



## Full Length Article

# Effect of late diesel injection on close-coupled SCR + ASC during DPF regeneration period

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## ABSTRACT

Future emission limits (Stage 6) for off-road engines will require more efficient removal of nitrogen oxides. The dual-SCR system has in addition of conventional main SCR catalyst after diesel oxidation catalyst (DOC) and particulate filter (DPF), a second SCR catalyst near to engine to enhance catalyst activity at low temperature periods. However, DPF regeneration requires periodic diesel fuel injection to DOC + DPF to oxidize carbonaceous particles at elevated temperatures. Late post-injection of diesel fuel was used during the regeneration period of a DPF. The study investigated how this strategy affects the performance of a close-coupled vanadium-based SCR with an ammonia slip catalyst. The exhaust aftertreatment system (SCR, DOC, DPF) was incorporated into the exhaust line of a high-speed, common-rail, diesel engine, designed for off-road applications fulfilling the latest emission legislation (Stage 5). Extensive bench experiments determined how late diesel injection through the close-coupled vanadium-SCR and ammonia slip catalyst affected the exhaust gas temperature, and whether high hydrocarbon concentrations from late diesel injection changed the catalyst performance. The SCR inlet temperatures ranged from 250 to 400 °C. Accumulation of hydrocarbons on the close-coupled vanadium-SCR catalyst at low exhaust temperatures was also examined. The study's overall conclusion is that the strategy of late diesel injection is feasible to adopt during the regeneration period of a particulate filter only at sufficiently high SCR-inlet temperatures ( $\geq 320$  °C). At lower temperatures, hydrocarbons might be stored in the catalyst. When the temperature increases again, exothermic reactions generated in the SCR may lead to notable catalyst deactivation.

## 1. Introduction

More effective exhaust gas aftertreatment systems are needed for the future abatement of emissions originating from internal combustion engines, such as diesels. Managing the exhaust gas temperature is a critical issue, helping aftertreatment catalysts work in their most effective temperature range. There are several methods for thermal management of exhaust gases. Hu et al. [1] divided these methods into either engine-based or device-added technologies that alter the exhaust gas temperature using external energy. A short warm-up period for catalysts during an engine cold-start is a main requirement. Exhaust gases must also attain the target temperature levels for the combination of a diesel

oxidation catalyst (DOC) and a diesel particulate filter (DPF) during engine operation, without cooling down during regeneration, when the soot combustion temperature of around 600 °C must be reached [1].

Diesel particulate filters are commonly used for collecting the solid particulates from the exhaust gas stream. The filter needs to be cleaned periodically to remove the accumulated particulates. This entails raising the exhaust gas temperature ( $>550$  °C) to the level required for soot oxidation for active DPF regeneration. Alternatively, soot is also oxidized passively at lower temperatures ( $>250$  °C) by nitrogen dioxide (NO<sub>2</sub>) during most driving conditions. Late diesel injection (LDI) is a common engine-based strategy to reach the high exhaust gas temperatures necessary for active DPF regeneration [2,3,4,5]. Most of the fuel from the LDI period during the late expansion stroke does not have time

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### Nomenclature

|                  |   |
|------------------|---|
| ASC              | ammonia slip catalyst                   |
| CARB             | California Air Resources Board          |
| CC               | close-coupled                           |
| DOC              | diesel oxidation catalyst               |
| DPF              | diesel particulate filter               |
| ds               | Downstream                              |
| EPA              | Environmental Protection Agency         |
| EU               | European Union                          |
| FID              | flame ionization detector               |
| FTIR             | Fourier-transform infrared spectroscopy |
| HC               | Hydrocarbon                             |
| LDI              | late diesel injection                   |
| N <sub>2</sub> O | nitrous oxide                           |
| NOx              | nitrogen oxides                         |
| NRMM             | Non-Road Mobile Machinery               |
| SCR              | selective catalyst reduction            |
| THC              | total hydrocarbons                      |
| us               | Upstream                                |
| V-SCR            | vanadium-based SCR                      |
| VEBIC            | Vaasa Energy Business Innovation Centre |

to burn in the cylinders end thereby enter the engine exhaust as fuel vapor. Consequently, this increases the concentrations of unburned hydrocarbons (HC) in the exhaust gases. Moreover, LDI has negative impacts on the engine's fuel economy, when brake specific fuel consumption increases with the amount of injected fuel per working cycle [4,5].

Together with particulate filters, different kinds of catalysts with diverse catalyst materials are used for the abatement of gaseous pollutant emissions from diesel engines. Selective catalytic reduction (SCR) is used in conjunction with an aqueous urea solution to reduce nitrogen oxides (NOx) from exhaust gases by turning them to less harmless gaseous components. The standard reaction in an SCR catalyst involves the NOx, ammonia (NH<sub>3</sub>) carried by the urea-water solution, and residual oxygen (O<sub>2</sub>), producing nitrogen and water [6]. The NOx conversion is the measure for the SCR capability to reduce NOx. A DOC is used to oxidize hydrocarbons and carbon monoxides from diesel engines. The correct order of exhaust aftertreatment devices in the exhaust pipeline is essential in thermal management. The DOC usually is placed upstream of the SCR for exhaust aftertreatment in heavy-duty applications. [7]. This layout means the DOC will also provide additional NO<sub>2</sub> to promote SCR reactions [8]. When LDI is used, more hydrocarbons end up in the exhaust and are oxidized by the DOC, thus increasing the downstream temperatures for DPF soot regeneration [4,5]. This paper discusses a study that utilized the LDI-assisted DPF regeneration cycle of an off-road engine in an SCR-focused study. Therefore, this period is referred to as LDI regeneration in this paper.

However, the concept of a close-coupled (CC) SCR system places the first, small SCR catalyst directly after the engine, instead of conventional location after DOC [7]. These dual-SCR (or twin-SCR) systems consist of small closed-coupled SCR before and larger main SCR catalyst after DOC + DPF units, to improve low temperature NOx removal to reach future emissions limits. This CC position means the SCR catalyst is heated faster, starting NOx conversion earlier. However, it also means the SCR catalyst is exposed to a different environment compared to its usual downstream position. Critically, the higher concentrations of hydrocarbons [6], carbon monoxide, and particulates may cause deactivation of the SCR catalyst [9]. Ding et al. [10] suggest that hydrocarbons may be adsorbed on the SCR catalyst with NH<sub>3</sub>. The hydrocarbons absorbed into the catalyst prevent the oxidation of NO. As a result of this process, NOx conversion decreases [10,11].

The three most commonly used SCR catalysts are based on copper-zeolite, iron-zeolite, and vanadium on titania-tungsten. Vanadium-based SCR catalysts (V-SCR) are known for their chemical tolerance against sulfur, whereas zeolite-based copper and iron catalysts are known for their resistance to higher exhaust gas temperatures [12]. The dependence on NO<sub>2</sub> for the NOx reduction activity varies by SCR catalyst types. A CC-V-SCR (i.e., without a preceding DOC) has been found to have poor NOx reduction performance, especially at low exhaust temperatures [13]. That study reported that the performance of a CC-V-SCR on a heavy-duty engine's exhaust declined when the exhaust gas temperature was below 280 °C. The low-temperature performance improved when an ammonia slip catalyst (ASC), whose main function is to oxidize any NH<sub>3</sub> remaining from the SCR reaction (see e.g. [6]).

HC species from diesel exhaust may be adsorbed onto an SCR catalyst, especially at low exhaust temperatures. This accumulated HC blocks the catalyst pores and active sites, reducing NOx conversion efficiency. Thermal treatment of a catalyst at high temperatures with the presence of O<sub>2</sub> can remove the carbonaceous deposits and recover the SCR performance. However, not only do the accumulated deposits have a negative impact on NOx conversion, but their rapid oxidation can lead to exotherms which can thermally damage the SCR catalyst [14].

