Review

An Overview of Lean Exhaust deNOx Aftertreatment Technologies and NOx Emission Regulations in the European Union

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Abstract: This paper reviews the recent advances in the management of nitrogen oxide (NOx) emissions from the internal combustion engine of light-duty and heavy-duty vehicles, addressing both technical and legal aspects. Particular focus is devoted to the often-virtuous interaction between new legislation imposing more restrictions on the permitted pollutant emission levels and new technologies developed in order to meet these restrictions. The review begins first with the American and then European directives promulgated in the 1970s, aimed at limiting emissions of pollutants from road transport vehicles. Particular attention is paid to the introduction of the Euro standards in the European Union for light- and heavy-duty vehicles, used as a legal and time frame reference for the evolution of emission aftertreatment systems (ATSs). The paper also describes governmental approaches implemented for the control of pollutant emissions in circulating vehicles, such as market surveillance and in-service conformity. In parallel, it is explained how the gradual introduction of small-scale devices aimed at the NOx control, such as lean NOx traps (LNTs) systems, and, most of all, the selective catalytic reduction (SCR) of NOx, permitted the application to road-transport vehicles of this ATS, originally designed in larger sizes for industrial usage. The paper reviews chemical processes occurring in SCR systems and their advantages and drawbacks with respect to the pollutant emission limits imposed by the legislation. Their potential side effects are also addressed, such as the emission of extra, not-yet regulated pollutants such as, for example, NH_3 and N_2O. The NOx, N_2O, and NH_3 emission level evolution with the various Euro standards for both light- and heavy-duty vehicles are reported in the light of experimental data obtained at the European Commission's Joint Research Centre. It is observed that the new technologies, boosted by increasingly stricter legal limits, have led in the last two decades to a clear decrease of over one order of magnitude of NOx emissions in Diesel light-duty vehicles, bringing them to the same level as Euro 6 gasoline vehicles (10 mg/km to 20 mg/km in average). On the other hand, an obvious increase in the emissions of both NH_3 and N_2O is observed in both Diesel and gasoline light-duty vehicles, whereby NH_3 emissions in spark-ignition vehicles are mainly linked to two-reaction mechanisms occurring in three-way catalysts after the catalyst light-off and during engine rich-operation. NH_3 emissions measured in recent Euro 6 light-duty vehicles amount to a few mg/km for both gasoline and Diesel engines, whereby N_2O emissions exceeding a dozen mg/km have been observed in Diesel vehicles only. The present paper can be regarded as part of a general assessment in view of the next EU emission standards, and a discussion on the role the SCR technology may serve as a NOx emission control strategy from lean-burn vehicles.

Keywords: DeNOx; SCR; EU regulation; NOx

1. Introduction

Nitrogen oxides are a group of highly reactive gaseous compounds containing nitrogen and oxygen in different proportions. Among these, NO, NO_2, and N_2O are the most abundant in the atmosphere and thus more interesting from an environmental protection point of view. N_2O is a strong greenhouse gas, with a global warming potential (GWP) approximately 300 times higher with respect to the one of CO_2, when considered over a 100-year period and the single most important ozone-depleting substance (ODS) [1]. On the other hand, NOx (as the sum of NO and NO_2 is commonly referred to) has direct effects on human health and the environment; some non-exhaustive examples are protein oxidation, cell membrane damage, alteration of the immune system, green leaves ageing, and reduction of photosynthetic activity and biomass production [2,3].

NOx species are classified both as primary pollutants, being directly emitted in different industrial sectors (including all conventional combustion processes [4]), and secondary ones leading to the formation of harmful compounds such as nitric and nitrous acid or acting as a precursor of photochemical smog [3]. The road transport sector is one of the main sources of NOx emissions in Europe (39% in the EU-28 in 2017) [5]. In the European Union (EU), the control of emissions from mobile sources is implemented by improving fuel quality and promoting and integrating environmental protection requirements into the transport and energy sectors. In particular, the EU's air quality directives [6] set pollutant concentration thresholds that shall not be exceeded in a given period of time. For NO_2, thresholds have been established at 200 μg/m^3 hourly—not to be surpassed more than 18 times per year—or 40 μg/m^3 in a calendar year. Overall, 16 of the EU Member States recorded NO_2 concentrations above the annual limit value in 2017 [5].

Aiming at curving the concentrations of air pollutants in Europe, the EU has introduced since the early 1990s a series of directives and regulations, commonly referred to as Euro standards (Euro 1 to Euro 6d for light-duty vehicles (LDVs) and Euro I to Euro VI-E for heavy-duty vehicles (HDVs)), that prescribe limits for the emissions of a series of air pollutants including NOx. To meet the requirements laid down by the procedures present in these emission standards, vehicle manufacturers have equipped their products with different emission control systems. In particular, to reduce NOx emissions vehicles have been equipped with systems such as three-way catalytic converters (TWCs), selective catalytic reduction systems (SCRs), and/or lean NOx traps (LNTs). However, while reducing the emissions of the target compounds, these systems can lead to the emissions of other pollutants that are not regulated from vehicles in the EU, e.g., NH_3 and N_2O [7,8].

The introduction of new legal and technical procedures for the control of pollutants and greenhouse gas emissions will be more extensively discussed in this paper. These new procedures are largely based on the legal request that vehicles are type-approved and controlled on new real-world driving emission (RDE) testing.

RDE data show that the new norms are working worldwide and are effectively reducing Diesel NOx emissions up to 70–90% compared to pre-Euro 6d regulations [9]. New regulations continue to be introduced and implemented throughout the world. China has revised its New Energy Vehicles (NEVs) policy and has acknowledged the role of hybrids in meeting future CO_2 and criteria pollutant targets. Early implementation of China 6/VI has started. Elements of post-Euro 6 regulations are becoming clearer. India is implementing Bharat Stage (BS) 6/VI norms starting in 2020, and filters and SCR systems are expected to be adopted this coming year on new Diesel vehicles as well. While following the general European framework, key changes are foreseen in order to better represent local driving conditions [9,10].

In summary, it is clear that the implementation of policies aimed at the reduction and control of NOx pollution, among other pollution sources, has become a paramount challenge for the authorities worldwide. It is also clear that, in parallel, the development of targeted technologies for a drastic reduction of NOx pollution derived from internal combustion engine (ICE) emissions has led to the production and commercialisation of vehicles able to face the conflicting exigencies of increasing mobility by the public on one

hand, and the increasingly stringent air pollution limits required by the environmental policies on the other.

The present paper aims at summarising the policies and technological aspects of the challenge set by the reduction of nitrogen oxide emissions from the transport section in the last few years when the selective catalytic reduction systems appear to have become crucial.
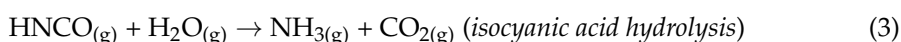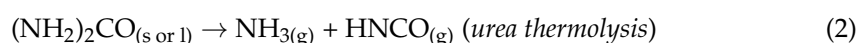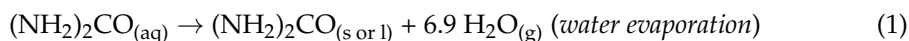
2. Fundamentals of SCR Operation and Future Applications

Selective catalytic reduction of NOx using NH_3 as reducing agent, originally developed for stationary applications (e.g., power generation plants) and first introduced in the late 1970s in Japan, has become a widely applied process also in Europe, starting from its early adoption in 1985 in Germany [11,12].

SCR technology has been recently introduced in the automotive industry due to the enforcement of progressively more stringent regulations on NOx emissions, as widely discussed in the present review. The downscaling of this process to relatively smaller and inherently transient applications, such as those of internal combustion engines used in the transport and off-road machinery sectors, has posed significant technical challenges such as space limitations, requirements for high conversion efficiencies in a wide range of temperatures (150–550 °C) and under highly variable conditions of engine load/speed, availability of ammonia and its safe storage/handling, etc. [12]. In addition, aftertreatment systems (ATSs) in these sectors have to ensure robustness and adequate performance over the whole life cycle of the vehicle, which can be several years and several thousands of kilometres long (up to 160k km for light-duty and 160–700k km for heavy-duty according to EU regulations 2018/1832 [13] and 595/2009 [14]).
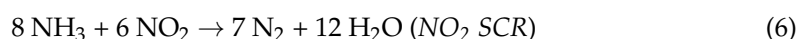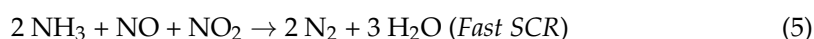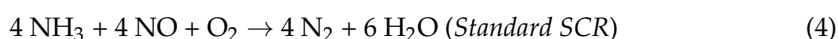
In the following sections, we will briefly address the main criticalities and specificities of the application of the SCR process to lean-burn internal combustion engines, with a particular emphasis on light and heavy-duty vehicles.

