

A study on the indirect urea dosing method in the Selective Catalytic Reduction system

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Abstract. This article presents the results of studies on concept solution of dosing urea in a gas phase in a selective catalytic reduction system. The idea of the concept was to heat-up and evaporate the water urea solution before introducing it into the exhaust gas stream. The aim was to enhance the processes of urea converting into ammonia, what is the target reductant for nitrogen oxides treatment. The study was conducted on a medium-duty Euro 5 diesel engine with exhaust line consisting of DOC catalyst, DPF filter and an SCR system with a changeable setup allowing to dose the urea in liquid phase (regular solution) and to dose it in a gas phase (concept solution).

The main criteria was to assess the effect of physical state of urea dosed on the NO_x conversion ratio in the SCR catalyst. In order to compare both urea dosing methods a special test procedure was developed which consisted of six test steps covering a wide temperature range of exhaust gas generated at steady state engine operation condition. Tests were conducted for different urea dosing quantities defined by the α equivalence ratio.

Based on the obtained results, a remarkable improvement in NO_x reduction was found for gas urea application in comparison to the standard liquid urea dosing. Measured results indicate a high potential to increase an efficiency of the SCR catalyst by using a gas phase urea and provide the basis for further scientific research on this type of concept.

1. Introduction

Increasingly more and more stringent Europeans emission standards aim to reduce the fuel consumption and toxic compounds from automotive exhaust gasses. It poses new challenges to OEM's in terms of refining combustion engines and exhaust after-treatment systems itself. In the light of Euro 6 legislation limits and their upcoming correlation factor to Real Driving Emission figures the main attention is paid to reduce nitrogen oxides emission what necessitated application into exhaust line an additional catalyst for NO_x conversion. In practice it concerns nearly all diesel applications and lean burn spark-ignition engines.

Currently there are two dominant methods of NO_x reduction in the exhaust gases. The first method is selective catalytic reduction (SCR) which uses an aqueous urea solution (AdBlue) as a reductant and the second is so-called DeNO_x Trap which adsorbs and stores NO_x during engine lean operation $\lambda > 1$ and subsequently reduces it in short phase of gas enrichment at $\lambda \approx 0.9$. These types of catalysts are also known as NSC (NO_x Storage Catalysts) or LNT (Lean NO_x Traps).



The SCR is the most effective method of catalytic NO_x reduction, but it requires carrying a tank on board the vehicle and dosing infrastructure, which makes the entire system more complex and extensive. The SCR catalyst is often wash-coated on the DPF substrate to integrate both catalysts (SCRf) and save the space within the vehicle's chassis and body.

DeNO_x traps are more compact in structure due to the fact that regular diesel fuel is used as the reductant. DeNO_x traps can be also wash-coated on a DOC substrate which reduces the size of the exhaust aftertreatment system.

The SCR and DeNO_x Trap systems allow to meet always tougher NO_x emission limits. An intensive research and development works carried out over last decades provided required efficiency and durability features, but still there are some technical issues to overcome.

2. Selective catalytic reduction

2.1. Introductory remarks

An SCR is nowadays the most effective method of NO_x conversion into nitrogen. In mobile applications the preferred reductant is an aqueous solution of nontoxic urea, which is used as an ammonia source. The so-called AdBlue solution is injected into the exhaust system where it is decomposed to NH₃ and CO₂.

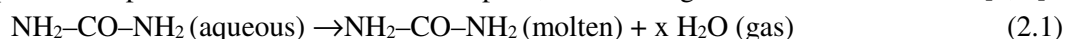
There are several complications in using urea-SCR. One of them is the need for efficient ammonia release from the urea solution and the related risks of urea deposits formation in the exhaust system. Another issue is the accurate ammonia dosage: there should be enough ammonia present on the catalyst to reduce all NO_x, but at the same time there must be no excess of ammonia, to prevent its slippage from the catalyst.

Depending on an SCR catalyst coating, the biggest NO_x reduction efficiency is typically achieved in a temperature window from 250°C to 450°C. Most commonly used SCR coatings developed for the Euro V emission limits were based on metal oxides: TiO₂-WO₃-V₂O₅, while for Euro VI requirements the coatings were based on zeolites: Cu-Zeolite for lower temperature range and Fe-Zeolite for higher gas temperature range.