CC-SCR systems with high NOx conversion efficiency are needed to meet the California Air Resources Board (CARB) upcoming Tier 5 emission standard for Non-Road Mobile Machinery (NRMM) [15]. Equally, these Tier 5 limits cannot be met without particulate filters as part of the exhaust aftertreatment system. For off-road engines from 56 kW to 560 kW, Tier 5 will require a 90 % reduction in NOx and a 75 % reduction in PM emissions compared to current Tier 4 limits set by the Environmental Protection Agency (EPA) of the United States. Tier 5 is scheduled to be phased into force, starting in 2029 [16].

This study investigates how LDI and high hydrocarbon concentrations resulting from its use affect the performance of a V-SCR catalyst combined with an ASC. In particular, the study examines the accumulation of hydrocarbons in a CC-SCR catalyst at low exhaust-temperatures. The objective is fill the knowledge gap relating to the combined use of CC-SCR catalysts when stressed periodically by high hydrocarbon and CO concentrations due to LDI. One pre-determined interest in the study related to the temperature window in which the SCR + ASC lets the LDI-derived HC through without shortcomings. The underlying assumption was that if LDI-derived HC pass the SCR + ASC unit, they might oxidize later in the following DOC increasing the exhaust temperature to a level of soot ignition temperature (~600 °C) for the last-positioned DPF. Another pre-determined interest was thus to establish if the SCR catalyst performance would be degraded by the use of LDI.

## 2. Experimental setup

This study was performed under laboratory conditions at the engine laboratory located in Vaasa Energy Business Innovation Centre (VEBIC), the interdisciplinary research facility of the University of Vaasa (Fig. 1).

### 2.1. Engine and exhaust aftertreatment devices

The examined exhaust gas aftertreatment system was incorporated into the exhaust line of an AGCO Power 49 AWF engine (Table 1). This is a state-of-the-art, turbocharged and intercooled engine, designed for off-road use. It is a high-speed, four-cylinder, common-rail diesel engine that meets the latest emission standard sets by EPA (Tier 4 Final, [17]) and European Union (EU Stage V, [18]). The engine was loaded with a Schenck W400 water-cooled eddy current dynamometer, controlled by a Horiba SPARC controller. The fuel was low-sulfur (<10 ppm) diesel which met the SFS-EN 590:2022 standard [19]. Throughout the study, the engine was operated at steady-state operating points.

The studied aftertreatment system consisted of a pre-SCR mixer; a vanadium-based CC-SCR catalyst, combined with an ASC (ceramic 400

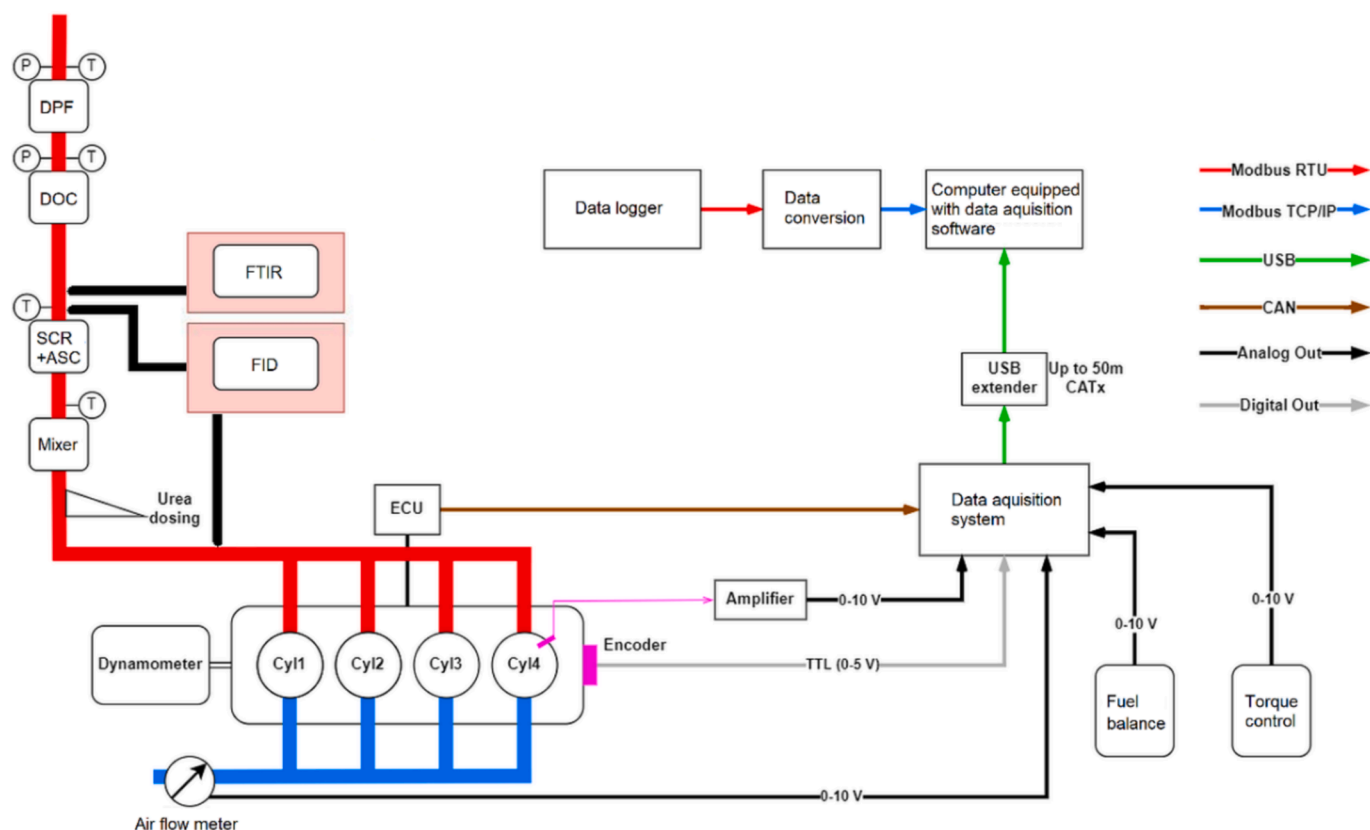


Fig. 1. Experimental scheme.

Table 1  
Engine specification.

| Type                              | AGCO Power 49 AWF                    |
|-----------------------------------|--------------------------------------|
| Rated speed (r/min)               | 2100                                 |
| Maximum power at rated speed (kW) | 141                                  |
| Maximum torque at 1500 r/min (Nm) | 800                                  |
| Cylinder number                   | four                                 |
| Bore (mm)                         | 108                                  |
| Stroke (mm)                       | 134                                  |
| Air intake                        | turbocharged, intercooled            |
| Fuel injection                    | common-rail                          |
| Emission standard compatibility   | EPA Tier 0, 2, 3, 4i, 4F, EU Stage V |

cpai, 4.6L) containing a low amount of platinum; a DOC (ceramic 400 cps, 4.6L) containing both platinum and palladium (4:1); and a DPF (ceramic 300 cps, 5.8L), arranged in that sequence. An aqueous urea solution – called AdBlue® in Europe, or diesel exhaust fluid (DEF) in the US – was injected into the exhaust gas stream directly into the pre-SCR mixer to promote the SCR. The purpose of the pre-SCR mixer was to assist the urea solution distribution, so that it is evaporated and decomposed into NH<sub>3</sub> before entering the catalyst. The platinum containing ASC integrated into the rear part of the SCR catalyst enables more aggressive NH<sub>3</sub>-dosing and higher NO<sub>x</sub> conversions by eliminating excessive NH<sub>3</sub> emissions.

