applied sciences

MDPI

Article

Real-Time Evaluation Method of Heavy-Duty Diesel Vehicle SCR System Based on Ammonia Storage Characteristics in Real-Road Driving Emission Test

Yan Lei [1], Chenxi Liu [1], Dongdong Guo [2,3], Jianglong Yang [2], Tao Qiu [1,*] and Guangyu Peng [4]

[1] Department of Automotive Engineering, Beijing University of Technology, Beijing 100124, China
[2] Beijing Vehicle Emissions Management Center, Beijing 100176, China
[3] School of Mechanical Engineering, Beijing Institute of Technology, Beijing 100081, China
[4] College of Mechanical and Electrical Engineering, Hunan Communication Polytechnic, Changsha 410132, China
* Correspondence: qiutao@bjut.edu.cn; Tel.: +86-18618323651; Fax: +86-10-67391985

Abstract: In China, where in-use heavy-duty diesel vehicles producing NOx and particulate emissions for air pollution are required to undergo emission spot inspection at check stations, it is significant to adopt a simple method to evaluate emissions due to traffic jams, especially in big cities. To realize convenient vehicle emission spot inspection, this paper investigates the effects of exhaust temperature on the Selective Catalytic Reduction (SCR) de-NOx conversion efficiency and presents a method for evaluating the SCR operation state based on ammonia storage characteristics. The paper proposes a real-road driving test procedure and verifies it by measuring NOx from a heavy-duty diesel vehicle in an on-road driving test. The results show that the SCR de-NOx efficiency experiences three operation states. In state I, SCR works and injects urea, resulting in high de-NOx efficiency (>90%); state III occurs during the cold, starting with the lowest de-NOx efficiency (<50%) due to a lack of NH_3; and state II is a transition stage caused by the ammonia storage, with a certain conversion efficiency (50–90%) when SCR de-NOx efficiency linearly relates to exhaust temperature. Whether the SCR works normally can be judged based on the SCRs operation states. This method is simple and easy to implement in different SCR operation states, and it is effective and repeatable.

Keywords: selective catalytic reduction (SCR); NOx; real-road test; ammonia storage; conversion efficiency; diesel vehicle

check for updates

Citation: Lei, Y.; Liu, C.; Guo, D.; Yang, J.; Qiu, T.; Peng, G. Real-Time Evaluation Method of Heavy-Duty Diesel Vehicle SCR System Based on Ammonia Storage Characteristics in Real-Road Driving Emission Test. *Appl. Sci.* **2022**, *12*, 11197. https://doi.org/10.3390/app122111197

Academic Editor: Jun Cong Ge

Received: 7 October 2022
Accepted: 2 November 2022
Published: 4 November 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

1. Introduction

Due to outstanding advantages such as high thermal efficiency and reliability, diesel engines are still the most powerful energy conversion devices widely applied in heavy vehicles, ships, locomotives, and generators [1]. In China, the number of trucks has increased from 7 million in 2000 to 26.209 million in 2020, and most trucks are powered by diesel engines [2]. Following the sustainable growth of diesel trucks, their emissions, especially NOx and PM emissions, have been one of the most important pollution sources. It was reported that in China, NOx emissions from motor vehicles reached 6.263 million tons, and the emission of NOx from diesel vehicles exceeded 80% of the total vehicle emissions in 2020 (China Mobile Source Environmental Management Annual Report in 2021). Nitrogen oxides are an important cause of photochemical smog, acid rain, the greenhouse effect, and ozone reduction [3,4]. To further control the emission of pollutants from diesel vehicles, China's National VI vehicle emission regulations, issued in June 2018, are stricter in terms of test conditions, procedures, and test device requirements. Moreover, to meet the strict emission regulations, diesel vehicles nowadays adopt aftertreatment technology to reduce emissions. Aiming at the control of NOx emissions from diesel engine exhaust, the selective catalytic reduction (SCR) technology has the advantages of low fuel consumption, strong

sulfur resistance, with few changes to the original engine and has become one of the most effective ways to reduce NOx emissions from heavy-duty diesel engines [5,6]. The SCR system is mainly composed of the urea supply system, related sensors, the SCR catalyst, the dosing control unit (DCU), and other components. As the operating environment of an SCR system is rather harsh, it needs to bear high temperature, high pressure, chemical poisoning, scale aging, mechanical external force damage, poor road conditions, etc., which will lead to the performance degradation of an SCR system. When it causes a fault, it will also lead to a further increase in vehicle pollutant emissions. Therefore, it is urgent to test the real-time emissions to evaluate the SCR system performance when diesel vehicles are driving on real roads.

For the diesel vehicle, the emissions from the test bench and the real-road driving test are not exactly the same. Ko et al. [7] tested the NOx emission from a Euro 6-compliant diesel passenger car on a chassis dynamometer over both the new European driving cycle (NEDC) and the more realistic worldwide harmonized light-duty test cycle (WLTC), and they found that the NO emission factor was lower for the NEDC than the WLTC. Yang et al. [8] tested emissions from seventy-three Euro 6 diesel passenger cars over both NEDC and WLTC, and they reported that most vehicles met the legislative limit of 0.08 g/km of NOx over NEDC, but the average emission factors rose dramatically over WLTC. These studies reveal that real-road NOx emissions differ from the legislative limits. For the vehicle emission evaluation, real-time experiments include both the test bench and the on-road driving emission test, which is required in emission regulations. Generally, there are two test methods to measure the real-time emissions of diesel vehicles, i.e., the Portable Emissions Measurement System (PEMS) and the NOx sensor monitored by an on-board diagnostic system (OBD).

Current China VI Emission Regulation, GB17691-2018 Emission Limits and Measurement Methods of Heavy Diesel Vehicles, requires that the Real Driving Emission (RDE) test be used as a supplementary test procedure to measure the real-time emissions of the vehicles. The test cycle of China VI emission regulation adopts the global unified transient cycle of heavy engines (WHTC) and steady cycle of heavy engines (WHSC). The emissions from the vehicles have been regulated for RDE testing using the Portable Emissions Measurement System (PEMS) during in-use field operations for on-highway diesel vehicle engines and model year designations [9,10].

In general, on-board diagnostic systems (OBD) monitor the vehicle's real-time running status to test the real-time NOx emissions under real-world driving conditions. The OBD system has a significant role in monitoring vehicle emissions and improving the reliability of the aftertreatment devices. In recent years, many researchers have focused on studying the OBD system. Canova et al. [11] designed a model-based control strategy of OBD for the lean NOx trap aftertreatment system, and OBD diagnosed the faults such as the sensor fault, system ageing, sulfur poisoning by comparing the predicted values with the measured data. Leonardo et al. [12] realized rapid and accurate diagnosis of SCR catalyst aging based on the OBD NOx sensor, and the control strategy corrected the urea injection amount as the catalyst ageing was diagnosed. Hofmann et al. [13] designed the OBD strategy of the SCR catalyst based on the NOx sensor and achieved the Euro V emission standard through bench calibration. Zhang et al. [14] proposed the OBD control strategy based on respectively NOx and NH_3 sensor monitoring and verified the OBD strategy for the urea-SCR system by a diesel engine test on a test bench. Therefore, OBD can effectively monitor the real-time emissions from the vehicle during on-road driving.

Moreover, a large number of real-road driving emission test results [15,16] have shown that, even if the diesel vehicle equipped with an SCR system worked, the NOx emissions were still far higher than the legal requirements. For example, Preble et al. [17] conducted emission tests on thousands of in-use heavy-duty diesel trucks on a main highway in San Francisco and found that the NOx emissions of most trucks exceeded the limits of the current emission standards. The International Committee on Clean Transport assessed the actual NOx emissions of 160 in-use heavy-duty diesel vehicles in the United States, and they reported

that when the vehicles were running at a speed of less than 40 km/h, the NOx emissions were more than five times the emission standard [18]. Thiruvengadam et al. [19] tested the heavy-duty diesel and natural gas vehicles equipped with, respectively, three different SCR models, and they revealed that the NOx emissions of these vehicles were five to seven times higher than the standard during transportation near the dock and in the local area. These above publications revealed the phenomenon of NOx emissions exceeding the standard limit even for those vehicles equipped with the SCR system. On the one hand, the reasons for this phenomenon are due to the ageing of the SCR system and its catalytic performance deterioration. The design of the system may not be adequate for all driving conditions or an auxiliary emission strategy may be triggered. On the other hand, one important reason for this phenomenon lies in the failure diagnosis, for example, the exhaust temperature sensor. Once the temperature sensor has a certain mechanical or electronic failure, or even cheating by artificial tampering, the effectiveness of the SCR system greatly decreases.

