, 2 July 2012, Bielsko-
Biała, Poland

[6] Stiebels S., Wendt C., Neubauer T., Molier-
Stach T.: Smart Catalyst Technologies for Fu-
ture Automotive Emission Control, presenta-
tion at the IAV MinNOx Conference, June
2012, Berlin

[7] Partridge W., Pihl L., Auvray X., Olsson L.,
Kamasamudram K., Yezerets A., et al.: Local
Ammonia Storage in a Monolithic SCR Cata-
lyst, presentation at the 9th Catalysts for Au-
tomotive Pollution Control (CAPoC) Confe-
rence, September 2012, Brussels.

[8] Li J., Szailer T., Watts A., Currier N.,
Yezerets A.: Investigation of the Impact of
Real-World Aging on Diesel Oxidation Cata-
lysts, SAE Inf. 1. Engines 5(3):2012,
doi:10.4271/2012-01-1094.

for Diesel Exhaust Performance and Perspec-
tives for High SCR Loadings, presentation at
the US Department of Energy Directions in
Engine Efficiency and Emissions Research
(DEER), Dearborn, MI, October 2012

Catalyst Systems for Light and Medium Duty
Diesels, 4th International Conference: NOx
Reduction - Current and Future Solutions for
On- and Off-Road Applications, 19-10 June,
2012, Detroit, MI.

al.: Study on Low NOX Emission Control Us-
ing Newly Developed Lean NOX Catalyst for
Diesel Engines, SAE Technical Paper 2007-

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