2.1. Basic Principles

The SCR is a catalytic process of reduction of oxidised compounds (NOx) in an environment in which oxygen presence is typically still abundant such as the exhaust stream of a lean combustion process (e.g., in a Diesel engine exhaust). This is a fundamental difference with respect to gasoline engine ATS in which, due to the stoichiometric combustion and the minimal oxygen content in the exhaust, is possible to accomplish oxidation and reduction functionalities in a single catalytic unit (i.e, the three-way catalyst (TWC)). Additionally, this is also the reason why, in the SCR process, a reducing agent is needed. In contrast to pure ammonia, which is used in stationary applications due to its high selectivity, a Diesel exhaust fluid (DEF) is employed in mobile applications, mainly for safety and space reasons, as better detailed in the 'Ammonia Supply', Section 2.2.2 of this paper. DEF, commercially known by the name AdBlue, is an aqueous solution of 32.5% of high purity urea (by weight) in deionised water. Ammonia is made available in the gas phase via the following set of reactions [15]:

$$(NH_2)_2CO_{(aq)} \rightarrow (NH_2)_2CO_{(s \text{ or } l)} + 6.9\ H_2O_{(g)}\ \textit{(water evaporation)} \tag{1}$$

$$(NH_2)_2CO_{(s \text{ or } l)} \rightarrow NH_{3(g)} + HNCO_{(g)}\ \textit{(urea thermolysis)} \tag{2}$$

$$HNCO_{(g)} + H_2O_{(g)} \rightarrow NH_{3(g)} + CO_{2(g)}\ \textit{(isocyanic acid hydrolysis)} \tag{3}$$
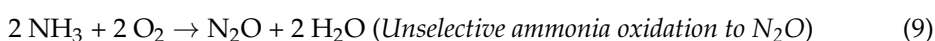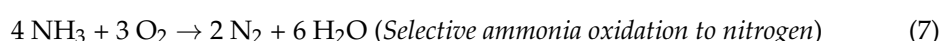
Overall, the SCR process is then based on the following set of global reactions occurring via species in the gas or adsorbed phase:

$$4\ NH_3 + 4\ NO + O_2 \rightarrow 4\ N_2 + 6\ H_2O\ \textit{(Standard SCR)} \tag{4}$$

$$2\ NH_3 + NO + NO_2 \rightarrow 2\ N_2 + 3\ H_2O\ \textit{(Fast SCR)} \tag{5}$$

$$8\ NH_3 + 6\ NO_2 \rightarrow 7\ N_2 + 12\ H_2O\ \textit{(NO_2 SCR)} \tag{6}$$
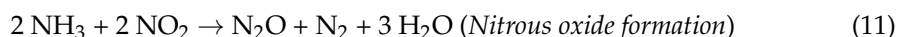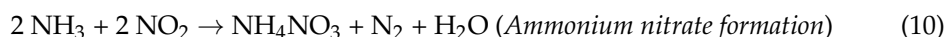
Among those, the highest reaction rates are achieved in the case of Fast SCR, i.e., when an equimolar amount of NO and NO_2 are present in the exhaust gas. For this reason, a dedicated catalytic unit, the so-called Diesel oxidation catalyst (DOC), has been introduced in order to ensure the oxidation of NO to NO_2. DOCs are gaining more attention in recent studies targeting the next level of regulations. This will be discussed in the 'Diesel Oxidation Catalyst (DOC)', Section 2.2.1 below. Finally, particularly for the Standard SCR reaction (R4), the fundamental redox reaction mechanism has yet to be clarified, and this has led, in recent years, to a lively and prolific discussion in the specialised literature. More details concerning the latest development in SCR chemistry can be found in [16–18].

In addition to the above-mentioned reactions, different sets of unwanted reactions can occur. In particular, ammonia can be selectively oxidised to nitrogen (7), leading to an overconsumption of reducing agent, or unselectively converted to NOx (8) and (9), further reducing the overall process conversion [12].
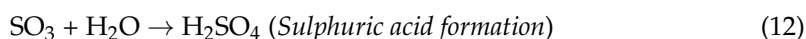
$$4\,NH_3 + 3\,O_2 \rightarrow 2\,N_2 + 6\,H_2O \;\; (\textit{Selective ammonia oxidation to nitrogen}) \tag{7}$$

$$4\,NH_3 + 5\,O_2 \rightarrow 4\,NO + 6\,H_2O \;\; (\textit{Unselective ammonia oxidation to NO}) \tag{8}$$

$$2\,NH_3 + 2\,O_2 \rightarrow N_2O + 2\,H_2O \;\; (\textit{Unselective ammonia oxidation to } N_2O) \tag{9}$$

These reactions are normally relevant at high temperatures (>400 °C) and in the absence of NO_2 in the feed.

On the contrary, a large presence of NO_2 in the feed at low temperatures might lead to the unselective formation of ammonium nitrate and N_2O, according to (10) and (11) below [12]:

$$2\,NH_3 + 2\,NO_2 \rightarrow NH_4NO_3 + N_2 + H_2O \;\; (\textit{Ammonium nitrate formation}) \tag{10}$$

$$2\,NH_3 + 2\,NO_2 \rightarrow N_2O + N_2 + 3\,H_2O \;\; (\textit{Nitrous oxide formation}) \tag{11}$$

In general, ammonium nitrate formation is critical below 180 °C, limiting, together with urea decomposition, the applicability of the SCR process at low temperatures. Ammonium nitrate can be reduced by NO at low temperature (200 °C), producing NO_2 and thus enabling the occurrence of a Fast SCR reaction. This has been proposed [19] as a way to boost the low-temperature performances of catalytic systems, in particular for Fe–zeolites and V_2O_5–WO_3/TiO_2 for which best performances are normally obtained in the 300–400 °C range.

Finally, the presence of sulphur in the fuel, combined with the oxidative function of DOC, can lead to the formation of SO_3 and subsequently to the formation of sulphates and sulphuric acid (12)–(14), as also detailed in the 'Catalysts and Supports for SCR', Section 2.3 [12]:

$$SO_3 + H_2O \rightarrow H_2SO_4 \;\; (\textit{Sulphuric acid formation}) \tag{12}$$

$$NH_3 + SO_3 + H_2O \rightarrow (NH_4)HSO_4 \;\; (\textit{Ammonium bisulfate formation}) \tag{13}$$

$$2\,NH_3 + SO_3 + H_2O \rightarrow (NH_4)_2SO_4 \;\; (\textit{Ammonium sulfate formation}) \tag{14}$$

These salts tend to accumulate on the catalyst leading to pore blocking and deactivation, reversible upon temperature increase. Sulphuric acid might lead to corrosion of the ATS components and the formation of harmful aerosols.

2.2. General Architecture of Lean-Burn ATS

In the following, we will provide a brief overview of the typical components constituting the ATS of a Diesel engine. The scope of this section is not to provide an exhaustive review of the basic functioning and technological evolution of each one of these components but to present their principal role and the impact they have on the functioning and technical implementation of the SCR technology.

2.2.1. Diesel Oxidation Catalyst (DOC)

A DOC promotes oxidation of exhaust components such as CO, hydrocarbons (HC), and NOx, using platinum-group metal (PGM)-based catalysts. This is typically the first component in the Diesel ATS and serves multiple functions. First, it converts any unburned species such as CO and HC to CO_2 and water. Second, the reactions are exothermic, and the heat generated can be used for elevating exhaust temperature to trigger soot regeneration in the downstream particulate filter, or to enable earlier urea dosing for the SCR [20]. Finally, a DOC oxidises NO to NO_2, to support both passive regeneration of the filter and to increase the rate of the SCR reaction through the "Fast SCR" mechanism, (R5) above, which is most pertinent to the topic of this paper.

Traditionally, DOC was placed in an underfloor position. The progressively more stringent limits imposed by regulations and the pursuit for catalysts with smaller volumes (and, thus, costs) has led to positioning this component in a closed-coupled position, near to the engine out, or in a pre-turbo configuration [20].

The most common PGMs used in the DOC washcoat formulation are Pt, Pd, and, less frequently, Rh. The latter is typically used in TWCs to implement NOx reduction functionality but might be used, although expensive, in DOC to limit sintering at high temperatures [20,21]. Interestingly, due to the lower operating temperature with respect to a conventional TWC, PGM in DOC might be up to three times higher at comparable space velocities [20,21], making the optimisation of this component very important. In general, Pt shows better performances with HC molecules and good oxidation activity also in presence of SO_2, provided that the temperature is kept under control. However, at extreme temperatures (such as those obtained to trigger Diesel particulate filter (DPF) regeneration) Pt might undergo degradation [20,22]. On the contrary, Pd has displayed higher activities in the oxidation of light molecules (i.e., CH_4, C_3H_8) and an increased resistance to sintering at high temperatures [20]. Due to complementary properties, and also in an attempt to substitute the more expensive Pt with Pd, mixtures of Pt/Pd have been systematically studied in the specialised literature [20,23,24]. In general, all Pt/Pd mixtures show better light-off and thermal stability with respect to monometallic ones. NO_2 production was found to be proportional mainly to Pt content, with a negative effect of Pd addition. Similarly, no dramatic improvement of light-off temperatures has been observed after a Pt:Pd ratio of approximately 80:20 is reached [25], except for very high Pd loadings. Another interesting concept applied in order to reduce the PGM loading of the catalyst is to use non-uniform metal distributions or zone-coating. In this way, it is in principle possible to use different amounts of metal along the axial section. It has been demonstrated that this will lead to lower light-off temperatures, reduced thermal stresses, and a light-off closer to the inlet section [20]. Indeed, an uncontrolled thermal event might result in metal sintering and also volatilisation, leading to PGM migration from DOC downstream to SCR at higher temperatures. It has been shown that minimum quantities of PGM can significantly reduce SCR performance due to over-oxidation of NH_3 [26–28].