In China, the NOx emission control for diesel-engine vehicles has been a big issue due to their huge vehicle numbers. Wu et al. [20] investigated the total NOx emissions for the Beijing heavy-duty diesel vehicles (HDDV) fleet and estimated the total increasing NOx emissions for the Chinese HDDV fleet. Furthermore, the total NOx emissions increase with the age of the in-use diesel vehicles. It is necessary to understand the NOx emission characteristics of in-use diesel vehicles as they run on the real road. To check in-use vehicles exceeding the emission standard level, in-use diesel vehicles are required to stop for emission inspection at many roads check stations in China. However, it is difficult for vehicle emissions to be executed under environmental supervision and administration in China due to the serious traffic jams, especially in large cities. If the vehicle is asked to stop for the real-time official inspection in the highways and city road check stations, it is impossible to install the PEMS device or use OBD on the vehicles under inspection. The emission characteristics of the in-use vehicle should be investigated by the portable test devices and evaluated by a simple and actionable method. Therefore, it is necessary to investigate the most suitable method to evaluate the SCR operation performance in the in-use diesel vehicles for the official inspection at road check stations.

This work aims at the real-time relationship between the SCR conversion efficiency and the exhaust temperature during real-road driving conditions because the SCR conversion efficiency mainly depends on the exhaust gas temperature [21]. This work presents an experimental investigation of a real-road driving emission test of a heavy-duty diesel vehicle and proposes a real-time evaluation method of SCR operation performance.

2. Real-Time Evaluation Method of a Diesel Vehicle SCR System

2.1. Analysis of the NOx Conversion Process for a Real-Road Vehicle Test

In the urea-SCR system for the diesel vehicle, the injector injects the urea aqueous solution into the catalyst converter, where the urea aqueous solution undergoes evaporation, pyrolysis, and hydrolysis to finally produce ammonia (NH_3) for catalytic reduction [22]. Equations (1)–(3) present the evaporation, pyrolysis, and hydrolysis reactions, respectively.

$$CO(NH_2)_2 \cdot 7H_2O(aqu) \rightarrow CO(NH_2)_2\ (s) + 7H_2O(g) \quad (1)$$

$$CO(NH_2)_2\ (s) \rightarrow NH_3(g) + HNCO(g) \quad (2)$$

$$HNCO(g) + H_2O(g) \rightarrow NH_3(g) + CO_2(g) \quad (3)$$

For this SCR catalytic conversion process, the hydrolysis reaction requires the highest temperature, which challenges the emission control in the cold-start stage of a diesel engine. The urea aqueous solution first produces HNCO after evaporation and pyrolysis, and then it is hydrolyzed to NH_3 for catalytic reduction. Generally, the hydrolysis reaction only begins at 150 °C and continues until it reaches 200 °C and releases ammonia. Moreover, the adsorption efficiency of NH_3 on the catalyst is low at low temperatures. When the exhaust temperature is lower than 200 °C, urea cannot be fully pyrolyzed and hydrolyzed, and by-products such as cyanuric acid and urea crystallization are easily generated, so

that urea cannot be fully converted into NH_3. According to the Eley–Rideal mechanism, when NH_3 enters the catalyst, it is adsorbed to the active sites on the catalyst surface [23]. There are two active sites on the catalyst surface: one is the Bronsted active site, where NH_3 is adsorbed in the form of NH_3^+-, and the other is the Lewis active site, where NH_3 is adsorbed in the form of NH_x- (x ranges from 1 to 3). When NH_3 enters the catalyst, it first is absorbed on the Bronsted and Lewis active sites until adsorption saturation of NH_3 is reached, and then continues to be absorbed on the inactive sites on the catalyst surface. The process of storing NH_3 on active and inactive sites is called ammonia storage [24].

Generally, the de-NOx mechanism of the SCR system includes both standard and fast SCR reactions, as the following equations show:

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \quad (4)$$

$$2NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O \quad (5)$$

$$8NH_3 + 6NO_2 \rightarrow 7N_2 + 12H_2O \quad (6)$$

Equation (4) is the standard SCR reaction, and it is the main reaction between NH_3 and NO in the SCR system [25]. Equation (5) is the fast SCR reaction, and it has a greater chemical reaction rate than the standard reaction because NO2 helps improve the reaction rate [26,27]. Equation (6) is the slow SCR reaction, and it works when the NO_2 amount exceeds the amount of NO [28].

The reduction reaction of the SCR catalyst needs a specific temperature window for effective NOx conversion, and different catalysts have different temperature windows. For example, the temperature window of a Cu-zeolite catalyst is about 200–500 °C, and the temperature window of a Fe-zeolite catalyst is about 350–550 °C. In a specific temperature window, the catalytic conversion efficiency first increases with the increase in temperature and then decreases once it is higher than the temperature of the maximum catalytic conversion efficiency [29] (Kim et al., 2012). For the SCR catalyst, once the temperature is not within the special temperature window, for example, if it is lower than 200 °C, urea cannot be fully hydrolyzed. Thus, the diesel SCR system has such a control strategy that the SCR system does not inject urea once the exhaust temperature is lower than the light-off temperature, i.e., the limit of the temperature window (generally $\leq$200 °C), and the SCR catalyst can only catalytically reduce NOx through the remaining NH_3 adsorbed on its catalyst surface. Therefore, as for the operation condition of lower exhaust temperatures, the SCR conversion efficiency decreases because of the worse decomposition rate of urea, limited urea injection, and poor catalyst activity.

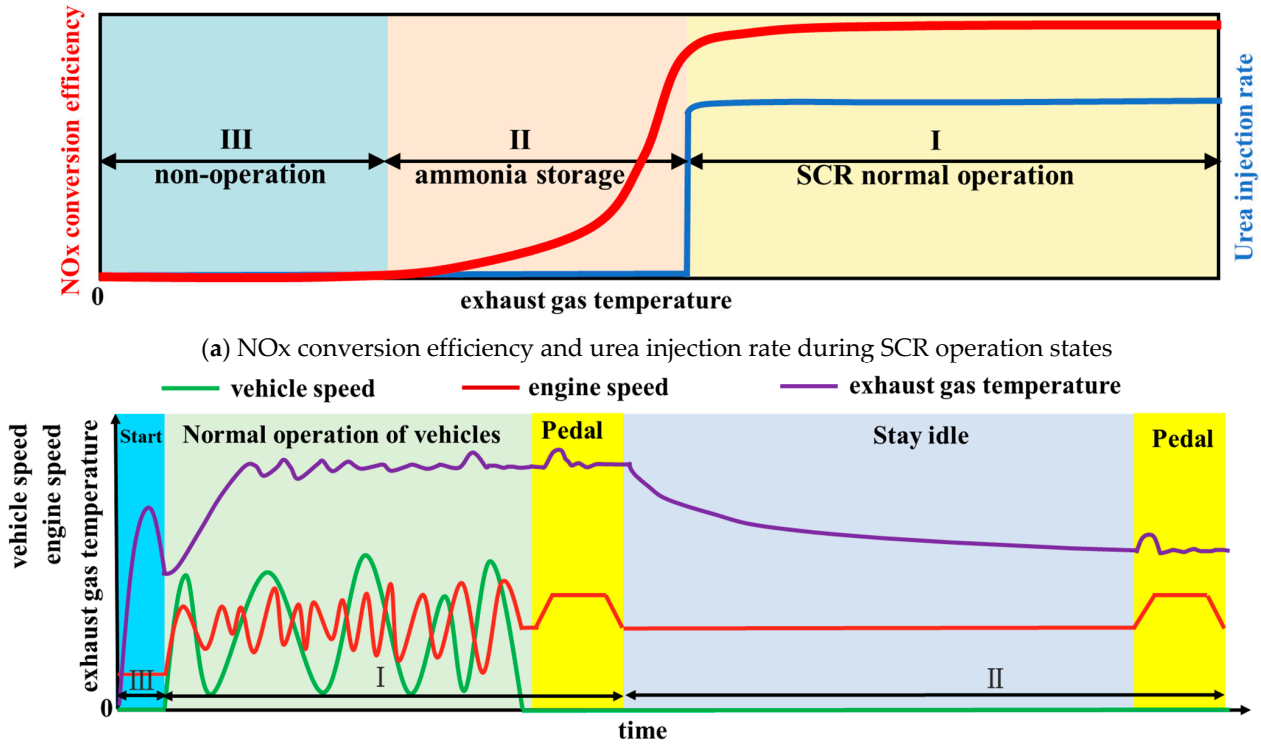
For the real-road diesel vehicle driving process, the SCR system undergoes three operation states, i.e., state I: the SCR normal state, state II: the SCR ammonia storage state, and state III: the SCR non-working state, as shown in Figure 1.