2.2. SCR chemistry

In the SCR applications an aqueous urea solution (32.5% urea) is injected into the hot exhaust gas upstream of the SCR catalyst. The decomposition of urea into ammonia and carbon dioxide precedes the SCR reaction.

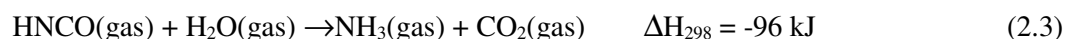
The first step is the evaporation of water from the droplets, thus leading to solid or molten urea: [4, 6]:



Molten urea will then heat up and decompose thermally according to:



Equimolar amounts of ammonia and isocyanic acid are thus formed. Isocyanic acid is very stable in the gas phase, but hydrolyzes easily on many solid oxides reacting with water vapor originating from the combustion process:



The thermo-hydrolysis of urea is globally an endothermic process. The reactions (2.1) and (2.2) may also occur in the gas phase upstream of the catalyst, whereas the hydrolysis of the isocyanic acid (reaction 2.3) proceeds mainly on the SCR catalyst itself.

3. Concept of the indirect urea dosing

Studies were carried out on heavy duty diesel engine with exhaust after-treatment consisted of a DOC, DPF filter and an SCR system with the standard and development urea dosing methods.

The concept of indirect urea dosing assumed to inject the urea into a mixing module fitted upstream of SCR catalyst. The module was made of aluminium alloy in shape of gas carburettor and had an inbuilt gallery with a number of holes at its internal periphery. The working principle was that the injected liquid urea solution before reached the exhaust gas was flowing first inside the module's gallery what give an extra time for the urea evaporation and then the vapour escaped through the holes and mixed with exhaust. The mixing module induced a pressure drop which facilitated to disperse the vapour urea in an exhaust upstream of the SCR catalyst. Figure 3.1 presents the exhaust system layout with a concept urea dosing that was set up for the test purposes on the engine test bed.

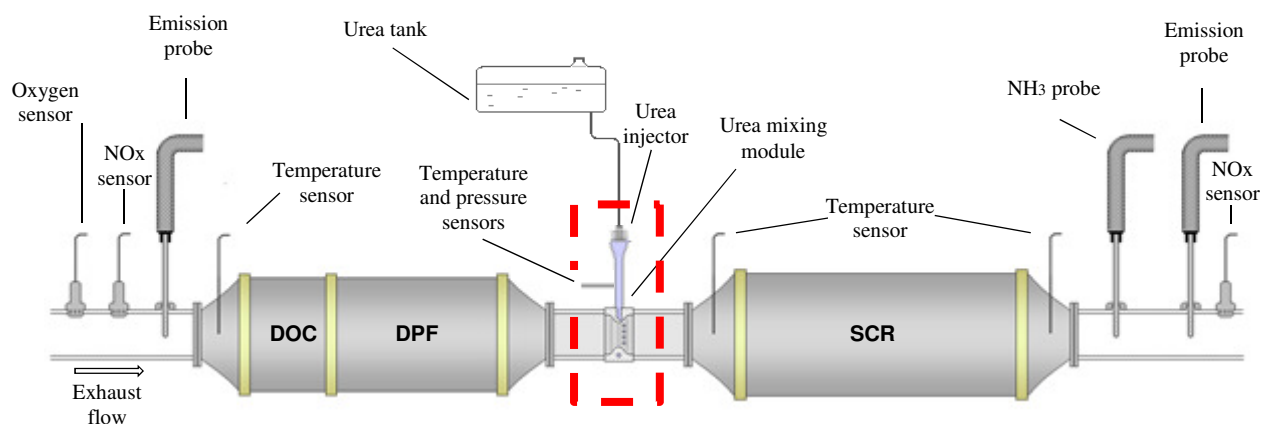


Figure 3.1. Concept of indirect urea dosing in the SCR system.

In a concept solution standard urea multi holes injector was used and dosed liquid urea into cone-shaped funnel directly connected to the mixing element via straight piece of metal tube. During the test run pressure and temperature measurements of urea dosed were taken at the inlet of the mixing module.