As shown in the 'Results and Effects of Regulation Adoption', Section 4, and in [7,8,29], DOC can produce relevant amounts of N_2O. It has been shown that C_3H_6 is able to decrease NO reduction to N_2O. However, this effect is counterbalanced by the presence of CO that can promote propylene oxidation, increasing also the light-off temperature for N_2O formation [29]. Pd addition has a beneficial effect on N_2O production while reducing overall NO to NO_2 oxidation performance, however. A detailed review on DOC chemistry, kinetic modelling, and issues connected to deactivation and poisoning can be found in the comprehensive work of Russell et al. [20]

2.2.2. Ammonia Supply

NH_3 is the main reducing agent used in the SCR process. In mobile applications, the use of different reducing agents such as hydrocarbons [30] or hydrogen [31,32] has been explored as potential alternatives; however, with limited commercial success mainly due to excessive fuel penalty in the first case and technical complexity in the latter.

In stationary applications, anhydrous ammonia (commercial grade, 99.5% ca. purity), aqueous ammonia (at 29.4%, i.e., the solubility limit at ambient conditions of 30 °C and 1 atm), and urea are commonly used as reducing agents [12]. However, anhydrous ammonia is corrosive (classified GHS05 according to the Globally Harmonised System of Classification and Labelling of Chemicals), highly toxic (GHS06) and dangerous for the environment (GHS09) and must be stored under pressure. In addition, it is flammable, has an autoignition temperature of 651 °C at 1 atm, and might form explosive mixtures with air (16–26% v/v at 1 atm). Occupational long-term and short-term exposure limits (LTEL/STEL) in the European Union are 20 ppm and 50 ppm, respectively [33,34].

Urea ($(NH_2)_2CO$), on the contrary, is non-toxic, non-corrosive, and can be easily handled as an aqueous solution. For these reasons, in mobile applications, a standard mixture of deionised water and 32.5% w/w urea, known as Diesel exhaust fluid (DEF) or commercially as AdBlue, is commonly used. First patented applications of urea solutions in mobile SCR were registered in 1990 [35], but some criticalities related to its use still need to be solved. In particular, (i) urea full decomposition requires sufficiently high temperatures (170–180 °C) limiting NH_3 availability during cold start phases; (ii) urea dosing and uniform mixing with exhaust flue gas is inherently more complex with respect to gaseous NH_3 and, if not well controlled, can lead to solid deposits in the pipes or on the catalyst with issues of pore blocking and deactivation; (iii) NH_3 storage density of DEF is only 1/3 with respect to pure NH_3 increasing the space needed for storage; (iv) DEF composition lead to a freezing point of −11 °C, which constitute an issue in many cold countries and, in addition, storage tanks must be designed to account for DEF volumetric expansion upon freezing (ca. 7%) and to rapidly melt urea for a quick start of the system; (v) DEF long-term storage at more than 30 °C may lead to hydrolysis and to an increase in pressure with the formation of ammonia—in general, storage temperature should not exceed 25 °C and direct sunlight must be avoided [36]. The shelf life of DEF decreases significantly (down to six months) if stored at temperatures between 30 °C and 35 °C. This is an additional issue in countries with a hot climate.

In order to solve some of the above-mentioned issues, different alternatives are currently under investigation. They include solid urea [37,38], ammonium formate [38–40], ammonium carbamate [38,41,42], guanidinium salts, and metal ammine chlorides [38,43]. Although they might overcome some of the issues typical of urea-based solutions, these methods also present some new challenges.

Solid urea presents very high NH_3 storage densities when compared to traditional DEF. Nevertheless, its use is extremely challenging because the dynamic dosing required in mobile applications is very hard to achieve in the case of solids. Moreover, small solid urea pellets have a high tendency to form conglomerates, which makes the storage demanding [38].

The addition of ammonium formate to urea solutions can significantly decrease the freezing point down to about −20 °C/−30 °C (DeNOxium-20/DeNOxium-30) while increasing the amount of stored NH_3 in solution (from 0.184 kg/kg of reference DEF up to 0.205/0.207 kg/kg for DeNOxium-20/DeNOxium-30) [38–40]. However, when evaporating it forms formic acid, which is not only the most corrosive halogen-free organic acid, but it might also form unwanted secondary products such as methanamide, (a teratogenic compound) or hydrogen cyanide (extremely toxic) [38].

Ammonium carbamate has the advantages of solid precursors (avoid freezing issues, higher NH_3 storage density), without the need to be contacted with a catalyst to favour its decomposition. The ammonium carbamate can store up to 0.436 kg_{NH3}/kg [38]. Moreover, in certain applications [42] allow early dosing of NH_3 at temperatures as low as 50 °C, in principle well before the light-off temperature of conventional metal exchanged zeolite catalysts normally used in SCR. Despite the interesting developments, there are no technological solutions commercially available at the time being.

Guanidinium formate can form very stable aqueous solutions (from −30 °C up to 60 °C) with an NH_3 storage capacity which can be roughly 1.5 times that of commercial

DEF [44]. Unfortunately, due to its stability, its full decomposition requires a dedicated hydrolysis catalyst with dedicated heating. Moreover, the kinetics and decomposition mechanism need further investigation, also to avoid problems similar to those experienced for ammonium formate, as already discussed [38]

In applications using metal ammine chlorides, gaseous NH_3 is reversibly adsorbed as a ligand to a metal atom contained in salt, from which it can be desorbed upon heating, being the release endothermic. Some of the salts considered due to their high storage capacity include $Mg(NH_3)_6Cl_2$, $Ca(NH_3)_8Cl_2$, and $Sr(NH_3)_8Cl_2$. Among the first pilot applications, Amminex, whose technology is based on $SrCl_2$, allows releasing up to seven NH_3 molecules at a temperature as low as 80 °C, which can be achieved by using directly the engine coolant as a heat source. However, with this solution, pressures as high as 6 bar can be achieved in the NH_3 storage cartridge, which requires a strong containment [38].

2.2.3. Ammonia Slip Catalyst (ASC)

In the SCR process, gaseous NH_3 is used as a reducing agent to convert harmful nitrogen oxides back to N_2 and H_2O. However, unreacted ammonia can slip from the SCR catalyst leading to undesirable emissions at the tailpipe. This phenomenon can have different causes, for example:

- The occurrence of transients causing rapid increases in exhaust temperature;
- Progressive reduction of the NH_3 storage capability of SCR catalyst due to ageing;
- Overdosing of urea, normally done in modern units to achieve the high conversions required by legislation;
- Suboptimal design or operation of the DEF dosing system leading to solid deposits that can then, upon temperature increase, release NH_3 in an uncontrolled way.

ASC catalysts are normally constituted by honeycomb monoliths supporting washcoat containing PGMs, given their relevant oxidation capabilities. These catalysts can lead to N_2 formation according to Reaction (15):

$$4\,NH_3 + 3\,O_2 \rightarrow 2\,N_2 + 6\,H_2O \ (NH_3\ oxidation\ to\ N_2) \qquad (15)$$
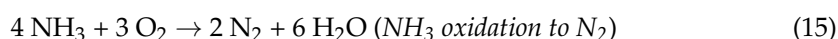
However, this is normally done with average selectivity and possible side reactions involve the unselective oxidation of NH_3 to NO or N_2O, as described in (R8) and (R9).

In addition, it was shown that high NO/NH_3 ratios, which can occur due to NH_3 oxidation in SCR catalyst such as Cu-exchanged zeolites, suboptimal DEF injection or poor mixing, can lead to significant N_2O production according to the following unselective Standard SCR reaction [45,46].

$$2\,NH_3 + 2\,NO + 3/2\,O_2 \rightarrow 2\,N_2O + 3\,H_2O \ (unselective\ Std.\ SCR) \qquad (16)$$

Latest developments in ASC catalysts technology have permitted to reduce by 80% the amount of PGM loading, resulting in a relevant cost decrease with a slight increase in overall selectivity to N_2, as shown in Kamasamudram et al. [47] and reviewed by Johnson [48].

An interesting implementation of ASC technology is constituted by a dual-layer architecture in which the PGM washcoat layer is placed below an SCR catalyst. This solution presents advantages both in terms of NH_3 overall conversion but also with respect to N_2 selectivity. Indeed, the bottom PGM layer carries out the oxidation of NH_3 to N_2 but also NOx. These latter compounds have then to diffuse back in the above layer in which they are converted by the excess NH_3 typically stored by SCR catalysts [49,50]. The positive interaction of the two chemistries has been extensively studied in [45,46].