State I: SCR normal state. Both the exhaust temperature and the NOx conversion efficiency remain high;

State II: SCR ammonia storage state. As the exhaust gas temperature decreases, the de-NOx efficiency declines;

State III: SCR non-operation state. The exhaust temperature is the lowest, and the NOx conversion efficiency is close to zero.

Given the above, the three operation states of the diesel SCR system occur during the real-road vehicle test according to the exhaust gas temperature. Based on this relation between temperature and NOx conversion efficiency, the operation state of the SCR system can be identified once the exhaust temperature and the NOx emission before/after the SCR catalyst carrier are tested. Thus, according to the real-time exhaust temperature, the operation state of the SCR system can be confirmed. Furthermore, the corresponding theoretical NOx conversion efficiency should be deduced based on the real-time SCR operation state.



(**a**) NOx conversion efficiency and urea injection rate during SCR operation states

(**b**) Proposed real-road test method

Figure 1. Proposed real-road test method based on operation states of the SCR system.

2.2. Real-Time Evaluation Method of the Real-Time SCR Operation State

The three operation states of the SCR system happen when the diesel vehicle runs on a real road. According to the emission standards, the NOx emissions can be tested by regulatory test procedures. In China, all the vehicles are tested according to the global unified transient cycle of heavy engines (WHTC) and the global unified steady cycle of heavy engines (WHSC) for evaluation and certification, according to the emission standard GB-17691-2018 Pollutant Emission Limits and Testing Methods for Heavy Diesel Vehicles (China's Sixth Stage). These complex test cycles (WHTC and WHSC) take much more time and require the PEMS (Portable Emission Measurement System) test device. However, as the government officers' conduct on-the-spot inspections of the in-use vehicles in the highways and city road check points, it is difficult and impossible to install the PEMS device on those vehicles. Moreover, for heavy traffic in cities, especially Chinese big cities such as Beijing, Shanghai, etc., there are so many vehicles on real roads and the traffic is so heavy that it is impossible and unthinkable to inspect every vehicle by driving at varied low, medium, high, and super high vehicle speeds like the WHTC/WHSC test cycle. Nowadays, a practical test method for inspectors is to first stop the vehicle and then test the emissions while they still in place by inserting a sampling device into the exhaust tail pipe. Therefore, a practical and simple test method should be investigated to evaluate the SCR system operation states for the standing-still vehicle emission test.

This work proposes a new and simple test method to evaluate SCR operation states based on their ammonia storage characteristics. The designed test procedure is illustrated in Figure 1:

(1) Start the vehicle;
(2) After the vehicle runs normally on the road for a period of time (several minutes), it pulls over and stops, ready for an on-site emission inspection. The engine maintains idle for several minutes while the test sampling device is well placed;
(3) The driver rapidly presses the pedal fully for at least 3 s and then slowly releases the pedal until the engine is stable;

(4) Maintain high idling speed (1000–1500 rpm) for about 10 min;
(5) The driver again presses fully on the brake pedal and slowly releases it.

This proposed test procedure may reveal the three states of the SCR system. As for the road driving test, when the vehicle first starts (cold start), the exhaust temperature is lower than the activating temperature, and the SCR does not inject urea, so it is in state III, the non-operational state. As the vehicle drives on the road, the exhaust temperature increases up to the catalyst activation temperature, and the SCR works. This is the state I normal operation state. As for the stop check, the full pedal pressing may make sure the exhaust gas temperature ranges in the temperature window, and this is still in state I. After a certain time of idling, the engine exhaust temperature decreases to be lower than the activating temperature, and the SCR stops injection of urea. However, the previously injected ammonia storage may work, and this is state II.

3. Real-Road Diesel Vehicle NOx Emission Test

Given the above, the three operation states of the diesel SCR system occur during the real-road vehicle test according to the exhaust gas temperature. This paper carried out a real-road vehicle emission test to investigate the SCR operation states during the real-road driving.

3.1. Test Vehicles and Devices

In this work, we used a heavy-duty diesel vehicle made in China that meets the China National VI emission standard. To effectively control the NOx emissions of the diesel vehicle, this work collected second-by-second on-road emission test data by using portable emission measurement systems (PEMS) and the OBD method together. In this work, the Horiba OBS-ONE-GS12 was used, which is the latest Portable Emissions Measurement System (PEMS) designed for engine/vehicle certification under real road conditions. This PEMS device measures concentrations of emissions (CO, CO_2, THC, NOx, and NO_2), the particulate number (PN), exhaust flow rate, GPS data, environmental conditions (atmospheric temperature, humidity, and pressure), and calculates mass emissions. In this work, the PEMS device measured the real-time parameters in the exhaust pipe, including the NOx emissions. Table 1 gives the basic vehicle and engine specifications, and Table 2 presents the PEMS characteristics.

Table 1. Specifications of test vehicle.

Type		Specification
Vehicle	Model	ZLJ5335JQZ25E
	Manufacturer	China Zoomlion Heavy Industry Science & Technology Co., Ltd. (Changsha, China)
	Overall dimensions (L × W × H)	12,870 × 2550 × 3580 mm
	Mass	33,110 kg (Deadweight in driving condition)
	Wheelbase	4525 + 1350 mm
	Departure angle	18°
Diesel Engine	Model	WP8.320E61
	Manufacturer	China Weichai Power Co., Ltd. (Weifang, China)
	Engine type	Inline 6-cylinder, four-stroke engine
	Cylinder number	6
	Displacement	7.8 L
	Aspiration	Turbocharged and intercooled
	Injection system	Electronically controlled high-pressure common rail
	Maximum power	235 kW
	Maximum torque at speed (RPM)	1400 N·m at 1200–1600 r/min
	Emission standards	Euro VI

Table 2. PEMS specifications.

Type	Specification	
Model	SEMTECH ECOSTAR	
Manufacturer	Sensors Co., Ltd. (Saline, MI, USA)	
Primary function	Measure NO and NO_2	
Operation principle	Non-dispersive ultraviolet (NDUV)	
Gas	NO	NO_2
Range of measurement	0–3000 ppm	0–1000 ppm
Resolution	0.1 ppm	0.1 ppm
Accuracy	±2% rdg or ±0.3%	±2% pt or ±0.3%
Linearity	Intercept $\leq$ 0.5% of range 0.990 $\leq$ Slope $\leq$ 1.010 SEE $\leq$ 1.0% of range $R^2 \geq 0.998$	
Repeatability	±1% rdg or±1% of FS	
Noise	<1 ppm	
Span Drift (over 8 h)	±2% span value	
Zero Drift (over 1 h)	≤2 ppm	
Response time	$T_{10–90} < 3$ s	

3.2. Real-Road Test Procedure

Figure 2 shows the diesel vehicle real-road emission test procedure.