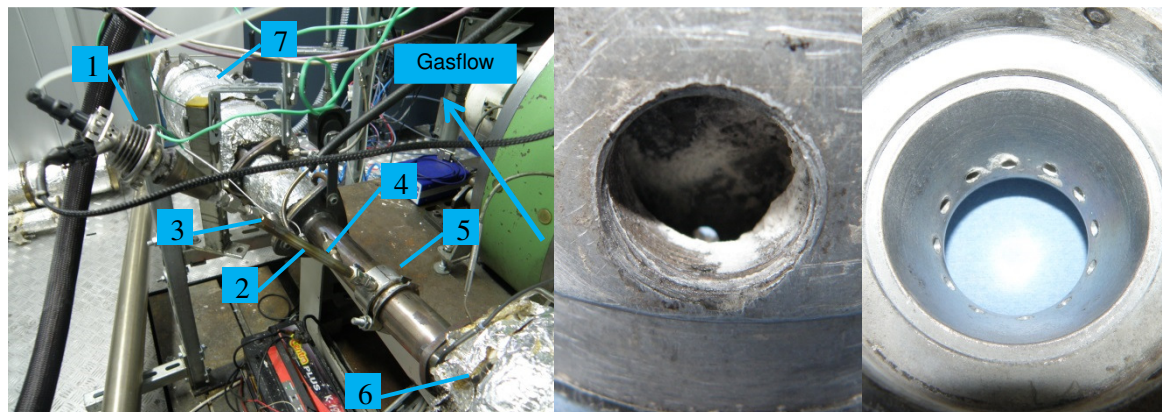


Figure 3.2. General view on the indirect urea dosing system: 1 – urea injector, 2 – urea temperature port, 3 – urea pressure port, 4 – tube, 5 – mixing module, 6 – DPF filter, 7 – SCR catalyst.

Figure 3.3. General view on the urea mixing module.

Standard urea dosing is shown in Figure 3.4, where the urea is injected directly into the exhaust gas. Between the injector and the SCR catalyst, a urea mixer is fitted which is made of metal blades with fixed geometry and which helps to break up urea droplets and achieve (as much as possible) even urea distribution on the SCR catalyst face.

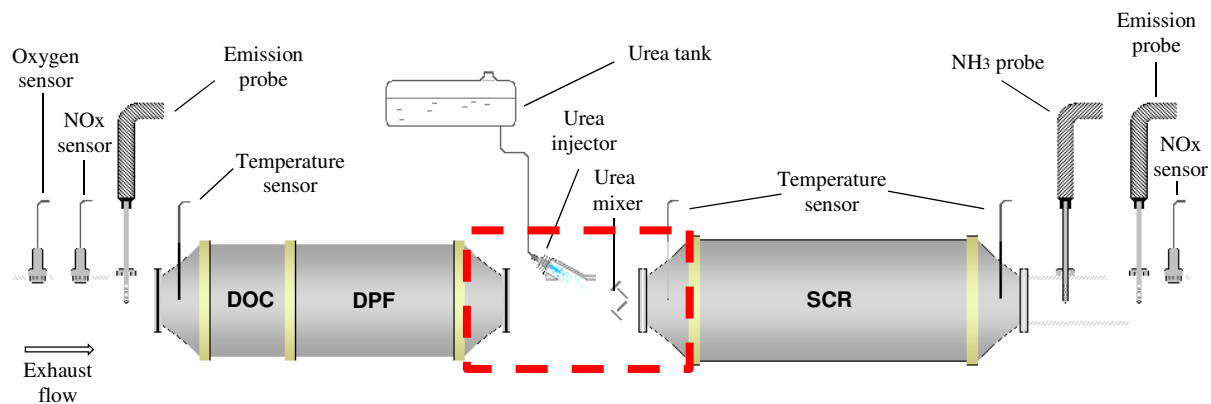


Figure 3.4. SCR system with a standard urea dosing in a liquid phase.

4. Test methodology

The study on the influence of urea dosing method on the SCR performance was carried out under steady-state engine operation. A dedicated test procedure was prepared, covering a wide range of exhaust gas temperatures and the test was run with both standard and concept urea dosing methods. As indicated by the dash line on Figures 3.1 and 3.4 urea dosing systems were changed over accordingly while the rest of exhaust layout remained unchanged. In the first approach standard urea dosing was tested and afterwards the concept dosing was put under the test.