## 2.2. Analytical procedures

All emission components shown in Table 2 were sampled from the wet exhaust gas. A Fourier transform infrared spectrometer (FTIR, DX4000 by Gaset, Vantaa, Finland) was used to measure nitrogen oxide (NO), NO<sub>2</sub>, NH<sub>3</sub>, and N<sub>2</sub>O concentrations downstream of the CC-SCR + ASC. An electrically heated sampling probe (PSP4000-H by M&C, Ratingen, Germany) was connected to the pressure-reducing unit to get

Table 2  
Analytical instruments.

| Component  | Analyzer                                | Technology      | Accuracy* |
|--|---|-----------------|-----------|
| NO, NO <sub>2</sub> , NH <sub>3</sub> and N <sub>2</sub> O | Gaset DX4000                            | FTIR            | ± 2 %     |
| Raw NO <sub>x</sub>  | Bosch NO <sub>x</sub> sensor ACX248097A | Electrochemical | n/a       |
| THC  | Cambustion HFR500                       | Fast FID        | ± 1 %     |

\*Accuracy provided by manufacturer.

the sample from the exhaust gas to the FTIR spectrometer, preventing the sample gas from cooling and condensing. FTIR's portable sampling unit was used to pump the sample gas from the sampling point. After the sampling unit, the sample gas was directed into the FTIR spectrometer that was connected to an external computer through an RS232 interface.

A NO<sub>x</sub> sensor (ACX248097A by Bosch) measured the raw NO<sub>x</sub> concentration upstream of the pre-SCR mixer, with a second similar sensor positioned upstream of the DOC. Exhaust gas temperatures were recorded at four points: upstream (us) and downstream (ds) of the CC-SCR + ASC, and upstream and downstream of the DOC and the DPF.

The concentrations of total hydrocarbons (THC) were analyzed from the exhaust gas sampled from upstream and downstream of the CC-SCR + ASC by using a fast flame ionization detector (FID, HFR500 by Cambustion, Cambridge, United Kingdom). The FID analyzer's detectors were located in the sampling heads near the sampling points. The sampling heads were connected to a control unit via a conduit containing the necessary connections for the detectors. A vacuum pump drew the sample gas into the detector through a heated probe. The FID analyzer was connected to its own control software via a RS-485 interface and provided an analog output signal from 0 to 10 V DC.

The engine control unit recorded the engine speed, torque, air mass flow, and urea dosing. The fuel flow was determined with a fuel balance

(733S by AVL, Graz, Austria). A data acquisition system (DewesoftX by Dewesoft, Trbovlje, Slovenia) collected and stored the measurement data from the FID analyzer, NOx and temperature sensors, engine control unit, and the fuel balance. The LDI quantities, urea dosing and regeneration functions were controlled via an engine management software (WinEEM).

### 2.3. Phases of experimental study

#### Defining load points, maximum NOx conversions and NH<sub>3</sub>-to-NOx ratios

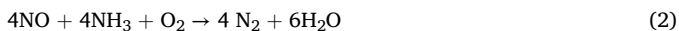
The research started with experiments to determine the correct operating points (speed, load) to achieve the targeted exhaust gas temperatures of 250, 280, 320, 350, 400, and 450 °C. The CC-SCR + ASC performance experiments were then conducted at steady-state driving modes, based on these operating points (Table 3).

These studies established the urea injection quantity that allows to reach the maximum NOx conversion in the CC-SCR. In order to find out the quantities, the similar procedure was accomplished separately at each load point. Raw NOx emission was first recorded by running the engine without urea dosing. Secondly, the raw NOx concentration value was used to determinate the difference between actual and target tail-pipe NOx. Third, based on the previous result, the theoretically required (stoichiometric) dosage amount of an aqueous urea solution containing 32.5 % urea was determined as follows [20]:

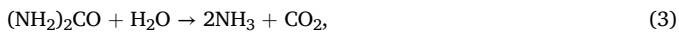
$$\dot{m}_{\text{urea solution, stoic}} = \frac{M_{\text{urea}}}{MF_{\text{urea solution}}} \cdot \frac{SR_{\text{NO}_2}}{2 \cdot M_{\text{NO}_2}} \cdot \delta\text{NOx} = 2.008 \cdot \delta\text{NOx} \quad (1)$$

where  $M_{\text{urea}} = 60.06$  g/mol,  $M_{\text{NO}_2} = 46.0055$  g/mol, and urea mass fraction of the urea solution  $MF_{\text{AdBlue}} = 0.325$ .  $SR_{\text{NO}_2}$  depends on the  $\text{NO}_2/\text{NOx}$  ratio.  $SR_{\text{NO}_2} = 1$ , if  $\text{NO}_2/\text{NOx} < 0.5$  [20].

The injected urea decomposes in SCR to NH<sub>3</sub> through several chemical paths [6]. During the third step of the procedure to find out the optimal urea dosage amount, it was assumed that the dominant chemical reaction in SCR happens only between NO and NH<sub>3</sub> with oxygen promotion. This reaction has been considered the main or standard SCR reaction [6,21].



NO was allowed to represent all NOx here and the mole ratio was assumed to be thus 1:1 for NOx:NH<sub>3</sub> stoichiometry. Moreover, the overall urea decomposition as a source of NH<sub>3</sub> was assumed to happen via the reaction



which is in line with the general understanding of urea decomposition pathway, see e.g. [22]. For urea to NH<sub>3</sub> stoichiometry, the mole ratio was assumed to be thus 1:2.

Then, while the engine was running, urea dosing was increased stepwise until the NOx conversion no longer increased, or started to drop. The next appropriate urea injection quantity was approximated by using the ratio of the injected urea amount and the stoichiometric urea amount for complete NOx removal. The NH<sub>3</sub> concentration after catalysts varied by the catalyst and feed conditions. NOx conversion was allowed to stabilize before initiating the measurements after changes in

**Table 3**  
Target temperatures and corresponding engine speed and load points.

| Operating Point  | 1    | 2    | 3    | 4    | 5    | 6*   |
|--|------|------|------|------|------|------|
| Target exhaust temperature at the inlet of the SCR + ASC unit (°C) | 250  | 280  | 320  | 350  | 400  | 450  |
| Speed (rpm)  | 1500 | 1500 | 2100 | 2100 | 2100 | 2100 |
| Load (Nm)  | 210  | 260  | 275  | 315  | 410  | 490  |

\*Operating point 6 (450°C) was used only during 40 min of engine operation in Phases B–C.

urea dosing. In addition to NOx conversion, N<sub>2</sub>O and NH<sub>3</sub> downstream of the CC-SCR + ASC were recorded. The molar ratio of the fed ammonia amount to feed NOx is denoted NH<sub>3</sub>-to-NOx ratio.

#### The effect of late diesel injection on exhaust gas temperatures and CC-SCR + ASC performance

Phase B examined how late diesel injection through the CC-SCR + ASC affected the exhaust gas temperatures. The target temperature after the DOC (i.e., at the DPF inlet) was 570 °C. Phase B also investigated whether the high concentrations of hydrocarbons associated with LDI degrade the CC-SCR catalyst performance. If so, this phase sought then whether 40 min of engine operation at a high exhaust temperature (450 °C) is sufficient to restore SCR performance. This was the highest inlet temperature which was chosen for the entire studied exhaust gas aftertreatment system in order to maintain the temperature of the excess HC-containing exhaust gas at a suitable level if first passing through the SCR and then through the DOC and DPF. However, this study was limited to the SCR + ASC only. Phase B's experimental matrix used the maximum NH<sub>3</sub>-to-NOx ratios which were determined in Phase A (Table 4).

#### Hydrocarbon accumulation in a CC-SCR catalyst at low exhaust-temperatures

Phase C aimed to investigate hydrocarbon accumulation on the SCR catalyst surfaces during LDI regeneration at 280 °C. First, the engine was run a 30-minute LDI regeneration period (Step II, Table 4). After regeneration period, the engine was operated at high load so that the exhaust gas temperature climbed to 450 °C for 40 min (Step IV, Table 4). Temperature differences over the CC-SCR + ASC and DOC were determined for both the exhaust heat-up period and the subsequent 40 min high-temperature operation.