Step 1: 0–t_1. At first, the driver started the vehicle. This is state III due to the cold start and low exhaust temperature;

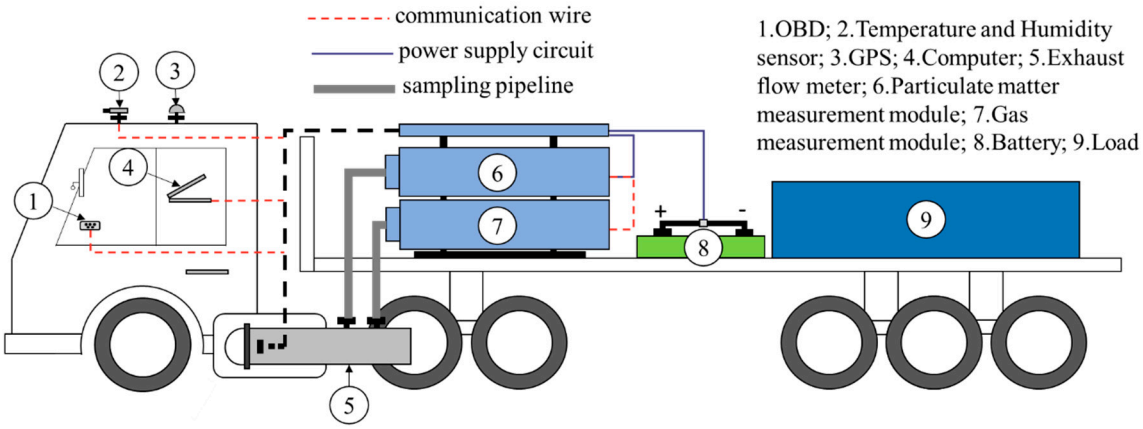
Step 2: t_1–t_2.Then, the driver drove the vehicle freely on the real road according to local traffic. This vehicle driving process was designed to increase the exhaust temperature;

Step 3: t_2–t_3. After the exhaust temperature rose, the vehicle was stopped, and the driver rapidly floored the pedal three times. Each free pedal maintains at least 3 s. This rapid pedal was designed to make sure the exhaust temperature rose enough. From t_1 to t_3, this is state I due to the high exhaust temperature;

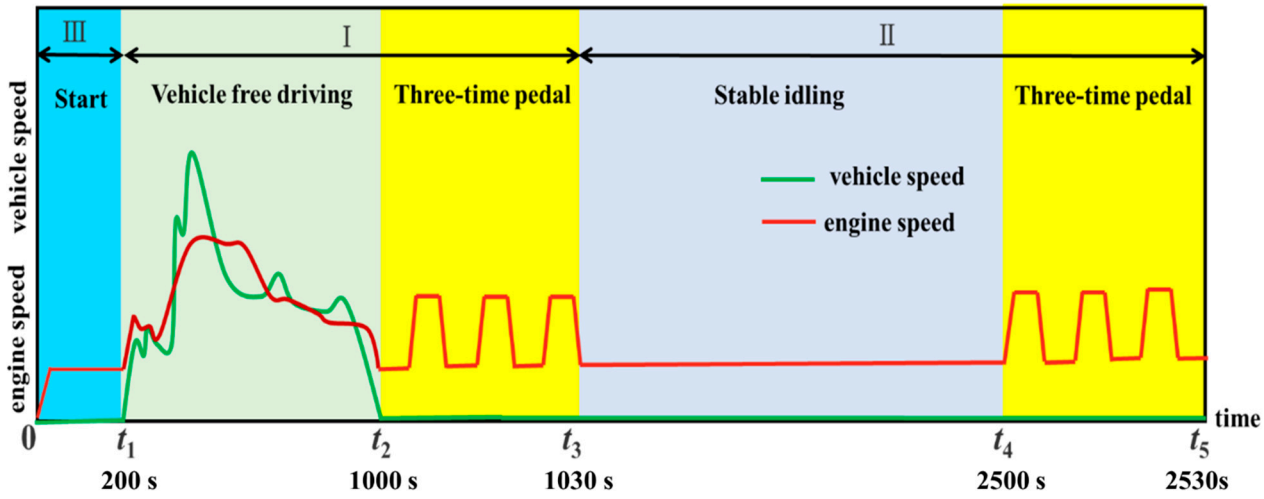
Step 4: t_3–t_4. The driver maintained the engine at a high idling speed, for example, 1000 r/min. This high idling speed is designed to decrease the exhaust temperature because more fresh air may be introduced into the cylinder to cool the exhaust gas;

Step 5: t_4–t_5. The driver repeated flooring the pedal three times. This is the end of the test procedure. From t_3 to t_5, this is state II because the exhaust temperature decreases from the high temperature in state I to a lower temperature.

From step 1 to 5, it is a whole test procedure. To ensure accuracy, this study repeated this test procedure three times. The first cycle included steps 1–5, but the second and third cycles included steps 2–5 except step 1 (cold start).



(**a**) Schematic of test devices and vehicles

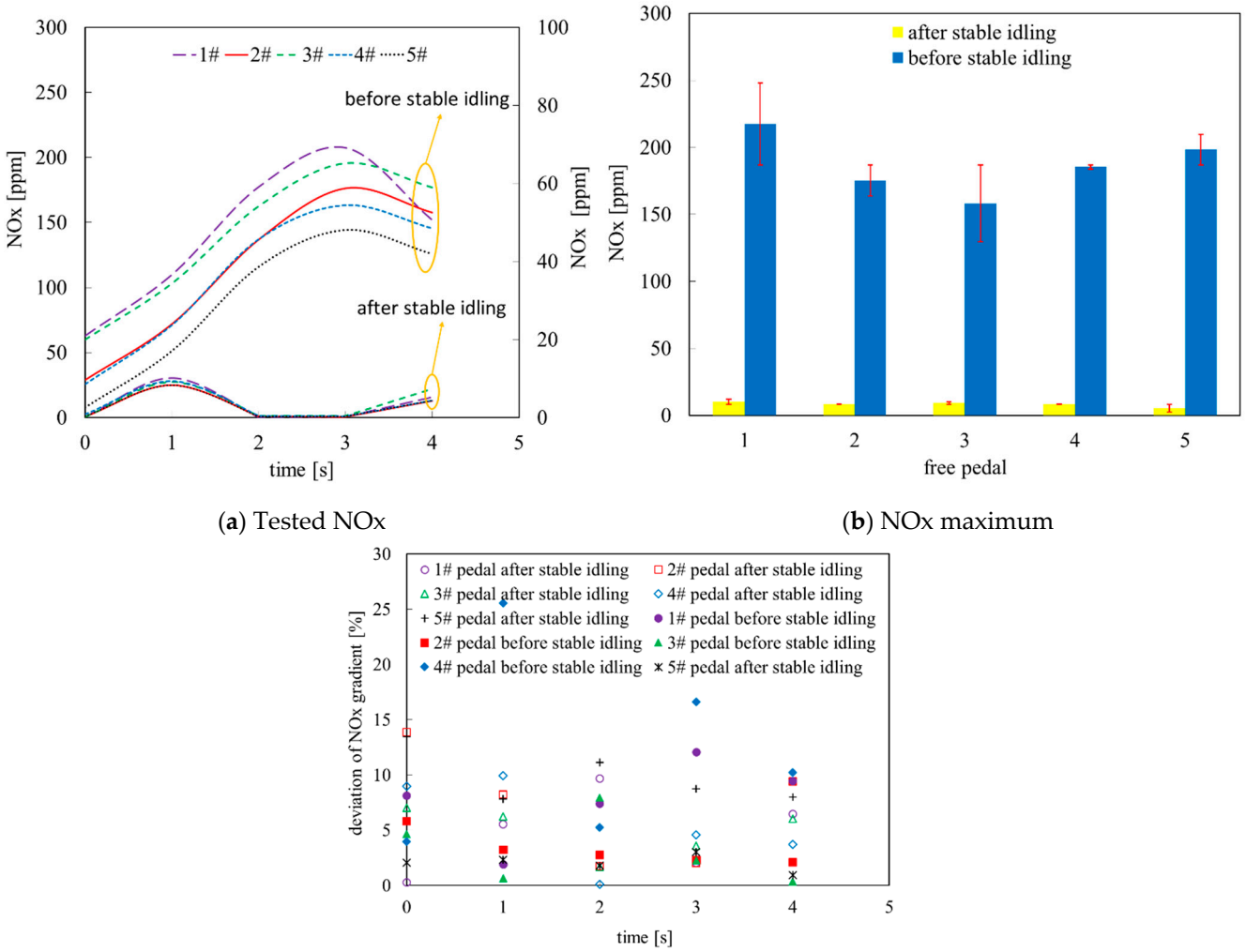


(**b**) Sequence of test procedures

Figure 2. Test devices and test procedures.

4. Results and Discussion

In this test procedure, the free pedal is quite important when the vehicle stops for on-site emission inspection. To analyze the measured deviation of the test, first the free pedal was repeated five times (test numbers 1#, 2#, 3#, 4#, 5#), respectively, before and after the stable idling. In this test procedure, each free pedal is maintained 3–5 s. Figure 3 shows the tested NOx of these five free pedal processes before and after the stable idling as well as the deviation. Figure 3a gives the test NOx of each test process. The results show that NOx emission changes slightly for different free pedal cases. It shows that the curves before stable idling have the same tendency with good following, and those after stable idling almost exactly coincide with each other. Figure 3b,c, reveals the uncertainty of the test. Figure 3b presents the NOx maximum of each test case, and Figure 3c gives the deviation. It reveals that most deviations from the maximum of NOx are less than 15%, and about 90% of the deviations are no more than 10%. This free pedal procedure depends on the drivers' driving habits, which have a great influence on the test emissions. For practical emission inspection, a deviation of 10% is acceptable.