The test itself lasted two hours and consisted of six 20-minute test steps covering exhaust gas temperature in a range from 180°C to 380°C. Test was carried out at fixed engine speed of 1900 rpm. Exhaust gas temperature was adjusted by changing the engine load in a range between 60÷400 Nm and it the gas temperature for each following step was greater by approximately 40°C than in the previous step. The engine was run under EGR valve shut-off conditions - therefore the NO_x concentration in the raw exhaust was high and varied from 580 ppm to 1100 ppm. Exhaust mass flow changed in the range between 230-400 kg/h.

Above test procedure allowed to compare NO_x conversion efficiency for both urea dosing methods in a function of exhaust gas temperature.

The quantity of urea dosed was expressed by a stoichiometric ratio α calculated as a quotient of the amount of ammonia molecules from the urea (NH₃IN) and the amount of nitrogen oxides molecules (NO_xIN) in the elementary exhaust gas mass flow.

$$\alpha = \frac{NH_3 IN}{NO_x IN} \quad (4.1)$$

Studies were carried out at three α ratios set to 0.6, 0.8 and 1.0. Exhaust gas emission was measured continuously at two points: at the engine outlet upstream of the DOC and downstream of the SCR catalyst, where the ammonia concentration was also measured. Further measurements were: gas temperature at SCR inlet and outlet, urea flow rate, temperature, pressure and a number of regular engine parameters to monitor and ensure the repeatability of the engine operation over the test time.

The quantity of urea injection corresponding to the α ratio was calculated by the control unit as a function of the actual exhaust mass flow rate and current NO_x concentration measured by the portable NO_x sensor fitted at the engine outlet. The urea solution was then injected at a pressure of approx. 5 bar by the multi-hole injector depending on the system configuration: directly into the exhaust gas stream (standard) or to the mixing element (concept).

Before each test was started, the entire exhaust line was carefully pre-conditioned in order to clean-up any urea deposits and carbon particles collected inside the DPF filter. It was also necessary to eliminate ammonia saturation of the SCR catalyst that could be left after previous test run and to ensure good

stability and repeatability of the initial test's conditions. The pre-conditioning was executed at high exhaust gas temperature generated by the engine running under high load conditions with the urea dosing system switched off.

5. Test results

5.1. Test results analysis

Obtained test data were processed and presented in a form of graphs with selected SCR operating parameters. The graphs directly compare the standard and concept methods of urea dosing for the test run. Test results were prepared separately for each α ratio and include the following parameters:

- NOx conversion efficiency calculated by the formula:

$$NOx\ conversion\ [\%] = \frac{NOxDOC_{IN} - NOxSCR_{OUT}}{NOxDOC_{IN}} * 100\% \quad (5.1)$$

- NH₃ concentration measured at SCR outlet.
- NOx concentration at DOC inlet and SCR outlet.
- Exhaust gas temperature and pressure at the inlet and outlet of the SCR.
- Urea solution mass flow.
- Gas urea temperature and pressure.

5.2. Test results under steady-state engine operation

The graphs below present modal analysis of test run under engine steady-state operation. The core parameter for test results evaluation was the NOx conversion efficiency as a function of the urea dosing method. Based on test data, it was stated that the concept urea system was beneficial in terms of NOx reduction over almost the entire range of the test cycle. This statement was further confirmed by the test runs with other α ratios.

The biggest benefits of concept dosing system for NOx reduction were obtained at α ratio equal to 0.8, where the difference in NOx reduction reached 28% at a gas temperature of 240°C.

The value of exhaust gas temperature measured at the SCR outlet was always greater than the one positioned at the SCR inlet. It indicates that the NOx reduction process is an exothermic reaction.

The first test was carried out for α ratio set to 0.6. During the first 130 seconds of the test at the lowest exhaust temperature of 180°C the NOx conversion for concept dosing was significantly lower compared to the standard one, but then it started to rise and had an advantage over the standard dosing for the majority of the test. Lower NOx conversion during the initial phase can be explained by the time delay of urea reaching the exhaust stream, due to the necessity of initial saturation of the mixing module with urea. The biggest difference in NOx conversion values for concept urea dosing was up to 10% within the gas temperature range 202-300°C. Ammonia slip was not detected at this α ratio.