The engine was run a total of three times in different days at each target exhaust gas temperature of 250 to 400 °C during the study. Maximum NOx conversion with corresponding NH<sub>3</sub> and N<sub>2</sub>O concentration was sought twice at each target exhaust gas temperature during Phase A of the engine runs. Each day, the exhaust gas temperatures downstream and upstream SCR + ASC unit and raw-NOx emission were recorded in 10-minute periods three times, but the maximum NOx conversion and corresponding concentrations of NOx after SCR + ASC,

**Table 4**  
Experimental matrix, Phase B.

| Step | Actions                    | Exh. Temp. us of SCR + ASC (°C)     | Duration | NH <sub>3</sub> -to-NOx Ratio   | Measurements (us = Upstream, ds = Downstream)  |
|------|----------------------------|-------------------------------------|----------|---------------------------------|--|
| I    | Emission measurements      | 250/<br>280/<br>320/<br>350/<br>400 |          | Maximum NH <sub>3</sub> -to-NOx | NOx conversion, N <sub>2</sub> O and NH <sub>3</sub> ds of SCR                       |
| II   | LDI regeneration           | 250/<br>280/<br>320/<br>350/<br>400 | 30 min   | 0                               | LDI quantity, HC us and ds of SCR, exhaust temp. us and ds of SCR + us and ds of DOC |
| III  | Emission measurements      | 250/<br>280/<br>320/<br>350/<br>400 |          | Maximum NH <sub>3</sub> -to-NOx | NOx conversion, N <sub>2</sub> O and NH <sub>3</sub> ds of SCR                       |
| IV   | Engine high load operation | 450                                 | 40 min   | 0                               | Exhaust temp. us and ds of SCR + us and ds of DOC                                    |
| V    | Emission measurements      | 250/<br>280/<br>320/<br>350/<br>400 |          | Maximum NH <sub>3</sub> -to-NOx | NOx conversion, N <sub>2</sub> O and NH <sub>3</sub> ds of SCR                       |

$\text{NH}_3$  and  $\text{N}_2\text{O}$  were determined once.

The uncertainty related to exhaust gas temperatures, raw-NOx was approximated by calculating the standard deviation of the exhaust gas temperature and raw-NOx concentration averages from each day, taken from each 10-minute recording. For the maximum NOx conversion and corresponding concentrations of NOx after SCR + ASC,  $\text{NH}_3$  and  $\text{N}_2\text{O}$ , the uncertainty was approximated by calculating the standard deviation of two daily values. The recordings of HC upstream and downstream of the SCR + ASC unit for Phase C was recorded only once.

### 3. Results and discussion

The results discussion is organized into the four research phases (A–C) outlined in the previous section. The first subsection presents the maximum NOx conversions and  $\text{NH}_3$ -to-NOx ratios that were detected. Then, the results for the high-temperature operating points are presented and discussed. The results from the more challenging low-temperature operating points are discussed last.

#### 3.1. Maximum NOx conversions and $\text{NH}_3$ -to-NOx ratios

Phase A aimed to find the correlation between NOx conversion and  $\text{NH}_3$  slip, and also to establish the maximum NOx conversion at target exhaust temperatures of 250–350 °C in SCR inlet (Fig. 2). As a rule, NOx conversion efficiency increased with exhaust gas temperature. The highest NOx conversion of 76 % was detected at 350 and 400 °C (Table 5). The space velocity (SV) was calculated as a ratio of the exhaust gas volume flow and the volume of the SCR + ASC catalyst in each operating point, including 400 °C.

Despite the ASC, the exhaust still contained relatively high  $\text{NH}_3$  concentrations after the SCR + ASC unit, even when NOx conversion was at its highest. Additionally, significant  $\text{N}_2\text{O}$  formation occurred at low exhaust-temperatures. The main contributors to  $\text{N}_2\text{O}$  from urea-based SCR units are expected to be the undesired reactions between NOx and  $\text{NH}_3$  over the SCR catalyst, and in this case particularly  $\text{NH}_3$  access into ASC, where a part of residual  $\text{NH}_3$  oxidized to  $\text{N}_2\text{O}$  [23].

**Table 5**

Maximum NOx conversions and corresponding  $\text{NH}_3$ -to-NOx ratios, exhaust gas mass flows, space velocities,  $\text{NH}_3$  slip, and  $\text{N}_2\text{O}$  formation at different operating points.

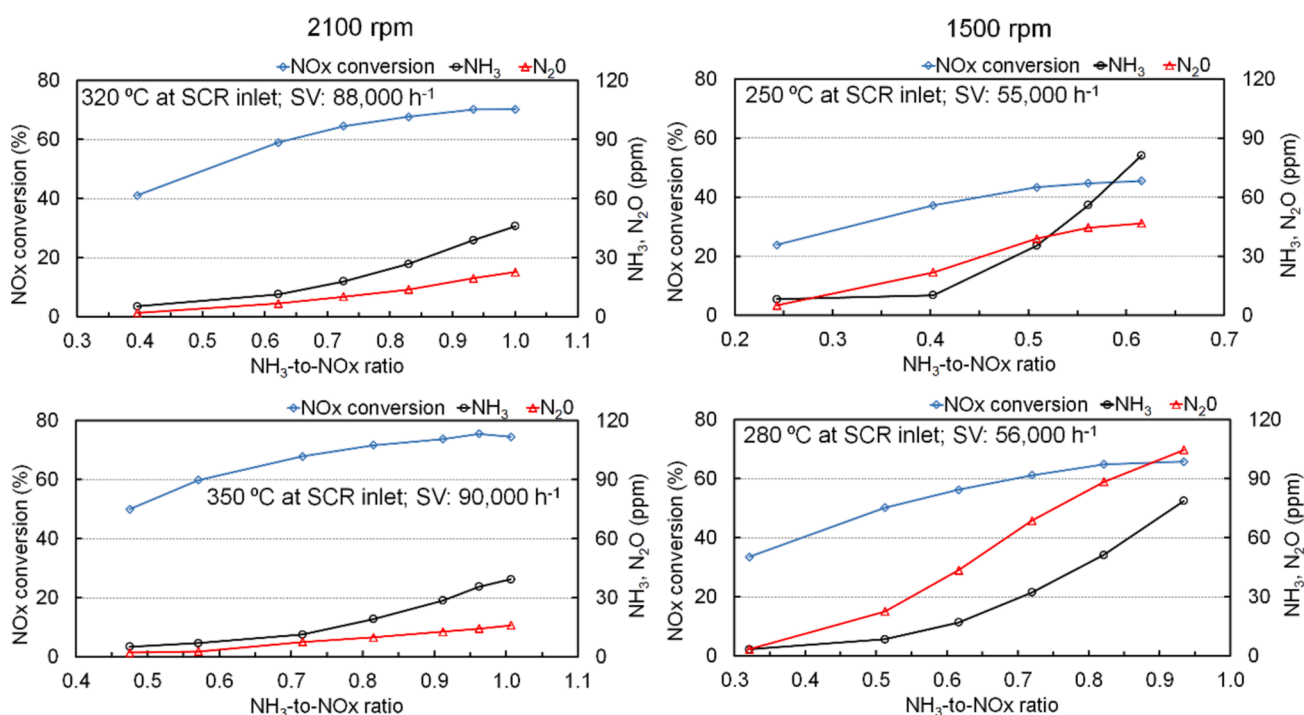
| Temperature at SCR inlet | Exhaust gas mass flow | Space velocity | Max. NOx conversion | $\text{NH}_3$ -to-NOx ratio | $\text{NH}_3$ | $\text{N}_2\text{O}$ |
|--------------------------|-----------------------|----------------|---------------------|-----------------------------|---------------|----------------------|
| °C                       | kg/h                  | 1/h            | %                   |                             | ppm           | ppm                  |
| 250                      | 328                   | 55,000         | 45                  | 0.55                        | 56            | 45                   |
| 280                      | 340                   | 56,000         | 65                  | 0.8                         | 51            | 89                   |
| 320                      | 528                   | 88,000         | 70                  | 0.95                        | 39            | 20                   |
| 350                      | 540                   | 90,000         | 76                  | 0.95                        | 36            | 14                   |
| 400                      | 590                   | 98,000         | 76                  | 0.9                         | 30            | 7                    |

At higher temperatures and the associated high SV, exhaust gases passing through the catalyst may not have sufficient residence time for catalytic reactions, thus reducing conversion efficiency. Moreover, to improve catalyst performance, it is important to provide enough time and distance for  $\text{NH}_3$  conversion and uniform distribution before the solution enters the catalyst [24]. This study used a mixer designed to mix the urea solution with the exhaust gas, although the mixing distance and size of the CC-SCR + ASC were not specifically optimized for this particular experimental setup. It should also be noted that the goal of the CC-SCR catalyst was not to achieve complete NOx reduction, but to be complemented by a larger main SCR + ASC unit after DPF to achieve target total NOx removal efficiency (>95–98 %).