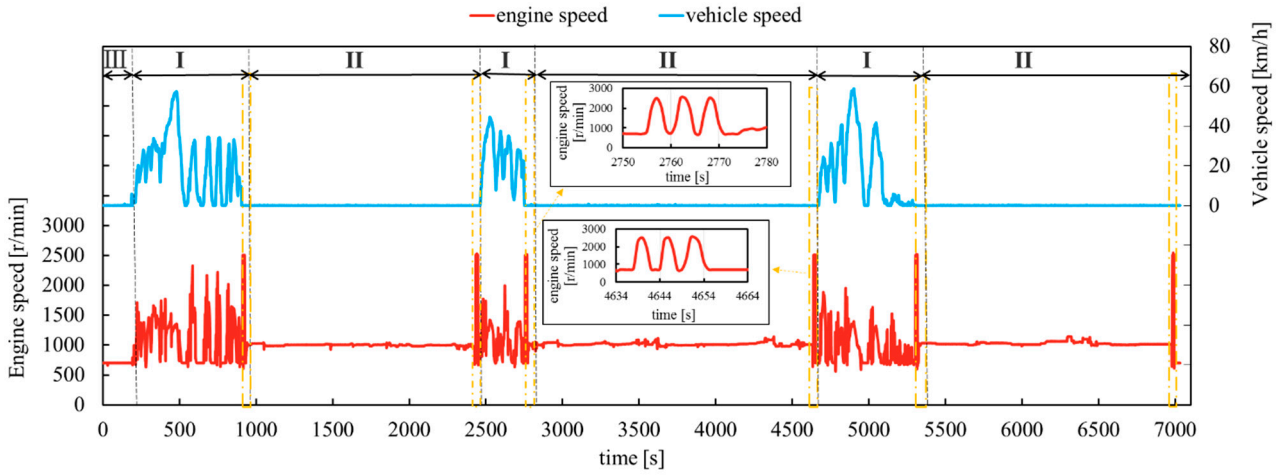


(**a**) Tested NOx (**b**) NOx maximum

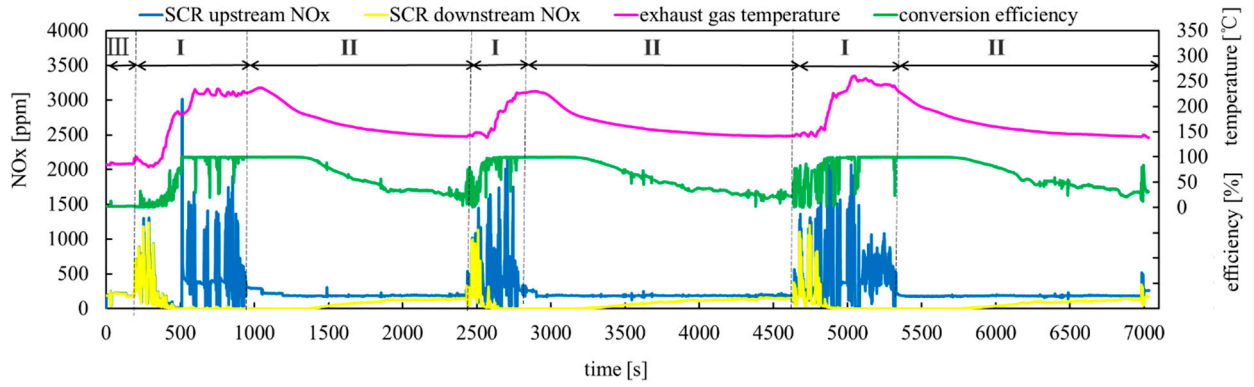
(**c**) Deviation of NOx gradient

Figure 3. Test deviation analysis.

Figure 4 shows the test results of the whole test procedure including three cycles with a total of 7000 s. It illustrates results for both the engine speed and the vehicle speed. There are several three-time flooring pedals marked by a dashed-line rectangle in this test, and the enlarged view of this three-time flooring pedal condition (in the second cycle) is also given. In addition, it shows the SCR upstream and downstream NOx and the SCR downstream exhaust gas temperature. It shows the exhaust gas temperature varies with the change in engine speed and vehicle speed. There are three states during the test process. State III occurs when, at first, the engine is in cold start. During this state III, the exhaust temperature is lower than 150 °C. The SCR downstream NOx and the upstream NOx are almost the same, which means there is no reduction in catalytic reaction in the SCR carrier, so it is in the non-operational state. After the vehicle drives on the road, the exhaust gas temperature increases to above 250 °C, and the SCR downstream NOx sharply decreases. This means the SCR system works and is in state II SCR normal operation. Then, the vehicle stops and runs at idle, therefore the exhaust temperature gradually declines from approximately 250–150 °C. During the temperature-decreasing stage, the SCR's downstream NOx emissions increase accordingly. This is a transitional stage between states I and III, i.e., state II ammonia storage.



(**a**) Vehicle speed and engine speed



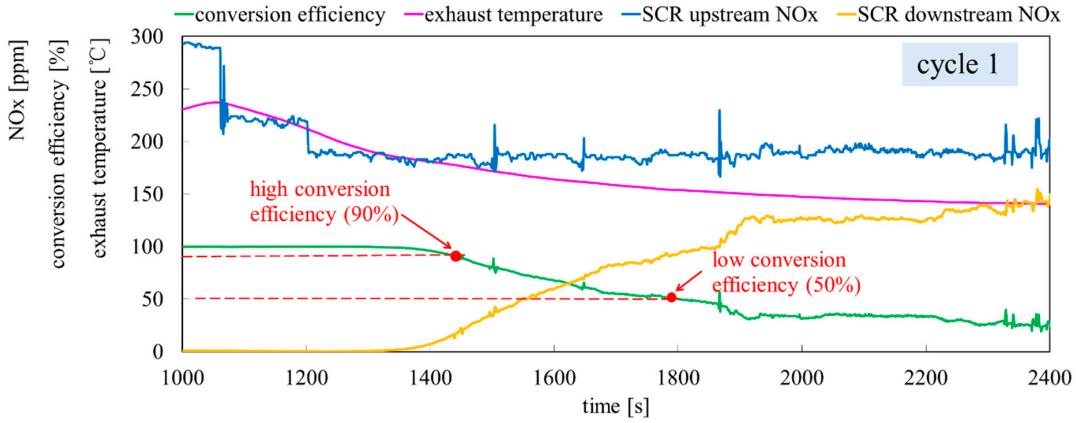
(**b**) NOx emissions, engine gas temperature and conversion efficiency

Figure 4. Test results.