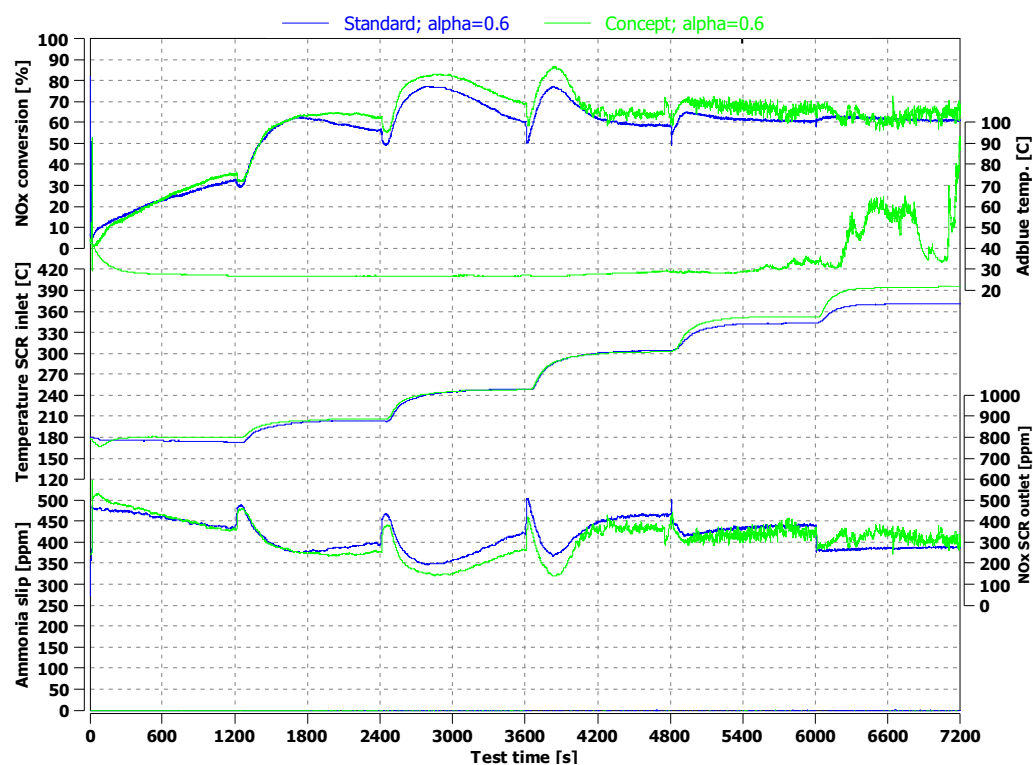


Figure 5.1. Comparison test results of SCR operating parameters for standard and concept urea dosing at $\alpha = 0.6$.

The following test with α ratio equal to 0.8 was most advantageous for concept dosing over the standard solution (Figure 5.2). The NOx conversion efficiency for the concept method was up to 28% greater than for the standard dosing, besides the initial 240s of the test where both conversion traces were quite in line. The ammonia slip was slightly higher for the concept solution.

In the last case of α ratio equal to 1.0 (Figure 5.3) the NOx conversion efficiency was lower by up to 9% for the concept dosing up to the exhaust temperature of 215°C. For the remaining part of the test the NOx conversion was greater by up to 11%. The ammonia slip was significantly higher for the concept solution.