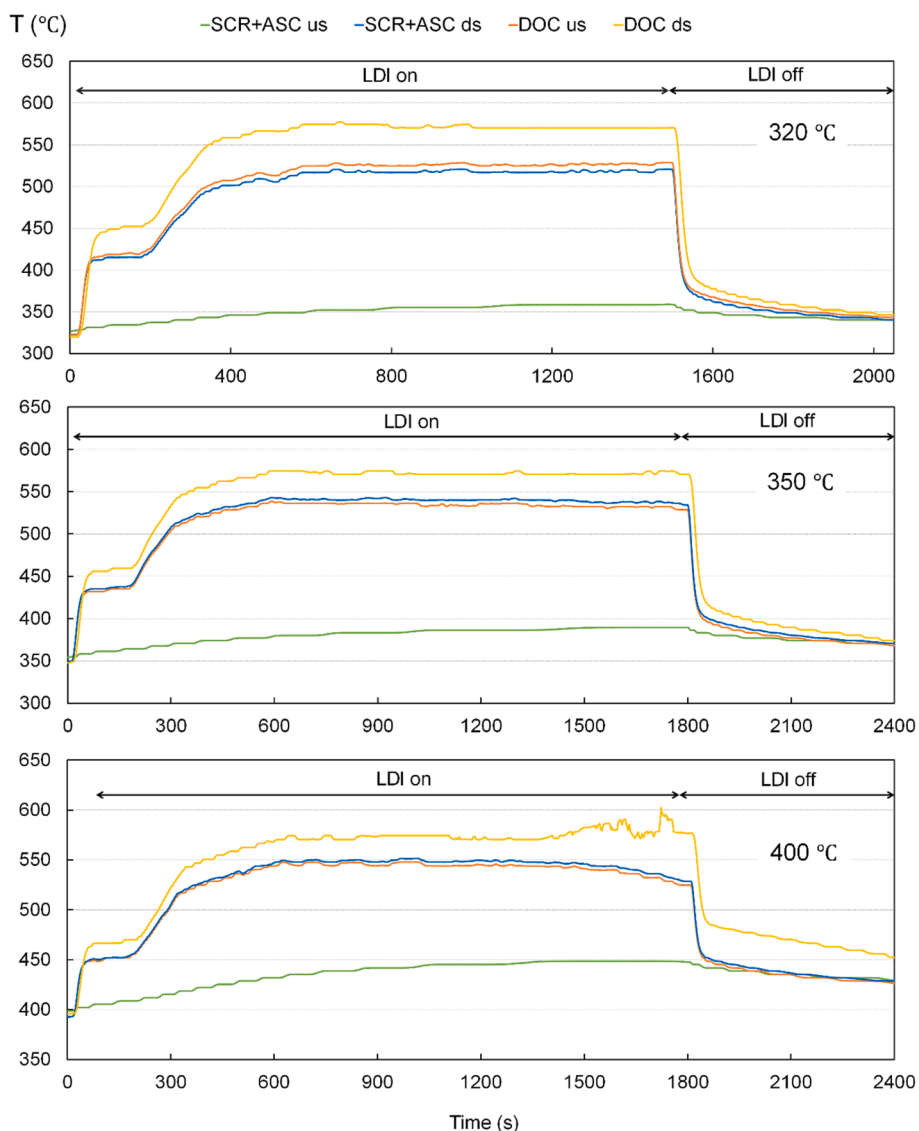
#### 3.2. The effect of late diesel injection at target exhaust temperatures of 320, 350 and 400 °C

The first part of Phase B was to establish how LDI affected exhaust temperatures, starting with LDI regeneration initiated at the higher-temperature operating points: 320, 350, and 400 °C (Fig. 3). The late diesel injection was continued for 25–30 min at each operating point. Urea injection was switched off during the LDI regeneration.

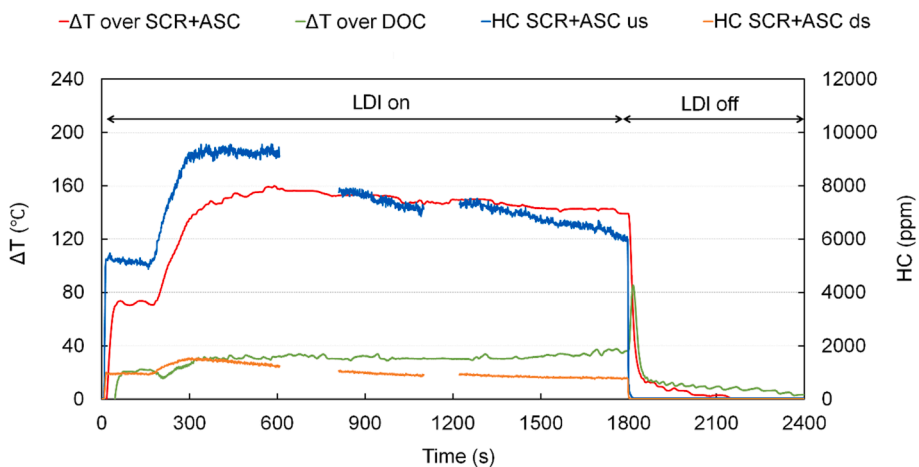
The 570 °C target temperature after DOC was reached in all cases.



**Fig. 2.** NOx conversion,  $\text{NH}_3$ , and  $\text{N}_2\text{O}$  at different operating points: target SCR inlet temperatures and space velocities are shown – The standard deviation of the  $\text{NH}_3$  averages was 43.3 % at 250 °C, 4.5 % at 280 °C, 1.0 % at 320 °C, 2.8 % at 350 °C and the  $\text{N}_2\text{O}$  averages 7.7 %, 8.4 %, 5.8 %, 0.2 %, respectively.



**Fig. 3.** Exhaust gas temperatures during LDI regeneration at the exhaust gas temperatures of 320 °C, 350 °C and 400 °C ( $\text{NH}_3$ -to- $\text{NO}_x$  ratio 0) – The standard deviation of the SCR ds temperature averages was 1.2 % at 320 °C, 0.8 % at 350 °C, 2.2 % at 400 °C and the SCR us temperature averages 2.6 %, 1.4 %, 3.9 %, respectively.



**Fig. 4.** Temperature differences over SCR + ASC unit and DOC; and HC concentrations upstream and downstream of SCR + ASC during LDI regeneration at 350 °C ( $\text{NH}_3$ -to- $\text{NO}_x$  ratio 0).

The maximum allowed SCR catalyst temperature (550 °C) was not exceeded at any operating point. At 320 °C, the maximum SCR ds temperature was 521 °C; at 350 °C it was 538 °C; and at 400 °C, it topped out at 548 °C.