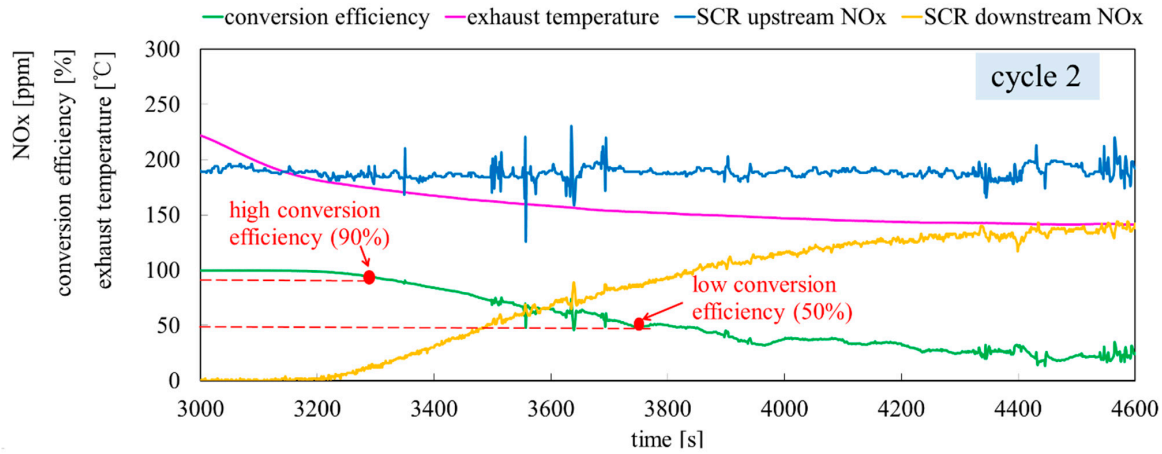
The NOx conversion efficiency is also presented in this figure. Here, taking the first cycle test results which range from 0 to 2500 s, as an example, the three-state NOx conversion efficiency characteristic is analyzed. During state III (cold start stage, time 0–200 s), the exhaust temperature is low (<100 °C) and the NOx conversion efficiency is quite low, nearly close to zero, which means the SCR system does not work in this state. As the vehicle moves, it comes to state I. The temperature increases rapidly along with the sharply increasing conversion efficiency, which quickly rises to its maximum (about 99%) in minutes. During state I, the SCR system works at a very high efficiency. Once the vehicle stops and runs idle for about 1000 s, the exhaust temperature tends to decline. As the time changes from 1000 to 1400 s, the temperature drops from 230 to 180 °C, while the NOx conversion efficiency maintains a high level (above 95%). However, as the temperature continues to drop, the conversion efficiency declines gradually. At the end of this state II (about 2450 s), the temperature decreases to about 140 °C, and the conversion efficiency is lower than 30%. This result reveals that the low conversion efficiency occurs due to the decreasing exhaust gas temperature. As the exhaust temperature is low, the SCR is designed to stop urea injection, but the conversion efficiency is not zero because the catalytic reduction reaction still happens due to the ammonia storage.

More details of the gradual decrease in the conversion efficiency in state II are investigated in this work. Figure 5 presents the results of state II in different test cycles (cycle 1, cycle 2, and cycle 3). It shows that each state II experiences about 1400–1600 s, and the exhaust gas temperature continues decreasing in this state. For these three different test cycles, the SCR upstream NOx maintains a constant of about 180 ppm while the SCR

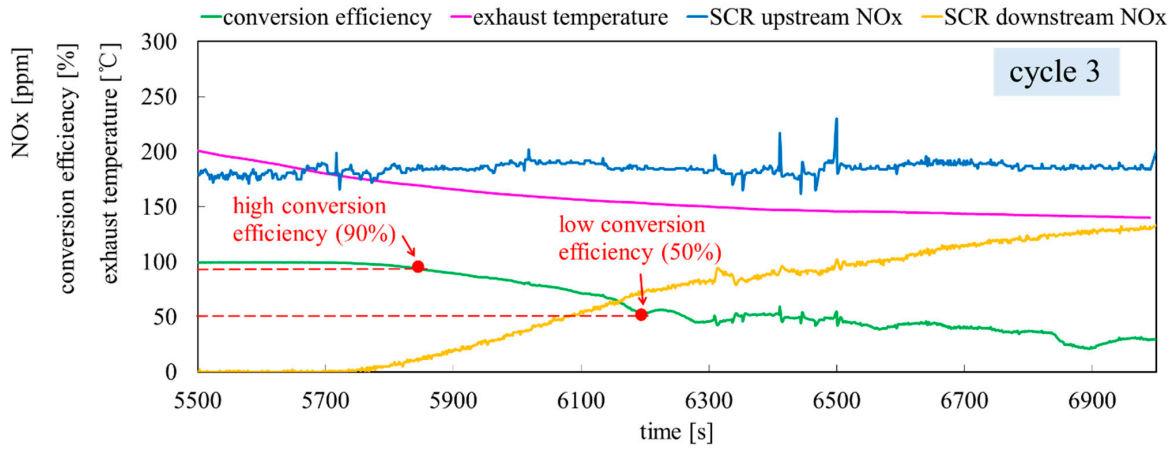
downstream NOx changes. At the beginning of 200 s, the SCR downstream NOx is low, and the conversion efficiency is high, close to 99%. After then, the SCR's downstream NOx increases, and the conversion efficiency drops gradually. At the end of state II for each test cycle, the SCR downstream NOx rises to about 140 ppm and the conversion efficiency declines to about 20%.



(**a**) Conversion efficiency, exhaust gas temperature and NOx emission in cycle 1



(**b**) Conversion efficiency, exhaust gas temperature and NOx emission in cycle 2

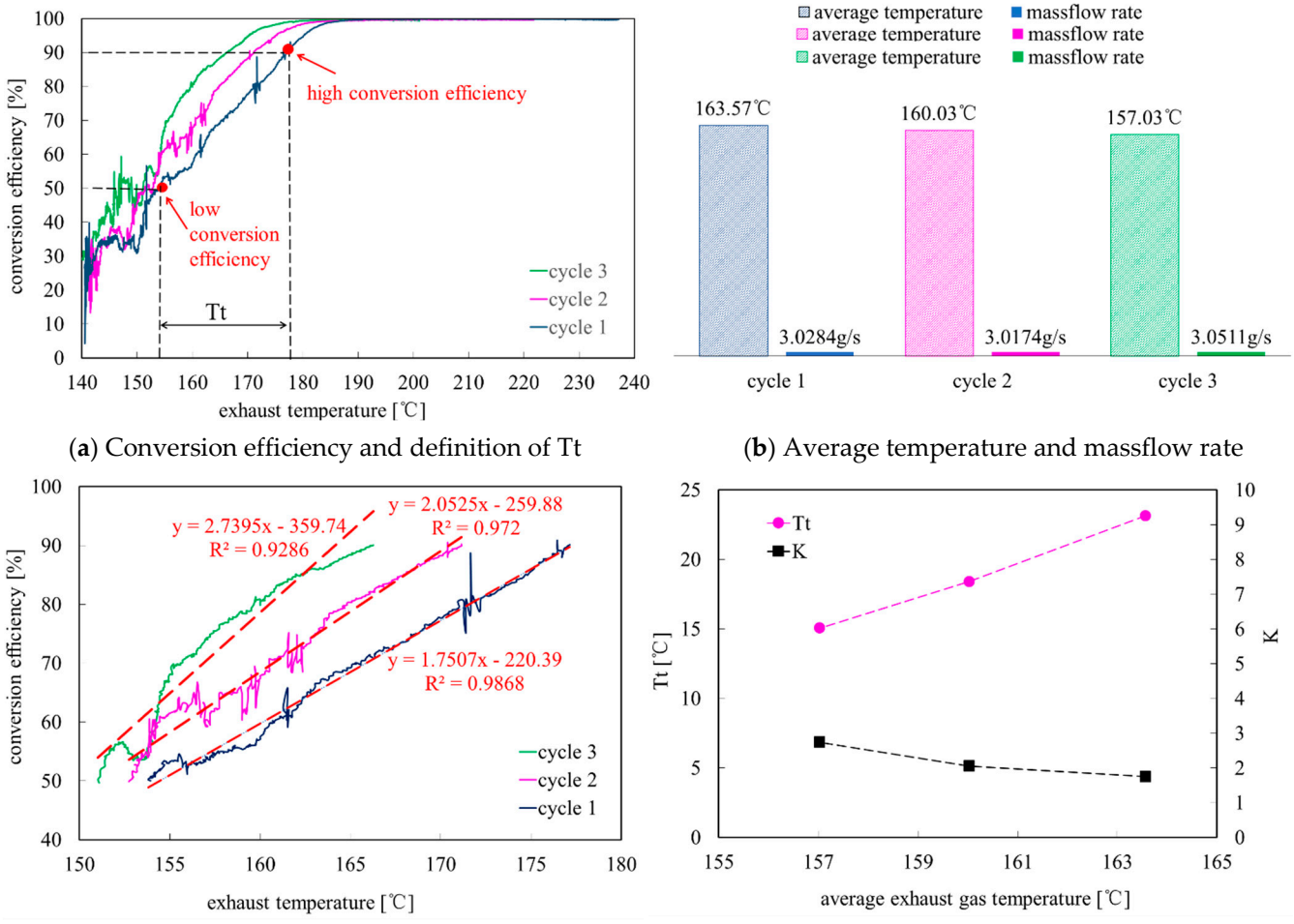


(**c**) Conversion efficiency, exhaust gas temperature and NOx emission in cycle 3

Figure 5. Test results for SCR state II.