Dual-layer ASC catalysts have an inherently more complex behaviour due to the coupled reaction mechanisms and, moreover, they are also affected in a significantly different way by hydrothermal ageing, as discussed in Kamasamudram et al. [51]. The possibility of combining NOx reduction and NH_3 oxidation functionalities in a single layer has also been investigated in the simulations published by Colombo et al. [52]. With respect

to the dual-layer architecture, mixed single layer solution greatly enhances the selectivity towards N_2, reducing the diffusional barrier encountered by NH_3 in reaching the PGM layer.

Irrespectively from the implementation, proper optimisation of these systems is becoming increasingly important given the progressive increase in NH_3 and N_2O emissions from both light and heavy-duty engines, as discussed in the 'Results and Effects of Regulation Adoption' Section 4 below, and in the specialised literature [7,53,54]. Recent studies are investigating the effects of combining ASC and DOC functionalities, which is of particular interest for advanced configurations (see the dedicated section) in which two SCR units might be present before and after the DOC/DPF units. This dual-layer solution is based on the presence of a PGM and an SCR layer, similar to what happens in conventional ASC, but it is designed to promote NO_2 formation (to be used in subsequent DPF and SCR units) with less parasitic consumption by NH_3 [55]. The system is able to ensure an increase of 10% in the NO_2/NOx ratio, in presence of NH_3 (NH_3 to NOx ratio of 0.4) at 350 °C with respect to the conventional system, without modifications in the N_2O selectivity profile.

2.3. Catalysts and Supports for SCR

A comprehensive review of catalysts used for SCR is beyond the scope of this paper, but we provide here some trends and technical considerations. Commonly, the catalysts are prepared either through extrusion as a homogenous monolith or washcoated on metallic and ceramic substrates. The geometry of the substrates is an important design choice as it directly impacts the distribution of the catalytic sites and the transport of reactants. Monoliths are honeycomb-structured reactors with thousands of parallel channels. The geometry is defined by the number of channels per square area—measured in 'cells per square inch' or cpsi and the wall thickness, measured in thousands of an inch or mils. Broadly, the trend has been towards higher cpsi to increase the geometric surface area, and thinner walls to decrease the pressure drop and thermal mass for rapid heat-up of the catalyst to operating temperature. Modern SCR catalysts for automotive applications are in the 400–600 cpsi range, while the wall thicknesses are in the 2–6 mil range. Modern SCR catalysts have to meet several competing requirements in order to deliver high NOx conversion throughout the vehicle life. These include high conversion at both low (<200 °C) and high temperatures (>500 °C), across a wide range of flow rates (space velocities) and transient driving conditions, durability under hydrothermal aging, resistance to chemical poisoning and sulphation, and low resistance to flow or pressure drop, to name a few. A wide variety of catalysts have accordingly been developed in the past several years and continue to improve. Leading examples include the use of vanadia–titania, zeolites exchanged with base metals such as copper and iron, and metal oxides. We provide here some exemplary catalyst developments in the past few years.

Copper–zeolite catalysts have been the leading choice due to the high conversion over a wide temperature window [48]. The use of small-pore zeolites such as chabazite (CHA) is known to offer especially good hydrothermal stability. In addition, small-pore zeolites such as CHA have shown significant resistance to HC poisoning and deactivation effects, as detailed in Selleri et al. [56]. Still, to address the next stage of regulations in advanced markets, current development is focused on further improving the low temperature (<200 °C) conversion, hydrothermal durability, and sulphur tolerance. Much progress is being reported on all fronts. For example, using aged Cu–zeolite SCR catalysts, two recent studies [55,57] reported NOx conversion of ~75% at 175 °C for the Standard SCR reaction (NO only), while also maintaining near 100% conversion up to 550 °C. A new LTA zeolite catalyst has been found to offer durability up to 900 °C. Zone coating of this Cu/LTA and the commercial Cu/SSZ-13 has been shown to provide a good combination of both low-temperature activity and hydrothermal stability [58]. Sulphur poisoning is a major drawback of Cu–zeolite catalysts and is getting increasing attention as new regulations are expected to substantially increase the durability requirements of aftertreatment systems. Broadly, most studies agree that sulphur is bound via both weak and strong interactions

with the Cu sites. The physically binding is expected to proceed through ammonium sulphate formation, which is released at temperatures above 350 °C. The most strongly, chemically bound sulphur is removed at much higher temperatures, greater than 550 °C. Thermal treatment can therefore be used to recover much of the activity. However, there is a fuel penalty associated with the regeneration step. A recent study cautions that even thermal aging does not completely recover the activity. Field-aged samples were thermally treated up to 550 °C and NOx conversion recovered to 76% at 200 °C. However, this was still not as good as the 96% conversion obtained on the reference degreened catalyst.

Iron–zeolite catalysts differ from Cu–zeolite primarily in the NOx conversion as a function of exhaust temperature. Cu–zeolites offer higher conversion at low temperatures, whilst Fe–zeolites are better at the high-temperature end. The latter observation is mostly attributed to reduced ammonia oxidation at high temperatures on Fe–zeolite catalysts. The low-temperature conversion can also be high for Fe–zeolite through an optimum 1:1 NO_2/NO ratio and the accompanying Fast SCR reaction. Fe–zeolite catalysts also have a lower affinity for sulphur as compared to Cu–zeolites and can therefore be better suited for applications requiring high sulphur resistance and low desulphation temperatures. Fe–zeolites also result in lower N_2O emissions compared to Cu–zeolites, and hybrid Fe–Cu SCR systems can offer a combination of high NOx conversion and low N_2O formation. One example is testing done on a 6.7 L engine with a 25% Fe–75% Cu catalyst, which was found to reduce the N_2O formation by half on the World Harmonised Transient Cycle (WHTC) [59]. There is a trade-off though, as adding Fe reduces the NOx conversion, and zone coating with Fe up to 20% of the inlet was found to be optimum for lower N_2O, beyond which NOx conversion is hindered [60].

Vanadia catalysts are generally preferred in markets with high-sulphur fuels due to their greater resistance to sulphation. Compared to copper zeolites, vanadia catalysts suffer from lower NOx conversion, especially at low temperatures. Furthermore, the key drawback is the stability of vanadia and its release at temperatures higher than ~500 °C [61].

Manganese-based catalysts are being explored to further improve low-temperature activity. Ce-Mn/TiO_2 catalysts have been tested in the laboratory and demonstrated to deliver >90% NOx conversion in the 140–260 °C range, while also delivering high sulphur resistance [62]. MnO_2/ZrO_2 catalysts are being examined to promote the in situ selective oxidation of NO to NO_2 [63]. A combination of 10% MnO_2/ZrO_2 and SCR catalyst was shown to increase the NO_2 and increased the NOx conversion at 150 °C by ~20%, while also reducing N_2O formation. This is expected to address the issue of competing demand for NO_2 for the SCR reaction and passive soot regeneration when SCR is coated onto filters.

2.4. Low-Temperature Challenges

NOx abatement in the lean exhausts of internal combustion engines at low temperatures is a technological challenge due to issues related to the availability of a reducing agent, salt depositions, and generally low catalytic activity. Essentially, to tackle this problem, different approaches can be followed: reduce as much as possible the heat-up time of the catalyst; avoid NOx emissions with additional catalytic systems such as adsorbers; provide a reducing agent in different forms, as already discussed in the previous section. In the following, a brief overview of the main advances on the first two strategies will be given.

2.4.1. Advanced Configurations

Typical modern Diesel ATS are conventionally composed of a DOC, a Diesel particulate filter (DPF) or a catalyzed DPF (cDPF) to trap soot particles, a DEF injection point with a mixer in order to achieve uniform NH_3, the SCR unit, and, finally, an ASC catalyst to limit the slip of unreacted NH_3 in the atmosphere. DeNOx ATSs have evolved significantly in the last few years, improving their performance at the expense of growing technical complexity, to comply with the progressively more stringent limits imposed by regulations. Indeed, several different configurations have been presented and discussed in the specialised literature and some examples will be discussed herein.

A first possibility is represented by a configuration in which the SCR is the first element of the ATS chain in a close-coupled position near the engine-out, followed by an ASC catalyst used to prevent oxidation of unreacted ammonia and then by a DOC, and a DPF. After this, the first set of components is placed in an additional DEF injection point and subsequently another SCR + ASC unit operating at lower temperatures [64,65]. These types of configurations give the possibility to reduce NOx emissions by up to 90% and N$_2$O emissions by 20% with a slight increase in fuel consumption (ca. 3%). Moreover, the close-coupled SCR can reach the injection temperature very quickly, reducing the cold start duration to less than 100 s. In these configurations, ASC and DOC functionalities can be in principle combined, as discussed below.