The exhaust gas temperature rose more in the CC-SCR + ASC than in the DOC, indicating that a large part of the HC was already oxidized in the SCR + ASC unit. HC oxidation in the SCR + ASC was also confirmed through HC measurements made upstream and downstream of the SCR + ASC (Fig. 4, at 350 °C). The behavior of these temperature differences across the SCR + ASC and DOC was very similar at 320 °C. At the 350 °C operating point, the SCR ds temperature decreased slightly during the LDI period (Fig. 4). The maximum HC concentration before the SCR reached 9,500 ppm. At the same instant, the HC concentration after the SCR was only 1,500 ppm. It should be noted that the FID had to be recalibrated during the measurements, due to its tendency to drift. These calibration periods appear as gaps in the HC curves in Figs. 4 and 5.

Compared to previous temperature (350 °C), the equivalent results were seen at the 400 °C (Fig. 5). Once again, the SCR ds temperature decreased and the DOC ds temperature increased during the last minutes of the LDI regeneration period. HC concentration upstream of the SCR + ASC decreased from their peak of 6,500 ppm to 3,500 ppm at the end of the period. HC oxidation over the CC-SCR + ASC was assumed to occur mainly via the platinum-based ASC. V-SCR catalysts have also been shown to be active in hydrocarbon oxidation (e.g., [25,26]).

### 3.3. The effect of late diesel injection on the CC-SCR + ASC performance

The second part of Phase B was to study the effect of late diesel injection on the CC-SCR + ASC performance at the 320, 350, and 400 °C operating points (Fig. 6). This was investigated through emission measurements made before LDI regeneration, after regeneration, and after 40 min of operation at 450 °C. LDI did not affect NOx conversion efficiency at 350 and 400 °C. However, NOx conversion fell from 67 % (before LDI) to 62 % (after LDI) at 320 °C. This decline in efficiency is attributed to exposure to high concentrations of HC associated with diesel fuel LDI regeneration. However, the original NOx conversion efficiency was fully restored and even improved after 40 min of engine operation at 450 °C made without urea dosing.

### 3.4. The effect of late diesel injection at the target exhaust temperatures of 250 and 280 °C

DPF regeneration procedure by LDI at low-temperature operating points proved to be more challenging (Figs. 7 and 8). In fact, at 280 °C, LDI had to be aborted after 660 s due to a considerable temperature

increase in the CC-SCR + ASC. The SCR ds temperature had reached the catalyst's maximum allowed temperature of 550 °C. This could possibly mean some HC was stored in the SCR at low temperature. At higher temperatures of 320 to 400 °C, the CC-SCR + ASC ds temperature stabilized approximately 500 s after starting LDI.

At 280 °C, it was seen that NOx conversion efficiency decreased by a clear 18 percentage points after this abbreviated LDI regeneration (Fig. 9). Significant increases in NH<sub>3</sub> and N<sub>2</sub>O concentrations were also detected. However, the original NOx conversion was fully restored and even improved after 40 min of running at 450 °C exhaust gas temperature. NH<sub>3</sub> and N<sub>2</sub>O also fell below their original levels.

### 3.5. Hydrocarbon storage on CC-SCR at 280 °C

Phase C of this study investigated hydrocarbon storage in a CC-SCR during LDI regeneration at low exhaust-temperature (280 °C). Temperature recordings us and ds of the SCR + ASC and DOC during exhaust heat-up and following the 40 min run at 450 °C were used to indicate potential HC storage and oxidation in the SCR catalyst. Unlike Phase B, the exhaust was heated-up immediately after LDI regeneration, i.e., there was no delay in exhaust gas heat-up due to emission measurements. No significant temperature peaks were detected in the SCR ds temperature although the temperature rose in the LDI regeneration phase. This may suggest that significant storage and oxidation of HC could not possibly occur in the SCR catalyst. However, it should be noted that the LDI period was very short, so it may have been insufficient for large quantities of HC storage.

The SCR + ASC ds temperature increased very slowly during LDI at the 250 °C compared to higher-temperature operating (Figs. 10 and 11). Low-Pt-ASC generally does not perform fully at 250 °C, promoting partial oxidation of HC and CO so that HC was oxidized in the DOC following the ASC. Accumulated HC in the ASC may also inhibit its function. [27].

The DOC ds temperature now increased more clearly, by up to 200 °C. This contrasts with the higher-temperature points, where DOC ds temperatures increased by only 20–60 °C. It might indicate that HC did not ignite in the CC-SCR + ASC at the initial exhaust inlet temperature of 250 °C, so more HC flowed through the SCR + ASC. Apparently, a significant part of the excess HC could also be stored in the SCR catalyst at low temperatures. When the temperature of SCR us reached 300 °C, the temperature of SCR ds increased uncontrollably (Fig. 11). This may have been due to very rapid oxidation of the stored HC.

Late diesel injection was aborted after 13 min (780 s) because the SCR ds temperature reached the maximum allowable 550 °C. However, the SCR catalyst temperature continued rising until the engine was

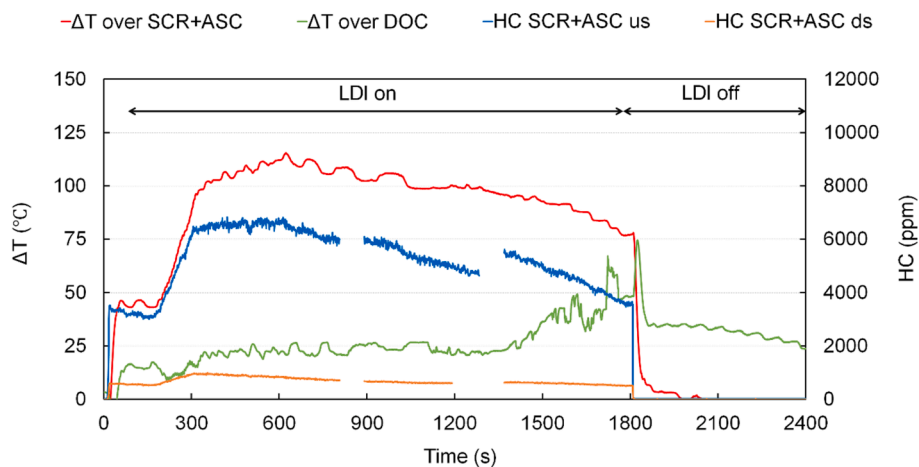


Fig. 5. Temperature differences over SCR + ASC and DOC; and HC concentrations upstream and downstream of SCR + ASC during LDI period at 400 °C (NH<sub>3</sub>-to-NOx ratio 0).

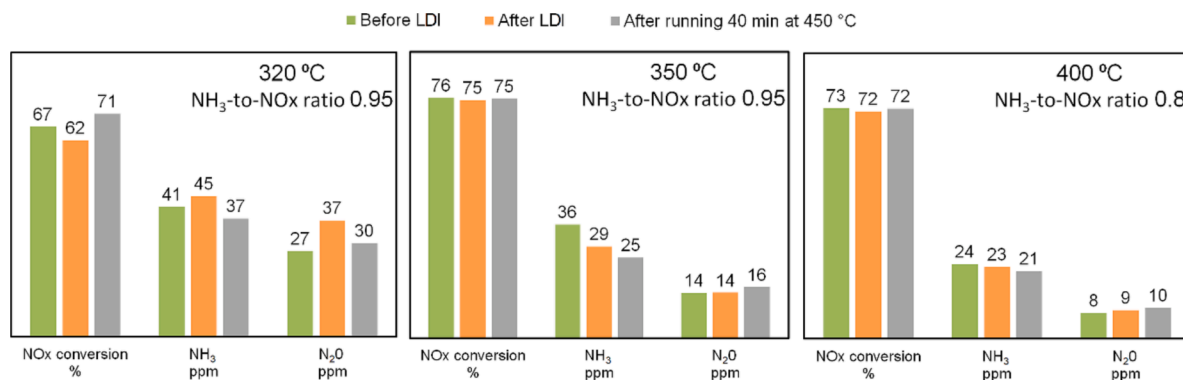


Fig. 6. NOx conversions and the concentrations of NH<sub>3</sub> and N<sub>2</sub>O at 320, 350 and 400 °C before and after LDI period, and after 40 min operation at 450 °C at the engine speed of 2100 rpm – The standard deviation of the NH<sub>3</sub> averages was 1.0 % at 320 °C, 2.8 % at 350 °C, 3.6 % at 400 °C and the N<sub>2</sub>O averages 5.8 %, 0.2 %, 0.8 %, respectively.