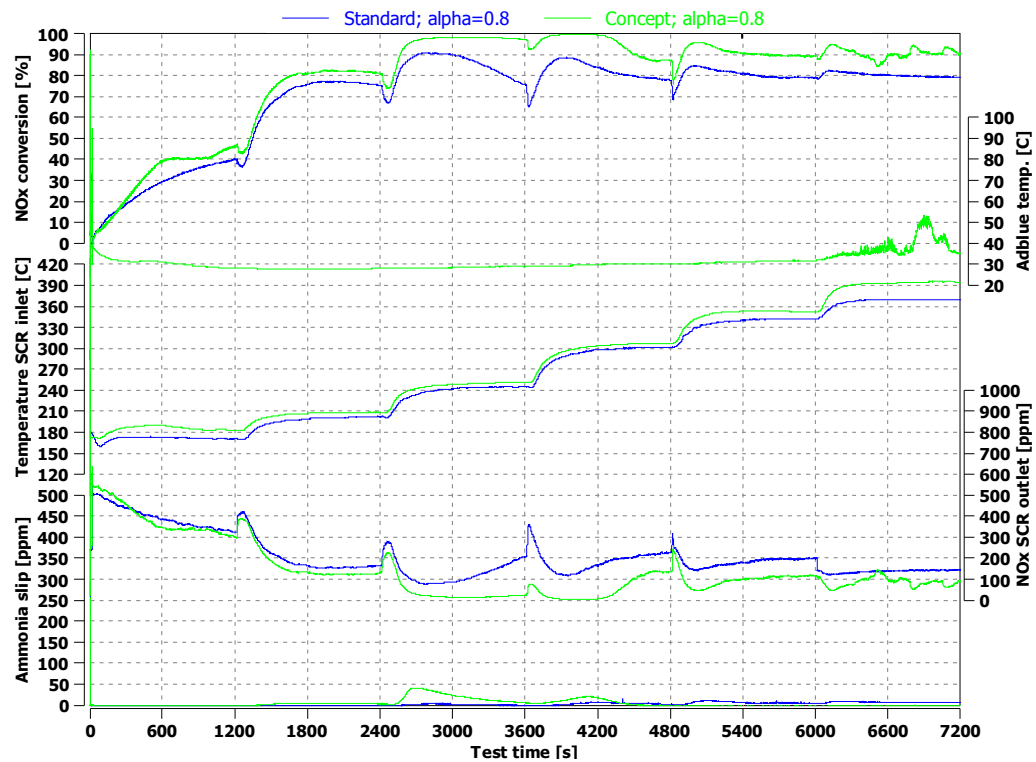


Figure 5.2. Comparison test results of SCR operating parameters for standard and concept urea dosing at $\alpha = 0.8$.

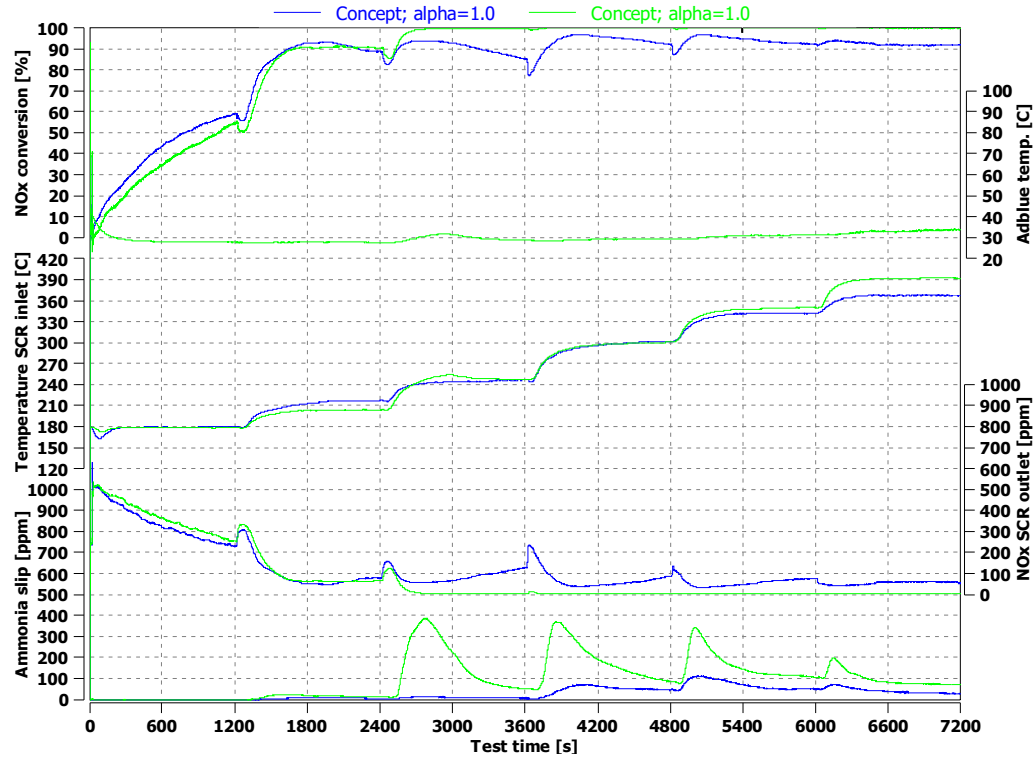


Figure 5.3. Comparison test results of SCR operating parameters for standard and concept urea dosing at $\alpha = 1.0$.

Considering the concept dosing method it was noticed, that for all tested α ratios at initial phase of the test the NO_x conversion rate was lower than for the standard solution. This fact can be explained by the time delay of urea reaching the exhaust.