Another option presented in Auld et al. [66] involves the combination of LNT and a close-coupled SCR on the filter unit. According to simulation results over RDE certification cycles, for a C-segment car, this system represents the best trade-off between emission performance, system costs, and fuel consumption penalty. For larger SUVs, an additional underfloor SCR can ensure better performances in NOx control on highway sections.

In this context of growing complexity and proliferation of potential options, model-based evaluation of different technologies is a fundamental tool [67,68]. With this approach, it is in principle possible to investigate different alternatives and optimise the most promising solutions. According to the simulations, some of the best-performing solutions in terms of tailpipe NOx emissions involve the use of a DOC and a passive NOx adsorber (PNA) followed by a mini-burner system to increase the exhaust temperature (see the following section) just before the DEF dosing point. An SCR on filter followed by a conventional SCR + ASC unit is present downstream. With this configuration, it should be possible to achieve 19 mg/bhp/h of tailpipe NOx emission with a fuel penalty of about 2%.

Finally, another option actively discussed in the literature is constituted by pre-turbo DOC/DPF placement [69–71]. Moving the DOC/DPF before the turbine drastically increases the thermal level across the units, allowing an overall improvement of about 15% in both HC and CO conversions in a New European Driving Cycle (NEDC). Additionally, almost 25% of the overall soot accumulated on the filter can be passively regenerated thanks to the higher temperatures produced. Finally, according to the simulations reported in Serrano et al. [71] pre-turbo DOC and DPF configuration permits to significantly reduce the volume of the units by up to 40% and 50%, respectively.

2.4.2. Active Heating Strategies

Different strategies can be devised to rapidly increase ATS temperatures and allow earlier urea injection. When evaluating these options, it is important to consider their overall impact on the vehicle, including additional fuel penalties or increased emissions of other pollutants. Among these, cylinder deactivation (CDA) can represent a solution to lower fuel consumption and consequently CO$_2$ emissions while, at the same time, increasing engine out temperature and thus warming up quicker the downstream catalytic units. In very general terms, this is obtained through an overall reduction of the air-to-fuel ratio, as detailed in Shaver et al. [72]. CDA in combination with a cylinder cut out and advanced ventilation strategies can increase turbine out exhaust temperature by 50–150 °C achieving, at the same time, about a 6% reduction in fuel consumption when compared to baseline [73]. Additional examples of implementation of the same approach have led, for an X15 6-cylinder Cummins engine with variable geometry turbine (VGT) and high-pressure exhaust gas recirculation (EGR), to an increase of 40–100 °C of the turbo-out temperature, with an overall reduction of roughly 20% in fuel consumption together with a simulated reduction of NOx going from 45% to 66% and a 1.5–3.7% decrease in CO$_2$ depending on the cycle considered (FTP (federal test procedure) or LLC (low load cycle), respectively) [74–76].

In order to shorten the time in which the SCR unit is not operative during cold start, the possibility to decompose DEF at temperatures below 180 °C has been explored, using glow plugs in a small reformer unit [77]. This approach uses six glow plugs of 70 W

each and allows to achieve a 60% conversion of NOx already at 160 °C on an otherwise conventional SCR system. The system is able to generate ammonia with an efficiency of more than 90% [77]. However, in order to proceed to an overall evaluation, the impact of such systems on fuel consumption and overall vehicle efficiency has to be addressed.

Another example of a solution that can be implemented to accelerate DEF injection is constituted by heated injection systems. In the configuration investigated in Kowatari et al. [78], part of the exhaust flow is diverted to an electrically heated bypass with a dedicated injector. In this way, the flow is firstly heated to facilitate urea thermolysis and then is passed through a hydrolysis catalyst to complete decomposition. This solution can provide NOx conversions up to 99% at 160 °C, although fuel penalties related to electrical energy consumption and increased complexity of the configuration also have to be addressed.

Sharp et al. [79] compared several options to achieve ultra-low NOx emissions on a 361 kW Volvo MD13TC engine with a fixed geometry turbocharger. Among others, a 2 kW electrically heated catalyst, followed by a hydrolysis catalyst alone or in combination with a 5 kW additional heater placed downstream the DPF and before the DEF injection point, was investigated and compared to an adjustable-power mini-burner going from 8 kW to 20 kW. These systems can bring, respectively, a 45%, 70%, and 80% potential reduction in the overall tailpipe NOx emissions at the expense of increased energy consumption that has to be carefully quantified.

2.4.3. SCR on Filters

SCR-coated Diesel particulate filters constitute an additional strategy for tackling high NOx emissions during low-temperature operations. These filters consist of a wall-flow monolith coated with materials that both enhance soot oxidation and reduce NOx. The advantage of this approach is that the two-way SCR–DPF catalyst (hereafter called SCR–DPF) can be placed immediately downstream the DOC and, thus, nearer to the engine and achieve a faster warm-up with respect to a more traditional layout in which the SCR unit is placed downstream the DPF. In addition, this novel configuration may downsize significantly the volume and, thus, the cost of the ATS of a Diesel vehicle and also contribute to better thermal management of the engine, resulting in reduced fuel consumption. Finally, a recent study also showed that the SCR–DPF configuration may also reduce the possible effects of urea injection on the particle number emission levels [80]. Typical materials used for simultaneously controlling NOx and soot are rare earth metal oxides, spinel-type oxides, hydrotalcites, perovskites, mixed transient metal oxides, and platinum-group metals. A comprehensive review of materials proposed for this application has recently been published by Castoldi [81].

The main challenge of an SCR–DPF is to handle competitive functions that occur in close vicinity. Specifically, the design of an SCR–DPF shall take into account the compatibility between NOx reduction (Fast SCR reaction activity) and the DPF passive soot oxidation reactions because both reactions consume NO_2. SCR reaction is faster than soot oxidation and consequently, the competitive effects are expected to influence the DPF regeneration. Indeed, numerous studies investigated the effect of soot loading on the SCR efficiency by performing experiments with model soot and synthetic gases [82,83] and with Diesel engine exhaust [84–86]. For ratios $NO_2/NOx \leq 0.5$ (Standard/Fast SCR reaction) the soot loading had slight [83] or no effect [82,84–86] on NOx conversion. However, soot deep-bed filtration may inhibit the mass transfer from the exhaust gas to the active catalytic sites [87,88]. Marchitti et al. [83] also noted the promotion of ammonia oxidation with model soot due to its oxygen content leading to a less efficient NOx conversion. On the contrary, soot-loaded compared to soot-free SCR–DPFs have a better de-NOx performance when $NO_2/NOx > 0.5$ (Standard SCR), possibly due to the soot–NO_2 interaction that drives the NO_2/NOx ratio closer to the optimal 1/2 [82,83,86,87,89].

Diesel particulate filters that continuously regenerate with NO_2 are expected to be strongly influenced by the SCR activity. Several studies investigated the soot oxidation in the presence of urea/ammonia and concluded that soot oxidation was inhibited at low temperatures [83,85,86,89–91]. Lopez et al. [84] measured the backpressure of a vanadia–zeolite SCR-DPF over 60 test cycles (20 h operation) in an engine bench using a DOC upstream the SCR–DPF. During the first 20 cycles, the backpressure increased but then stabilised, showing that passive regeneration with NO_2 occurred. A possible solution to the decreased filter passive regeneration observed by several authors consists of reducing the O_2-driven active filter regeneration temperature by coating the filter itself with appropriate catalysts. Park et al. [87] found that soot oxidation with O_2 started at 300 °C when using a Cu–zeolite catalyst. In two recent studies [92,93], the authors proposed a dual-layer configuration for handling low-temperature soot oxidation. Accordingly, they used two catalysts for the SCR–DPF; one for SCR reactions (Cu-, Fe-zeolite) and one for soot oxidation (K/CeO_2–PrO_2, K/ZrO_2–CeO_2). They managed to decrease the soot oxidation temperature by more than 150 °C by maintaining a high NOx reduction. However, the tests were powder-based, so possible implications on monolith-based tests have to be further investigated.

Lopez et al. [84] determined the NOx conversion efficiency of a V-zeolite SCR–DPF monolith to be ~70% for engine-bench tests, while Aryan et al. [94] installed a Cu–zeolite SCR–DPF on a vehicle and determined the NOx conversion efficiency to be ~60%. Sapio et al. [95] evaluated an ATS composed of a closed-coupled DOC followed by a DEF injector and an SCR–DPF with SiC substrate with synthetic gases. They found a maximum NOx conversion of 99% at 350 °C, 86% at 250 °C, and more than 40% at 180 °C. The possibility to use the SCR–DPF in a hybrid aftertreatment system has been investigated by several authors. Aryan et al. [94] substituted the original ATS of a commercial vehicle that was composed of two SCRs and a catalyzed DPF, with an SCR and an SCR–DPF. They found similar NOx conversion efficiencies, close to 70%, both for fresh and aged catalysts (50,000 miles road aging), although in the second case there was one component less. An ATS with DOC + SCR−DPF + SCR was also tested in [96] with Diesel engine exhaust. The combined maximum NOx conversion of SCR–DPF, and SCR was found to be 97% in the temperature range 210–367 °C when the NO_2/NO ratio was 0.5. An alternative approach was followed by Kang et al. [97], who compared the performance of an LNT–DPF against a hybrid LNT−DPF + SCR−DPF system. In the latter, both NOx efficiency and PM oxidation improved drastically. In summary, as also discussed in previous sections, several technical configurations are possible, and careful optimisation of the different subsystems is becoming more and more critical to achieving the required results in terms of conversion, durability, and selectivity.