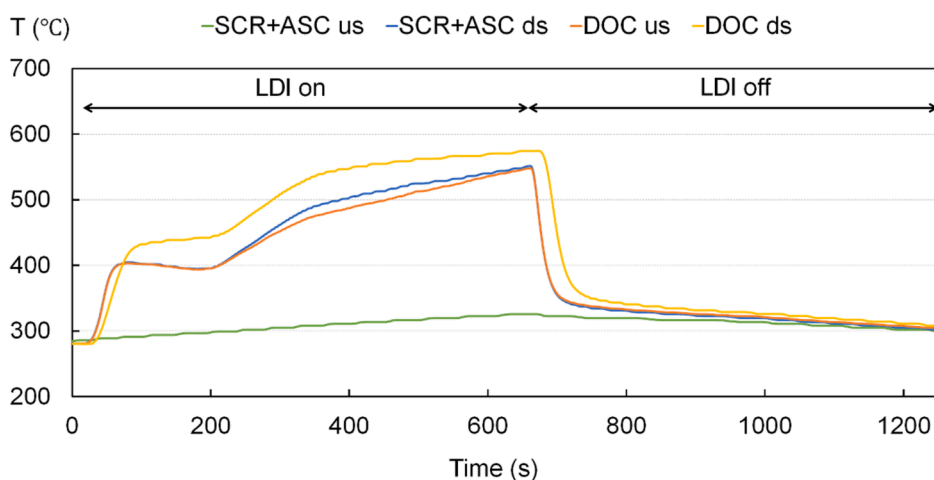


Fig. 7. Exhaust gas temperatures during LDI regeneration at 280 °C (NH<sub>3</sub>-to-NOx ratio 0) – The standard deviation of SCR ds temperature averages was 1.3 % and of SCR us temperature averages 1.6 % at 280 °C.

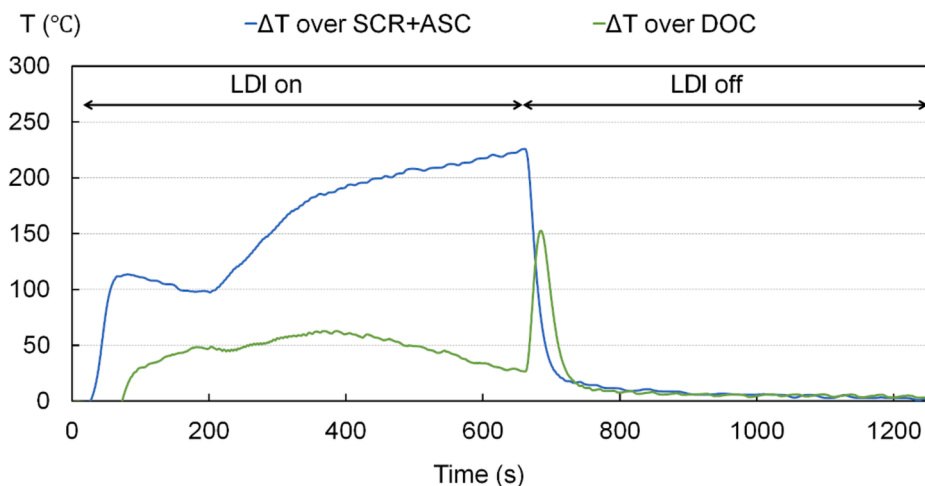


Fig. 8. Temperature differences over SCR + ASC unit and DOC during LDI regeneration at 280 °C (NH<sub>3</sub>-to-NOx ratio 0).

stopped 15 s after the end of LDI. The catalyst temperature rose close to 700 °C within this 15 s-period. It dropped below 500 °C after the engine shut-down, but restarting the engine caused it to quickly soar to over-temperature again, peaking at approximately 750 °C. Unfortunately, temperature recordings from this phase are missing, so the exact over-

temperature duration is unclear. Nevertheless, the SCR catalyst temperature had decreased to 250 °C after 12 min, for emission measurements during LDI period.

These consequences of LDI at 250 °C affected the performance of the CC-SCR + ASC (Fig. 12). Its NOx conversion efficiency dropped

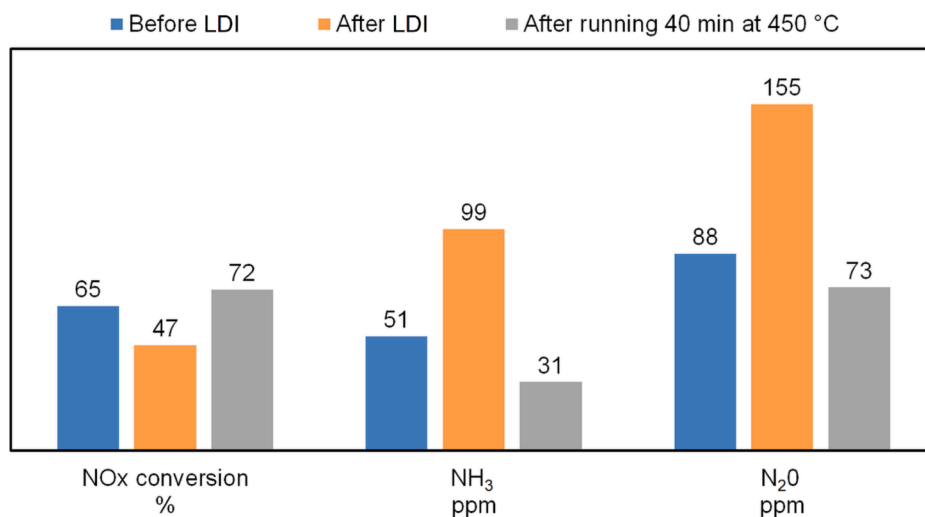


Fig. 9. NOx conversion and the concentrations of NH<sub>3</sub> and N<sub>2</sub>O at 280 °C and after LDI regeneration, and after 40 min operation at 450 °C – The standard deviation of the NH<sub>3</sub> averages was 4.5 % and of the N<sub>2</sub>O averages 8.4 %.

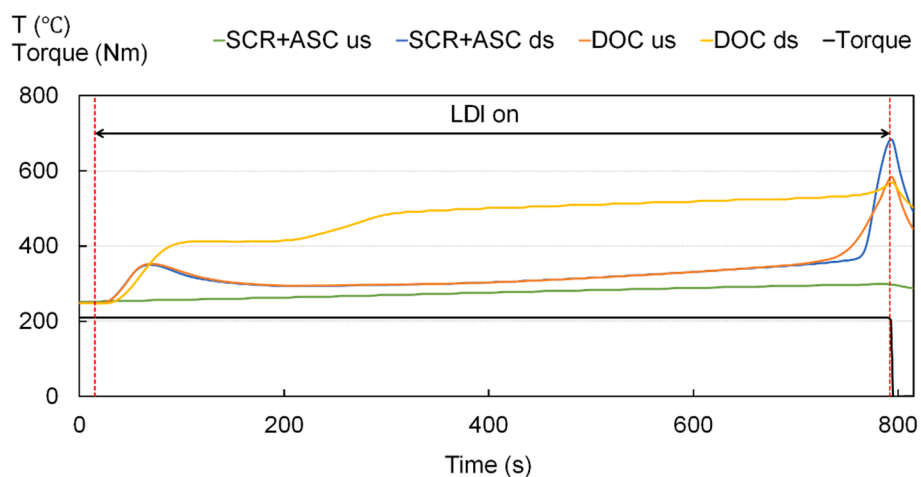


Fig. 10. Exhaust gas temperatures during LDI regeneration at 250 °C (NH<sub>3</sub>-to-NOx ratio 0) – The standard deviation of the SCR upstream and downstream temperatures averages were both 0.9 % at 250 °C.