Following the initial phase, the timing of which varied according to the α ratio, the NO_x conversion for concept system was greater and the difference in NO_x reduction was most evident in the middle and upper range of the exhaust gas temperature what corresponded to the test steps number 3-5.

Further improvement of concept solution should concentrate on optimization of the shape and volume of the mixing element in order to decrease the urea delay and also the exhaust back pressure.

Ammonia emission downstream of the SCR catalyst (NH₃ slip) is a critical parameter defining the operation properties of SCR system. The slip itself is difficult to control and often takes a form of a sudden release of volatile ammonia stored inside the SCR catalyst. The ability of ammonia storage within the SCR catalyst decreases with increasing temperature and vice versa – the lower the temperature, the greater the amount of ammonia that can be stored inside the catalyst. In the case of an increase in gas temperature, the ability to store ammonia is reduced, causing spontaneous ammonia release, even if the urea dosing was stopped. The ammonia slip may also occur if the urea is overdosed or if the NH₃ distribution across SCR face is uneven.

For the concept solution at dosing ratios of $\alpha=0.8$ and $\alpha=1.0$, ammonia concentration was higher than for the standard solution. The reason may be an uneven ammonia distribution on the SCR inlet face or possibly greater urea to ammonia conversion efficiency, which was essentially the gist of the concept solution.

6. Discussion

Test results obtained give a certain overview on a concept system performance under steady state operation. The concept has proven to be more efficient in NO_x reduction for a wide gas temperature range, but also can be disadvantageous at low gas temperature. The best combination was seen for the test at $\alpha=0.8$, in which the concept solution presents a significant increase in NO_x reduction.

The idea of an indirect urea dosing aimed for better NO_x reductant preparation before introducing it into the exhaust. Preliminary evaporation of urea by means of mixing element supposed to enhance the rate of urea decomposition into ammonia, what is currently the subject of much research.

Investigation on presented concept revealed that there are still many open questions which need to be resolved. Some critical conclusions can be pointed out, as follows:

- For the concept dosing, the NO_x conversion efficiency during low gas temperature was insufficient comparing to the standard dosing. This issue needs to be further investigated and improved.
- Secondly, the method of gas urea introduction into the gas stream via the mixing unit needs to be optimized to not create an excessive increase in the exhaust backpressure.
- Finally, it would be worth carrying out a study on the properties of the material the module is made of, as they might influence the pace of thermal urea decomposition. Selection of a material may be advantageous for enhancing urea to ammonia conversion before the reductant reaches the SCR catalyst.

Further research work requires an investigation on ammonia slip (in order to decrease it). Ammonia concentration measurements on the SCR face should be carried out and optimized to achieve (as much as possible) an even NH₃ distribution.

The final point is to verify the concept for deposit formation during regular operation.

7. Summary

The exhaust after-treatment with selective catalytic reduction system is a complex but very effective way of NO_x removal from combustion gases. The SCR method still requires development especially when it is operated under engine warm-up and idle conditions. Urea injection at low exhaust gas temperature is critical due to the limited ability to evaporate and chemical decomposition in the exhaust and further in the catalyst. An important in-service issue is urea deposit formation inside the SCR system, which leads to a deterioration in system functionality. Deposit formation is reversible and the solid fraction gets removed at high gas temperature.

The purpose of this study was to evaluate the effect of urea preparation on NO_x conversion in an SCR catalyst. The preparation process relies on indirect urea dosing via a mixing module in order to help it to evaporate prior to introduction upstream of the SCR catalyst. An expected effect was to accelerate thermal decomposition of urea and ultimately to increase NO_x conversion efficiency and possibility reduce urea consumption.

The study was conducted on a diesel engine and after-treatment with SCR system in which the urea dosing module was changeable between the standard and concept solutions. This allowed the influence of dosing method on SCR performance to be verified.

A custom made concept system was prepared and put under test. As it was a very simple solution it needed development works, but it was able to give an insight into achievable benefits.

It has been found that concept dosing method can increase NO_x conversion in the SCR system compared to standard liquid urea dosing. The gain was noticed especially in the gas temperature range from 220°C to 350°C under steady-state engine operation.

The studies carried out demonstrated a certain potential for the concept and the results obtained are a great incentive for further research on this subject.

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