2.4.4. Passive NOX Adsorbers

As extensively discussed in previous sections, the use of DEF as a source of NH_3 to reduce NOx currently sets a technological limit (180 °C) under which SCR applications are hardly possible, even with a non-negligible catalyst activity. A possible solution to this challenging issue is represented by passive NOx adsorbers (PNAs), i.e., catalytic devices able to temporarily store NOx and release them when the temperature is sufficiently high to convert them. The concept of storing and reducing NOx in distinct moments is an old idea already well established in lean NOx traps (LNTs) systems. However, PNAs are required to desorb NOx in lean conditions, avoiding cyclic operations, and in an appropriate temperature window. To this end, different combinations of PGMs, both as active and storing sites, and substrates are being investigated, and it is still unclear which will be the optimal solution, for instance, Pt/Pd deposited on alumina or ceria [98], Ag-based systems able to store NOx under rich conditions [99], or Pd zeolites [100]. Among these groups of materials, Pd-exchanged zeolites seem to be very promising due to their better resistance to sulphur poisoning. Indeed, it is known that PGMs deposited on Al_2O_3/CeO_2 are capable of easily oxidise sulphur, leading to the formation of stable sulphate species which drastically reduces the NOx storage capacity.

In general, however, the NOx adsorption and desorption chemistries on Pd–zeolites are far from being clarified and several aspects, such as the role of water or the effects caused by a realistic exhaust composition, need further investigation. Indeed, the topic has received significant attention in the specialised literature and has been reviewed in [100], in which the interested reader can find additional information. Finally, an important topic in PNA is the overall system cost. Indeed, currently investigated systems are based on precious metals and are realised with expensive synthesis methods [100]. These aspects should be carefully evaluated when comparing potential alternative strategies.

A possible alternative approach to PGM-containing PNAs is constituted by the so-called adsorption + selective catalytic reduction (AdSCR). This approach, firstly presented in Selleri et al. [101], consists in the combination of a NOx storage material similar to those traditionally used in lean NOx traps, such as, for example, BaO/Al_2O_3 or CeO_2/Al_2O_3, with a conventional SCR catalyst (i.e., metal exchanged zeolite). This system allows us to trap NOx in the form of nitrites, starting from room temperature and releasing them above 200 °C at which they can be actively converted by the SCR component. The process is enabled at T < 120 °C by the gas-phase mechanism of NO oxidation, which is characterised by negative apparent activation energy and is controlled by the confinement effect of the zeolite structure, as discussed in the literature [102,103].

Overall, preliminary studies [104] on these systems have shown promising performance. In some cold start simulated tests under model conditions, the authors have demonstrated a maximum trapping efficiency, defined as the ratio between the trapped NOx and the total NO entering the system, above 90% with a NOx breakthrough time of roughly 400 s. The system has demonstrated its capability to tolerate CO_2 and H_2O presence with some modifications. However, additional studies are necessary to demonstrate its applicability in more representative operative conditions.

2.5. Modelling and Control

The SCR process application to vehicles is characterised, as discussed previously, by continuously varying operating conditions, with changing temperatures, flow rates, and concentration of pollutants in the exhaust pipe. All these parameters ultimately affect the overall performance of the catalytic unit that is measured in terms of overall conversion and selectivity to nitrogen. At the same time, to achieve the stringent targets required by the regulation, deNOx systems and SCR in particular have become increasingly complex to control. They demand continuous management of DEF injection on the basis of the operative conditions. Traditionally, the first studies on the optimisation of injection strategies were based on look-up tables or dynamic feed-forward approaches [105–107], in which a subset of the system operating conditions was previously assessed and used as an interpolation basis to adjust to the current, in principle unknown, situation.

The first example of a more advanced approach based on a simplified simulation model is presented in Upadhyay et al. [108]. In this study, the SCR reactor is described with a continuously stirred tank reactor (CSTR) model with negligible mass transfer resistances and a simplified chemistry, accounting for only three main species (i.e., NH_3 in gas and adsorbed phases and gas-phase NO) and thus completely overlooking the role of NO_2 and thus of the fast-SCR reaction, which has become fundamental with the evolution of DOCs and the increased availability of NO_2 in the exhaust.

In order to limit the impact of unconverted NH_3 slip at the tailpipe, Schär et al. [109] proposed an approach which combined feed-forward and feedback controllers together with a one-dimensional homogeneous SCR converter model constituted by a set of two axial cells. The basic model includes a simplified reaction scheme involving NH_3/NO main reactions (adsorption/desorption, oxidation, reactivity).

In the papers of Ericson et al. [110] and Chi et al. [111], the models for SCR converter include a description of heat and mass transfer phenomena sacrificing, however, computational speed and making real-time control of the ATS system practically impossible. Indeed, while very detailed and complex descriptions of both SCR kinetics and heat and mass

transport problems exist [112,113], a significant part of the models available in the literature and developed for control purposes are based on the CSTR approach, with the inclusion of progressively more detailed kinetics (involving three or four species, i.e., including NO_2) [114–116] to keep the computational burden acceptable.

In the research of McKinley et al. [117,118], a switching procedure to keep the computational complexity under control is presented. The basic idea is to replace the equation for the coverage of adspecies (NH_3 in particular) with approximated pseudo-steady-state ones each time the time step necessary to solve the differential equations included in the model becomes shorter than a given threshold. This has allowed the utilisation of 1D heterogeneous PFR models with a detailed kinetic scheme also for real-time applications. Another example of progressive simplification of an SCR advanced model useful for model-based control can be found in the work of Gundlapally et al. [119].

A simplified orthogonal collocation approach is used in Selleri et al. [120] to discretise the washcoat coordinate in order to account for the diffusion-reaction problem in the washcoat real-time simulations. Its formal equivalence with the internal mass transfer coefficient approach presented by Balakotaiah [121–123] is demonstrated.

Another central topic, as also highlighted by in-service conformity (ISC) regulation (additional details can be found in Section 3.1.4), previously discussed and that can be addressed through modelling is related to durability and ageing of catalytic systems. Indeed, the topic is vast and complex. Most of all, it is extremely costly and complicated to perform durability experiments under in-field realistic conditions. In addition, apart from the issues related to hydrothermal stability of the catalysts, mostly related to the thermal load of the ATS system, different deactivation pathways (chemical poisoning, pore blocking, etc.) can occur and play an important role in the overall durability of the system. For these reasons, the development of a modelling tool to estimate catalyst durability is attractive, although complex. The work of Le Louvetel-Poilly et al. [124] presents a model describing, for example, the ageing of a TWC. The main idea is to identify a set of ageing parameters and related ageing laws which depends on the type of the PGM used and affects the connected chemistries. This set of parameters has to be calibrated in any case against a set of experimental data obtained in the lab or from on-road experiments. On the other hand, it presents the advantage to permit the utilisation of the same model for catalytic technologies involving different proportions of active elements, ultimately allowing model-based design (MBD) approaches. In a similar way, Dosda et al. [125] proposed a model for the whole exhaust after-treatment line of a Diesel engine, composed of a DOC, a closed coupled SCR on filter, and an underfloor SCR. In this latter work, a model accounting for hydrothermal ageing of the involved catalysts has been included permitting, in the end, the investigation of the optimal design of the system by optimizing line geometry and catalyst location as a function of the foreseen degree of ageing, based on the simulation output. In general, hydrothermal ageing in metal-exchanged zeolites has been extensively studied in the literature and simulated according to relatively simple approaches such as tuning the NH_3 storage capacity, depending on the ageing conditions [126]. Nevertheless, as shown in the literature, it is clear from the investigation of field-aged heavy-duty catalysts that is important to account, among other effects, for the deposition of chemical elements contained in the fuel, the impact of the lube oil, and the engine wear [127,128]. This makes the development of a predictive model for catalyst durability a challenge still not completely solved.