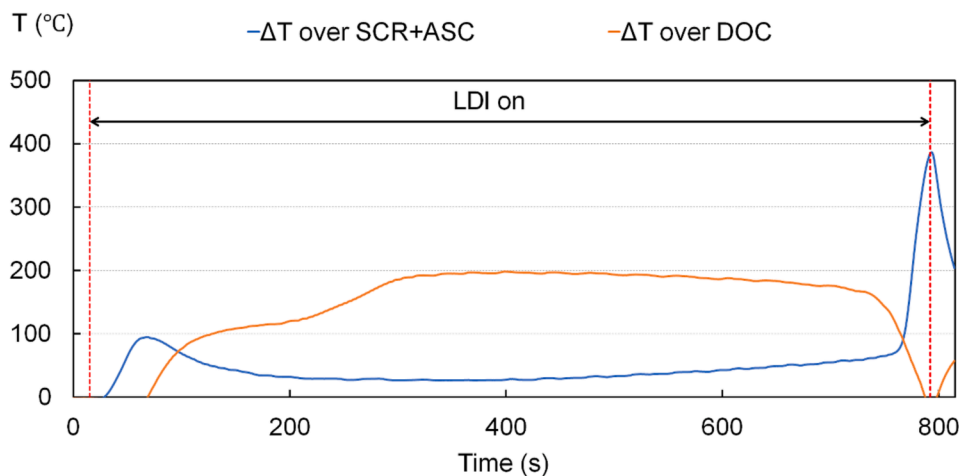
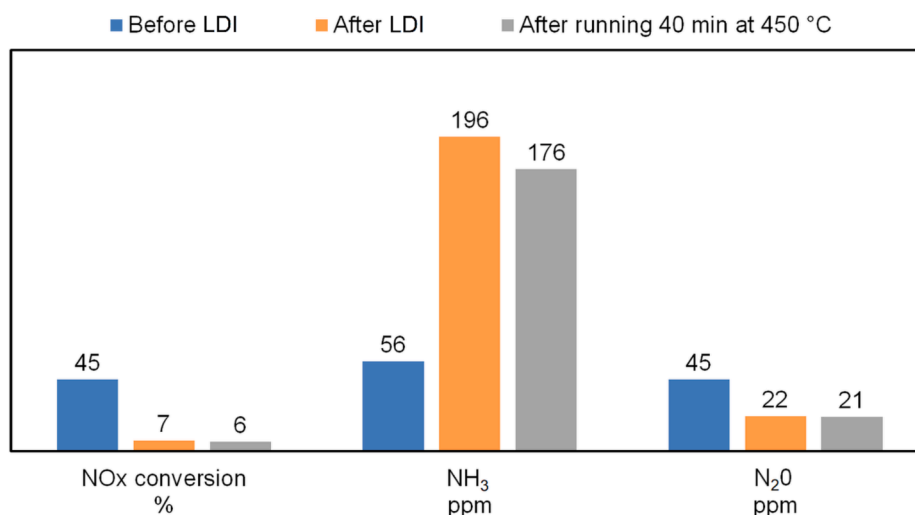


Fig. 11. Temperature differences over SCR + ASC unit and DOC during LDI regeneration at 250 °C (NH<sub>3</sub>-to-NOx ratio 0).



**Fig. 12.** NOx conversion and the concentrations of NH<sub>3</sub> and N<sub>2</sub>O at 250 °C (NH<sub>3</sub>-to-NOx ratio 0.55) before and after the low-temperature LDI regeneration, and after 40 min operation at 450 °C – The standard deviation of the NH<sub>3</sub> averages was 43.3 % and of the N<sub>2</sub>O averages 7.7 %.

dramatically, from 45 to 7 %. Additionally, NH<sub>3</sub> slip increased from around 50 ppm level to almost 200 ppm. Furthermore, the run at 450 °C for 40 min failed to restore the original NOx conversion efficiency, and NH<sub>3</sub> also remained high.

Further experiments at the 350 °C operating point confirmed that this apparent catalyst deactivation was most probably caused when the SCR + ASC temperature rose to around 700 °C at the end of the low-temperature HC accumulation test. Its NOx reduction efficiency at 350 °C declined from the original 76 % to 28 %, and NH<sub>3</sub> slip increased from 36 to 94 ppm. These results are in line with the hypothesis that a vanadium-based SCR has poor thermal stability with high-temperature exhaust gas (> 600–650 °C) and active DPF regeneration by HC/CO feed as high concentrations through closed-coupled SCR cause a risk for thermal deactivation. Such high temperatures are known to cause sintering and potential volatilization of vanadium, because the melting point of pure V<sub>2</sub>O<sub>5</sub> is 670 °C. The consequence is the loss of SCR catalytic activity [28,29].

In conclusion, the LDI is feasible to adopt during the regeneration period of a DPF only at sufficiently high exhaust-temperatures ( $\geq 320$  °C) in terms of closed-coupled V-SCR performance. At lower temperatures, oxidation of stored hydrocarbons can cause notable deterioration in catalyst performance due to the exothermic reactions generated in the SCR catalyst.

#### 4. Conclusions

The present study was related to design of exhaust gas after treatment systems for an off-road diesel engine. The system consisted of a close-coupled (CC) V-SCR + ASC, a DOC, and a DPF. The primary objective was to research how diesel fuel late diesel injection (LDI) affects the performance of a CC V-SCR + ASC during the active regeneration period of a DPF. The work also explored the impact of high hydrocarbon concentrations on the SCR + ASC performance and stability. The accumulation of hydrocarbons in the CC-SCR at low exhaust-temperatures was a particular focus. Engine bench experiments were carried out at SCR catalyst temperatures ranging from 250 to 400 °C. The principle findings of the study are:

- Regenerating a particulate filter by using late diesel injection through a CC-V-SCR is only feasible at exhaust temperatures of 280 °C and above.

- Late diesel injection for DPF regeneration proved to work appropriately in the CC-SCR + ASC and DOC when the initial exhaust inlet temperature of the SCR catalyst was sufficiently high ( $\geq 320$  °C).
- LDI did not affect the SCR catalysts NOx conversion efficiency at the highest exhaust temperatures. The slight decrease in NOx conversion efficiency (at 320 °C) was possible to fully restored to the original level by HC desorption and oxidation after 40 min' run at 450 °C
- The most notable increase in exhaust gas temperature occurred in SCR + ASC. This was assumed to occur due to the oxidation of LDI-derived HC in the platinum-based ASC.
- Active DPF regeneration by fuel injection through CC-SCR is a potential risk for overheating and deactivating vanadium-SCR catalyst (max. 550–600 °C).

#### CRediT authorship contribution statement

**Teemu Ovaska:** Writing – original draft, Visualization, Software, Methodology, Investigation, Data curation. **Kirsi Spoof-Tuomi:** Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation. **Seppo Niemi:** Writing – review & editing, Validation, Supervision, Methodology, Investigation, Funding acquisition. **Pauli Valkjärvi:** Software, Investigation. **Teuvo Maunula:** Writing – review & editing, Validation, Resources, Methodology, Funding acquisition. **Maciej Mikulski:** Writing – review & editing, Validation, Supervision, Resources, Project administration, Investigation, Funding acquisition. **Kati Lehtoranta:** Writing – review & editing, Validation, Resources, Project administration. **Jenni Alanen:** Writing – review & editing, Validation, Software, Resources, Methodology. **Matti Happonen:** Resources, Funding acquisition.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Data availability

The data that has been used is confidential.

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