It is worth noting that the moment when the SCR downstream NOx suddenly rises keeps pace with the moment when the conversion efficiency suddenly drops, there is no lag between these two moments. Therefore, it can be proved that the reason why the SCR's downstream NOx emissions increase sharply in a short time in state II during the idling phase of the vehicle is highly related to the conversion efficiency of the SCR. Because the exhaust temperature continues to drop in state II, the urea pump stops working due to the low temperature. Figure 5 shows that the SCR conversion efficiency does not drop directly from the high value to zero. This is because of the ammonia storage of the SCR catalyst carrier. The ammonia releases from the catalyst and takes part in the reduction reaction continuously, so that the conversion efficiency gradually declines and is far lower than that in the normal operation state. The results reveal that the conversion efficiency experiences a period of time where it decreases from a high to a low value. Here, high conversion efficiency is defined as >90%, while low conversion efficiency is defined as <50%. The conversion efficiency is closely related to the exhaust temperature.

Figure 6 presents the relationship between the conversion efficiency and the exhaust temperature in state II. The results reveal that the NOx conversion efficiency increases with the increase in the exhaust temperature and that it maintains a maximum value (above 98%) at high temperatures (>180 °C). For each test cycle, the range from the high to the low conversion efficiency covers a certain exhaust gas temperature. Here, the temperature range corresponding to the high and low conversion efficiencies is defined as Tt. Furthermore, it shows that the conversion efficiency is linearly related to the exhaust gas temperature. In addition, the slope of each line, here named K, varies for each cycle.



(**a**) Conversion efficiency and definition of Tt

(**b**) Average temperature and massflow rate

(**c**) Linear fitting of conversion efficiency

(**d**) Tt and K

Figure 6. Relationship between conversion efficiency and temperature in state II.

During this linearly increasing stage of the conversion efficiency, the diesel engine runs at idle speed with a stable engine speed and exhaust mass flow rate for each test cycle. The average exhaust mass flow rate and average temperature during the linear increasing stage for each test cycle are also presented, and during this linear rising stage, each cycle has a similar average mass flow rate and exhaust temperature.

During the idling stage, the exhaust gas temperature only changes a little, and the average exhaust temperature of each cycle varies within the range of 157–163 °C by no more than 8 °C. However, the parameters relating to the conversion efficiency, i.e., Tt and K, change. As the average exhaust temperature rises, Tt linearly increases, but the slope K slightly linearly decreases. These two parameters are affected by the capability of the ammonia storage of the SCR catalyst, which greatly depends on the operational temperature.

Figure 7 presents the effects of the exhaust gas temperature on the conversion efficiency. The results show that the conversion efficiency experiences three stages as the exhaust gas temperature decreases from 240 to 85 °C. When the exhaust temperature is higher than 216.6 °C, the conversion efficiency is high (above 98%) and stable. This stable, high-efficiency stage is exactly the SCR's normal operation state (state I). As the exhaust temperature drops below 216.6 °C, the conversion efficiency sharply decreases to a relatively low value (30–40%). This limited conversion efficiency is because the stored ammonia works and the SCR system has no urea injection during this stage with a temperature range of 216.6–88.1 °C, which is the ammonia storage state (state II). Once the exhaust temperature is lower than 88.1 °C, the conversion efficiency drops to its minimum. This near zero conversion efficiency shows that there is no catalytic reaction in this stage, and this stage is the SCR non-operation state (state III). The results prove that there are three states occurring for this real-road test method. Moreover, these three states of the SCR system are strongly related to the exhaust temperature.

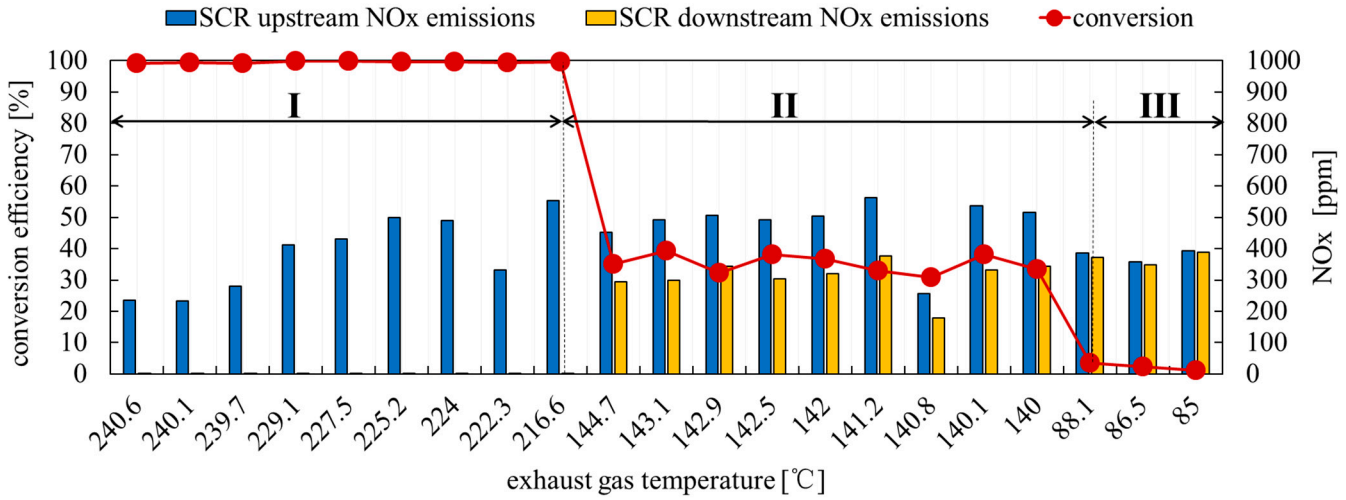


Figure 7. Effect of exhaust temperature on conversion efficiency.

5. Conclusions

This work proposes a simple real-road test method to evaluate the SCR system's operation states. We conducted a heavy-duty diesel vehicle real-road driving emission test and verified the proposed test procedure. The main conclusions are summarised as follows.

The SCR's de-NOx efficiency experiences three operation states according to the exhaust temperature. In state I, SCR works and injects urea, resulting in high de-NOx efficiency (>90%). State III occurs during the cold start and has the lowest de-NOx efficiency (<50%) because SCR injects no urea and no catalytic conversion happens due to the low exhaust temperature. State II is a transition stage and has a certain conversion efficiency (50–90%) caused by the ammonia storage. During state II, the SCR de-NOx efficiency is

linearly related to exhaust temperature; the slope of the conversion efficiency K declines while the temperature range Tt increases as the average exhaust temperature rises.

The different SCR three-state behaviors induced by ammonia storage can be used to judge whether the SCR works normally. The SCR works and injects urea in state I, and no urea injection occurs in state II. The method developed in this study is simple and easy to apply to different SCR operation states, and it is effective and repeatable. In the future, further simple and rapid test procedures based on this SCR state method may be applied to spot emission inspections.

Author Contributions: Conceptualization, Y.L.; methodology, Y.L. and T.Q.; software, J.Y.; formal analysis, C.L.; investigation, Y.L. and J.Y.; resources, D.G.; data curation, C.L.; writing—original draft preparation, Y.L.; writing—review and editing, G.P.; supervision, T.Q.; project administration, D.G.; funding acquisition, Y.L. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by [Beijing Vehicle Emissions Management Center] grant number [40005015202204].