3. Evolution of deNOx Regulation and Control Systems

3.1. Light Duty

3.1.1. Emission Standards (Euro 1 to Euro 6d)

The Emissions Directive 77/102/EEC (entered into force in 1976) [129] was the first emission policy that, for the first time, introduced a limit to NOx emissions from vehicles in Europe. This directive was followed by 78/665/EEC [130] and 83/351/EEC [131]. Together with the 70/220/EEC [132] and 74/290/EEC [133], these are known as the pre-

Euro emission legislations. The European Union introduced the Emissions Directive 91/441/EEC—Euro 1 [134] following its proposal to make unleaded gasoline available at gas stations by 1989, as such a proposal allowed the introduction of exhaust aftertreatment catalytic control systems (ATSs), i.e., the three-way catalysts (TWCs) for gasoline vehicles. This directive, the implementation of which was extended to all new passenger cars in 1993, (dates of implementation of the listed directives differ from country to country, depending on the approval status of the respective amendment in that country) presented, unlike the previous one, a combined limit for NOx and total hydrocarbons (THC) for both positive ignition and compression ignition engines, as briefly summarised in Figure 1. Euro 1 standards were followed by the wide introduction of TWC in gasoline vehicles, while no specific ATS was necessary for Diesel vehicles. Even though their size, position, precious metal load, electronic control, etc. have evolved since then, TWCs are still the most common ATS employed by all types of vehicles using positive ignition, stoichiometric, internal combustion engines (such as passenger cars, light-, and heavy-duty trucks).
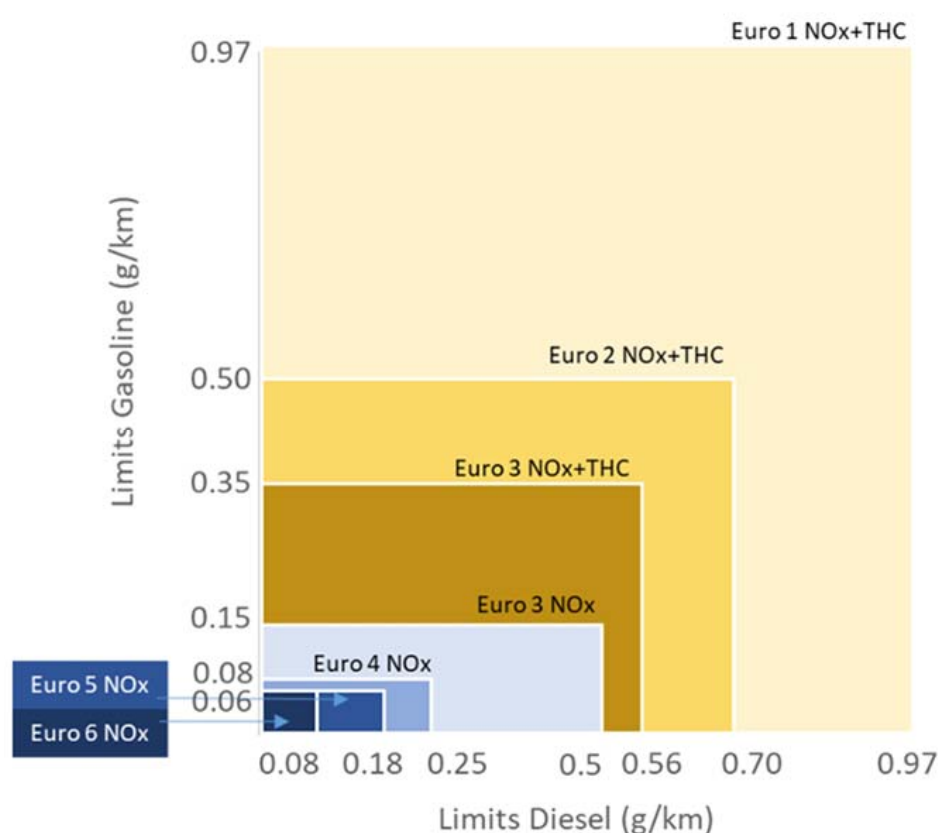

Figure 1. Evolution of NOx emissions limits enforced by EU regulation for gasoline and Diesel light-duty vehicles (LDVs).

Euro 2 standard for passenger cars was introduced with Directive 94/12/EC [135] and implemented for all new passenger cars in 1997. This standard reduced the combined limit of emission of NOx + THC by 50% and 38% from positive and compression ignition vehicles, respectively. Following the Euro 2 Directive, higher catalyst volumes or larger PGM loads were used on TWC by gasoline cars, and exhaust gas recirculation (EGR) was introduced in some Diesel vehicles.

The Euro 3 standard was covered under Directive 70/220/EEC [132] as amended by 98/69/EC [136], and the following adaptations and amendments: 99/102/EC [137], 2001/1/EC [138], 2001/100/EC [139], 2002/80/EC [140]. It was implemented for all new passenger cars in 2001. Euro 3 still presented the combined NOx + THC limit, with a 28% NOx + THC reduction. Two important aspects of the Euro 3 standard were that (i) it eliminated the 40-s engine warm-up period, resulting in the cold-start test 'New European

Driving Cycle' (NEDC); and (ii) it reintroduced a dedicated limit for NOx emissions from positive and compression ignition vehicles. To comply with Euro 3 limits, in gasoline vehicles, the TWCs were moved closer to the engine out, in the so-called close-coupled position, and their PGM loading was increased, while cooled EGR started to be widely used in Diesel vehicles.

Further reductions on the NOx emissions were introduced with Euro 4 (50% for both technologies), Euro 5 (25% reduction for positive ignition engines and 28% for compression ignition engines), and Euro 6 for Diesel vehicles (66% reduction only for compression ignition engines). The Euro 4 was introduced with Directive 2003/76/EC [141], and the Euro 5 and Euro 6 standards were introduced with Regulation 715/2007 [142] and its amendment Regulation 692/2008 [143]. They were implemented for all new passenger cars in 2006, 2011, and 2015, respectively. Euro 4 and Euro 5 vehicles met the NOx emission limits using new engine architectures and new engine strategies and controls, and by improving the exhaust treatment systems already in use (i.e., TWCs for gasoline and EGRs for Diesel). However, in order to meet the more demanding Euro 6 NOx limits, Diesel vehicles started using deNOx catalytic systems. Hence, the Euro 6b fleet comprises cars with positive ignition vehicles (gasoline, LPG (liquid petroleum gas), and CNG (compressed natural gas) cars) using TWC and Diesel cars with either LNT or SCR deNOx technologies. It should be noticed that one car manufacturer, Mazda, used no deNOx catalytic converter in their fleet to meet the Euro 6 limits. Typically, passenger light-duty vehicles with engine displacements smaller than 2.5 L would use LNT and those with a larger engine tended to use underfloor SCR.

The NOx limits required by this last regulation are those currently enforced in Europe. In summary, since the first implementation of the Euro 3 in January 2000, cold NOx emission limits have been reduced by 84% for Diesel vehicles and by 60% for gasoline passenger light-duty vehicles—from 500 to 80 mg/km for Diesel vehicles and from 150 to 60 mg/km for gasoline passenger cars. Although NOx emission limits have not been changed since 2015, in the past three years a series of improvements have been implemented in the European type-approval test procedures to make the driving cycle more representative of the conditions experienced on the road. The deNOx technologies have evolved with these procedures. The following sections will describe in more detail the latest emission procedures, namely, world harmonised light-duty test procedure (WLTP), RDE, and ISC, which constitute the basis for Euro 6d-TEMP and Euro 6d-ISC standards.

3.1.2. Worldwide Harmonised Light-Vehicles Test Procedure (WLTP)

The world harmonised light-duty test procedure (WLTP) and the real driving emissions (RDE) test procedure were introduced with Regulation (EU) 2017/1151 in September 2017 [144] in order to be more representative of the real-world operations and narrow the gap between laboratory emissions and real-world emissions. The WLTP and the corresponding worldwide harmonised light-duty vehicles test cycle (WLTC) replaced the NEDC procedure in the laboratory. It was implemented for all new passenger light-duty vehicles in September 2018. The WLTC was developed using real-world worldwide driving data and contains more dynamic and realistic driving conditions than the NEDC. These include higher maximum velocity, less idling time, and wider coverage of the engine map [145]. Other general elements introduced with the new procedure can be grouped in four categories, namely, (i) more representative road load settings; (ii) laboratory test set up and conditions, including new test procedures for hybrid electric vehicles, fuel cell vehicles, and battery electric vehicles; (iii) post-processing of the test results; and (iv) declaration of CO_2 emission results [146]. The introduction of the WLTP, together with the RDE's first, second, and third packages (see RDE, Section 3.1.3), resulted in the spread of the SCR deNOx technology in the European fleet. Some vehicles still kept using only LNT technologies to meet laboratory and on-road NOx requirements, but the use of SCR alone or combined with LNT became common practice [147].

3.1.3. Real-Driving Emissions (RDE) Test Procedure

The RDE test procedure was developed across four regulatory acts (commonly referred to as 'packages'). The first, second, and third packages, Regulation 2016/427 [148], Regulation 2016/646 [149], and Regulation 2017/1154 [150], respectively, became a mandatory part of the type-approval procedure for new passenger light-duty vehicles in September 2017. This aimed at complementing the laboratory Type 1 test (test performed using the WLTC at 23 °C) during the approval of light-duty vehicles in the EU. The RDE was implemented for all new vehicles in September 2019.