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Olabi, A.; Maizak, D.; Wilberforce, T. Review of the regulations and techniques to eliminate toxic emissions from diesel engine cars. *Sci. Total Environ.* **2020**, *748*, 141249. [CrossRef] [PubMed]
2. Shen, X.; Lv, T.; Zhang, X.; Cao, X.; Li, X.; Wu, B.; Yao, X.; Shi, Y.; Zhou, Q.; Chen, X.; et al. Real-world emission characteristics of black carbon emitted by on-road China IV and China V diesel trucks. *Sci. Total Environ.* **2021**, *799*, 149435. [CrossRef] [PubMed]
3. Li, X.; Ai, Y.; Ge, Y.; Qi, J.; Feng, Q.; Hu, J.; Porter, W.C.; Miao, Y.; Mao, H.; Jin, T. Integrated effects of SCR, velocity, and Air-fuel Ratio on gaseous pollutants and CO_2 emissions from China V and VI heavy-duty diesel vehicles. *Sci. Total Environ.* **2022**, *811*, 152311. [CrossRef]
4. Mahesh, S.; Ramadurai, G.; Nagendra, S.S. Real-world emissions of gaseous pollutants from diesel passenger cars using portable emission measurement systems. *Sustain. Cities Soc.* **2018**, *41*, 104–113. [CrossRef]
5. McCaffery, C.; Zhu, H.; Tang, T.; Li, C.; Karavalakis, G.; Cao, S.; Oshinuga, A.; Burnette, A.; Johnson, K.C.; Durbin, T.D. Real-world NOx emissions from heavy-duty diesel, natural gas, and diesel hybrid electric vehicles of different vocations on California roadways. *Sci. Total Environ.* **2021**, *784*, 147224. [CrossRef] [PubMed]
6. Yue, G.; Qiu, T.; Lei, Y. Experimental demonstration of NOx reduction and ammonia slip for diesel engine SCR system. *Environ. Sci. Pollut. Res.* **2022**, *29*, 1118–1133. [CrossRef] [PubMed]
7. Ko, J.; Jin, D.; Jang, W.; Myung, C.-L.; Kwon, S.; Park, S. Comparative investigation of NOx emission characteristics from a Euro 6-compliant diesel passenger car over the NEDC and WLTC at various ambient temperatures. *Appl. Energy* **2017**, *187*, 652–662. [CrossRef]
8. Yang, L.; Franco, V.; Mock, P.; Kolke, R.; Zhang, S.; Wu, Y.; German, J. Experimental Assessment of NO_xEmissions from 73 Euro 6 Diesel Passenger Cars. *Environ. Sci. Technol.* **2015**, *49*, 14409–14415. [CrossRef]
9. Feist, M.D.; Sharp, C.A.; Spears, M.W. Determination of PEMS Measurement Allowances for Gaseous Emissions Regulated under the Heavy-Duty Diesel Engine In-Use Testing Program: Part 1–Project Overview and PEMS Evaluation Procedures. *SAE Int. J. Fuels Lubr.* **2009**, *2*, 435–454. [CrossRef]
10. Bougher, T.L.; Khalek, I.A.; Laroo, C.A.; Bishnu, D.K. Determination of the PEMS Measurement Allowance for PM Emissions Regulated under the Heavy-Duty Diesel Engine In-Use Testing Program. *SAE Int. J. Engines* **2012**, *5*, 1371–1386. [CrossRef]
11. Canova, M.; Midlam-Mohler, S.; Pisu, P.; Soliman, A. Model-based fault detection and isolation for a diesel lean NOx trap aftertreatment system. *Control Eng. Pract.* **2010**, *18*, 1307–1317. [CrossRef]
12. Costa, L.D.O.; Santos, R.S. Impacts on the Emissions Monitoring System (OBD) Due to the Use of Biodiesel and Higher NOx Emissions. *SAE* **2011**. [CrossRef]
13. Hofmann, L.; Rusch, K.; Fischer, S.; Lemire, B. Onboard Emissions Monitoring on a HD Truck with an SCR System Using Nox Sensors. *SAE* **2004**, *113*, 559–572. [CrossRef]
14. Zhang, R.; Zhang, S. Development of the on-board diagnostics function of SCR after-treatment system for heavy-duty diesel engines. *Automot. Eng.* **2012**, *34*, 175–178. [CrossRef]
15. Anenberg, S.C.; Miller, J.; Minjares, R.; Du, L.; Henze, D.K.; Lacey, F.; Malley, C.S.; Emberson, L.; Franco, V.; Klimont, Z.; et al. Impacts and mitigation of excess diesel-related NOx emissions in 11 major vehicle markets. *Nature* **2017**, *545*, 467–471. [CrossRef] [PubMed]
16. Misra, C.; Collins, J.F.; Herner, J.D.; Sax, T.; Krishnamurthy, M.; Sobieralski, W.; Burntizki, M.; Chernich, D. In-use NOx emissions from model year 2010 and 2011 heavy-duty diesel engines equipped with aftertreatment devices. *Environ. Sci. Technol.* **2013**, *47*, 7892–7898. [CrossRef]
17. Preble, C.V.; Harley, R.A.; Kirchstetter, T.W. Control Technology-Driven Changes to In-Use Heavy-Duty Diesel Truck Emissions of Nitrogenous Species and Related Environmental Impacts. *Environ. Sci. Technol.* **2019**, *53*, 14568–14576. [CrossRef]

18. Badshah, H.; Posada, F.; Muncrief, R. Current State of NOx Emissions from In-Use Heavy-Duty Diesel Vehicles in the United States. International Council on Clean Transportation ICCT White Paper. 2019. Available online: https://theicct.org/sites/default/files/publications/NOx_Emissions_In_Use_HDV_US_20191125.pdf (accessed on 25 November 2019).
19. Thiruvengadam, A.; Besch, M.C.; Thiruvengadam, P.; Pradhan, S.; Carder, D.; Kappanna, H.; Gautam, M.; Oshinuga, A.; Hogo, H.; Miyasato, M. Emission Rates of Regulated Pollutants from Current Technology Heavy-Duty Diesel and Natural Gas Goods Movement Vehicles. *Environ. Sci. Technol.* **2015**, *49*, 5236–5244. [CrossRef]
20. Wu, Y.; Zhang, S.J.; Li, M.L.; Ge, Y.S.; Shu, J.W.; Zhou, Y.; Xu, Y.Y.; Hu, J.N.; Liu, H.; Fu, L.X.; et al. The challenge to NOx emission control for heavy-duty diesel vehicles in China. *Atmospheric Chem. Phys.* **2012**, *12*, 9365–9379. [CrossRef]
21. Schmieg, S.J.; Oh, S.H.; Kim, C.H.; Brown, D.B.; Lee, J.H.; Peden, C.H.F.; Kim, D.H. Thermal durability of Cu-CHA NH3-SCR catalysts for diesel NOx reduction. *Catal. Today* **2012**, *184*, 252–261. [CrossRef]
22. Koebel, M.; Elsener, M.; Kleemann, M. Urea-SCR: A promising technique to reduce NOx emissions from automotive diesel engines. *Catal. Today* **2000**, *59*, 335–345. [CrossRef]
23. Rajadhyaksha, R.A.; Hausinger, G.; Zeulinger, H.; Ramstetter, A.; Schmelz, H.; Knözinger, H. Vanadia supported on titania—Silica: Physical characterization and activity for the selective reduction on nitric oxide. *Appl. Catal.* **1989**, *51*, 67–79. [CrossRef]
24. Chen, P.; Simböck, J.; Schönebaum, S.; Rauch, D.; Simons, T.; Palkovits, R.; Moos, R.; Simon, U. Monitoring NH_3 storage and conversion in Cu-ZSM-5 and Cu-SAPO-34 catalysts for NH_3-SCR by simultaneous impedance and DRIFT spectroscopy. *Sensors Actuators B Chem.* **2016**, *236*, 1075–1082. [CrossRef]
25. Marbán, G.; Valdés-Solís, T.; Fuertes, A.B. Mechanism of low temperature selective catalytic reduction of NO with NH_3over carbon-supported Mn_3O_4: Active phase and role of surface NO species. *Phys. Chem. Chem. Phys.* **2004**, *6*, 453–464. [CrossRef]
26. Nova, I.; Ciardelli, C.; Tronconi, E.; Chatterjee, D.; Weibel, M. Unifying redox kinetics for standard and fast NH_3-SCR over a V_2O_5-WO_3/TiO_2catalyst. *AIChE J.* **2009**, *55*, 1514–1529. [CrossRef]
27. Tronconi, E.; Nova, I.; Ciardelli, C.; Chatterjee, D.; Weibel, M. Redox features in the catalytic mechanism of the "standard" and "fast" NH3-SCR of NOx over a V-based catalyst investigated by dynamic methods. *J. Catal.* **2007**, *245*, 1–10. [CrossRef]
28. Jung, Y.; Shin, Y.J.; Pyo, Y.D.; Cho, C.P.; Jang, J.; Kim, G. NOx and N_2O emissions over a Urea-SCR system containing both V_2O_5-WO_3/TiO_2 and Cu-zeolite catalysts in a diesel engine. *Chem. Eng. J.* **2017**, *326*, 853–862. [CrossRef]
29. Kim, Y.J.; Kwon, H.J.; Heo, I.; Nam, I.-S.; Cho, B.K.; Jin, W.C.; Cha, M.-S.; Yeo, G.K. Mn–Fe/ZSM5 as a low-temperature SCR catalyst to remove NOx from diesel engine exhaust. *Appl. Catal. B Environ.* **2012**, *126*, 9–21. [CrossRef]