While the first package introduced on-road testing using portable emissions systems (PEMS), the second introduced the not-to-exceed limit (NTE) concept. NTEs parallel the emission limits set for the laboratory Type 1 tests (under the WLTP) multiplied by so-called conformity factors (CFs). The CFs take into account the PEMS measurement uncertainties affecting the measurement of regulated pollutant emissions, assumed to be larger than the laboratory uncertainties for the same type of measurements. The third package introduced an NTE limit and the associated conformity factor for the solid particle number (SPN) emissions during the RDE test. Finally, the fourth package, laid down in Regulation 2018/1832 [13], introduced on-road emissions testing as part of in-service conformity (ISC) checks (see 'In-Service Conformity and Market Surveillance', Section 3.2.3) and lowered the conformity factor for NOx following a critical review of experimental data [151].

The conformity factor for NOx was initially set at 2.1. In 2018, also on the basis of data collected in Market surveillance activities at the Joint Research Centre laboratories of the European Commission, it was reduced to 1.43 [151]. This conformity factor will be applicable to all new vehicles by 2021. The vehicles type-approved using this conformity factor meet the Euro 6d standard. During the RDE phasing-in period (2017–2019), a temporary conformity factor of 2.1 for NOx emissions may be applied upon request of the manufacturer. Vehicle types approved using this requirement fall under the Euro 6d-TEMP standard.

Although there are Diesel vehicles that only use LNT as deNOx technology and have been type-approved under the Euro 6d-TEMP standard, to the best of our knowledge, all Diesel vehicles type-approved as Euro 6d use SCR as the main deNOx technology. The actual implementation of the SCR technology in various types of vehicles might differ and include single SCR, SCR combined with LNT, dual SCR and SCR on filter, any of the mentioned combined with ASC, etc. Analysing the refilling requirements reported by the OEMs, it is clear that the SCR units used in these vehicles, including the single SCR case, have a higher DEF consumption than those of Euro 6b vehicles.

3.1.4. Market Surveillance and In-Service Conformity

The vehicle emission standards described in the previous sections are aimed at limiting the amount of pollutants in vehicle exhaust. All major world vehicle markets have been concerned with increasingly stringent emission standards, reducing the legally permitted amount of air pollution resulting from all types of operating motor vehicles. Sold vehicles are required to demonstrate that they comply with the applicable standard by passing a certification test, a procedure known in Europe as 'type approval' (TA). On the other hand, more detailed and comprehensive analyses have documented significant and growing discrepancies between the amount of pollutants detected in vehicle exhaust during type approval tests and the amount that the vehicle emits in 'real-world' operation on the road, during normal driving. Differences between laboratory test results and on-road performance are admissible. However, too great a gap can signify the presence of a systematic problem, such as the unanticipated but consistent failure of emission control systems, or—in the worst case—a deliberate attempt to cheat the certification tests.

Independent of the background, excessive in-use vehicle emissions imply that public health is less protected. A persistent disparity between official and real adherence to the regulatory standard can compromise public trust in both official authorities and vehicle manufacturers. In order to avoid that, it should be ensured that vehicle emissions comply

with pollutant limits throughout the vehicles' normal useful life and under normal operating conditions and on the certification test. In-use vehicle compliance checks become then indispensable elements of consistent environmental policies concerning the transportation sector.

Market surveillance (Ma. Su.) and in-service conformity (ISC) testing are two essential aspects of the above-described programme.

Market surveillance refers to independent verification testing and inspection carried out by regulatory authorities on vehicles and components available on the market, in order to determine whether they continue to comply with exhaust emissions standards. Ma. Su. authorities check whether products made available on the market are manufactured according to the current law. In the U.S., this programme is referred to as in-use surveillance testing/in-use confirmatory testing or in-use surveillance [152]. For purposes of market surveillance, regulators should not be bound only to repeat the test procedure used for type approval but could put a vehicle through other tests not specified in advance, either in the laboratory (e.g., running the vehicle over alternate driving cycles) or on the road. Ma. Su. testing is particularly useful in identifying 'suspicious' vehicle families, which may emit more pollutants when in actual use than recorded upon type approval or in standard test procedures. Suspicious vehicle families can then undergo more accurate in-use testing, which is the object of ISC campaigns.

ISC testing refers to testing carried out by manufacturers on in-use vehicles and components, with the help of designated technical services or accredited laboratories, to verify compliance to type-approval procedures throughout a vehicle's lifetime. In the United States, this is referred to as an 'in-use verification programme/in-use confirmatory programme', or sometimes 'in-use test'. The ISC testing for light-duty vehicles (LDVs) essentially cross-checks the tailpipe exhaust emission tests conducted during type approval with the vehicle running on a chassis dynamometer in an emissions-testing laboratory, according to the aforementioned globally harmonised procedure (WLTP).

Since 2017, the European Commission (EC) has planned a vehicle compliance check programme requiring both Ma. Su. and ISC testing of LDVs in operation on the road, incorporating real-driving emissions (RDEs) testing with portable emissions measurement systems (PEMSs).

For heavy-duty vehicles (HDVs), on-road ISC testing using PEMS became mandatory with the introduction of the Euro VI standard in 2013/2014.

In the EU, some member states, including Germany, the Netherlands, Sweden, and the United Kingdom, have monitored in-use vehicle compliance through testing. Moreover, in the aftermath of the 'Dieselgate' scandal, a number of EU member states, including France, Germany, and the United Kingdom, have initiated or reinitiated market surveillance testing programmes. Since 2016, the European Commission proposed a new motor vehicle type-approval framework, bringing along fundamental and far-reaching changes to the earlier Framework Directive (Directive 2007/46/EC). The new EC Regulation 1151 approved in 2017 [144] established four essential novelties with respect to the existing framework. First, the proposed framework required EU member states to perform market surveillance testing of vehicles, whereby the EC retained the authority to determine the scale, scope, and frequency of the market surveillance testing that member states were required to perform. Second, the new regulation granted EU member states the authority to take measures against non-compliant vehicles sold in their own markets. Third, an EU-wide advisory body was created, called the 'Market Surveillance Forum'. This body aims at promoting cooperation among national regulatory authorities appointed by the EU member states with regard to market surveillance. Fourth, the proposed framework would require the EU member states to establish a national fee levied on the manufacturers that would cover the costs of market surveillance activities.

The EU type-approval framework has been updated in the last couple of years in order to establish a sound Ma. Su. and ISC programme also at the institutional level. The new type-approval Framework Regulation 2018/858 [153] and the new In-Service Conformity

Regulation 2018/1832 [13] introduce a European oversight on the vehicle type approval and in-service conformity processes with specific roles for the EC. In particular, the EC will have to carry out market checks independently of Member States. The Joint Research Centre (JRC) is the EC's service that carries out the compliance verification foreseen in Article 9 of Regulation 2018/858, with its official mandate starting in September 2020. Regulation 2018/1832 prescribes that Granting Type Approval Authorities (GTAAs) cooperate with the EC and designated technical services to ensure effective ISC testing aimed at the emission standard compliance assessment for entire vehicle families. These tests shall be carried out on in-use vehicles, with a mileage between 15,000 km and 100,000 km and between six months and five years old. Vehicle manufacturers are also supposed to co-operate with testing campaigns by providing relevant information in due time whenever required.

A concise review of the political approaches currently adopted in other countries worldwide was recently published by Joshi. [9] In the United States, in-use tests are performed by Environmental Protection Agency (EPA) on circulating vehicles for several years already [154,155]. No relevant changes are being currently applied to the present system.

In China, inspection/maintenance (I/M) programmes for in-use vehicle emission control have a longer history than the new vehicle emission standards [156]. The 6a light-duty standard is being phased in across China, while key areas are implementing 6b. Details of RDE are currently being worked out. It is expected that there will be further tightening of gas emissions, and common elements with post-Euro 6 regulations, such as the inclusion of sub-23 nm particles.

In India, RDE test boundary conditions have been aligned to the general European framework, with some key changes made to better represent local driving conditions.

Other regions are expected to begin improving fuel quality and moving to tighter regulations in the coming years. The ASEAN (Association of Southeast Asian Nations) region, and Thailand in particular, is poised for these changes. Current regulations in Thailand are at the Euro 4 level, and the country aims to achieve 10 ppm S fuel by 2023 with a feasibility study to move to a Euro 6 standard in the coming years [157].

3.1.5. Post-Euro 6

Figure 2 summarises the changes faced by the ATS applications and architectures for Diesel and gasoline, along with the introduction of more stringent limits required with the different Euro standards discussed in the previous section. The figure also shows some of the systems that experts from the emission control field suggest may be used by post-Euro 6 Diesel and gasoline passenger light-duty vehicles. As illustrated, SCR will be an important component of the ATS in Diesel vehicles, and it could potentially be introduced also for some gasoline applications, showing the importance of this technology in the years to come.

Indeed, some common trends could be identified, namely, (i) close coupling of the catalytic units in order to speed up their warm-up; (ii) the necessity for some active heating strategies in order to dose DEF at an early stage or to accelerate TWC light-off (see Section 2.4.2, 'Active Heating Strategies'); and (iii) the introduction of multiple DEF dosing points to increase overall deNOx performance and ensure additional flexibility in the control of the system.
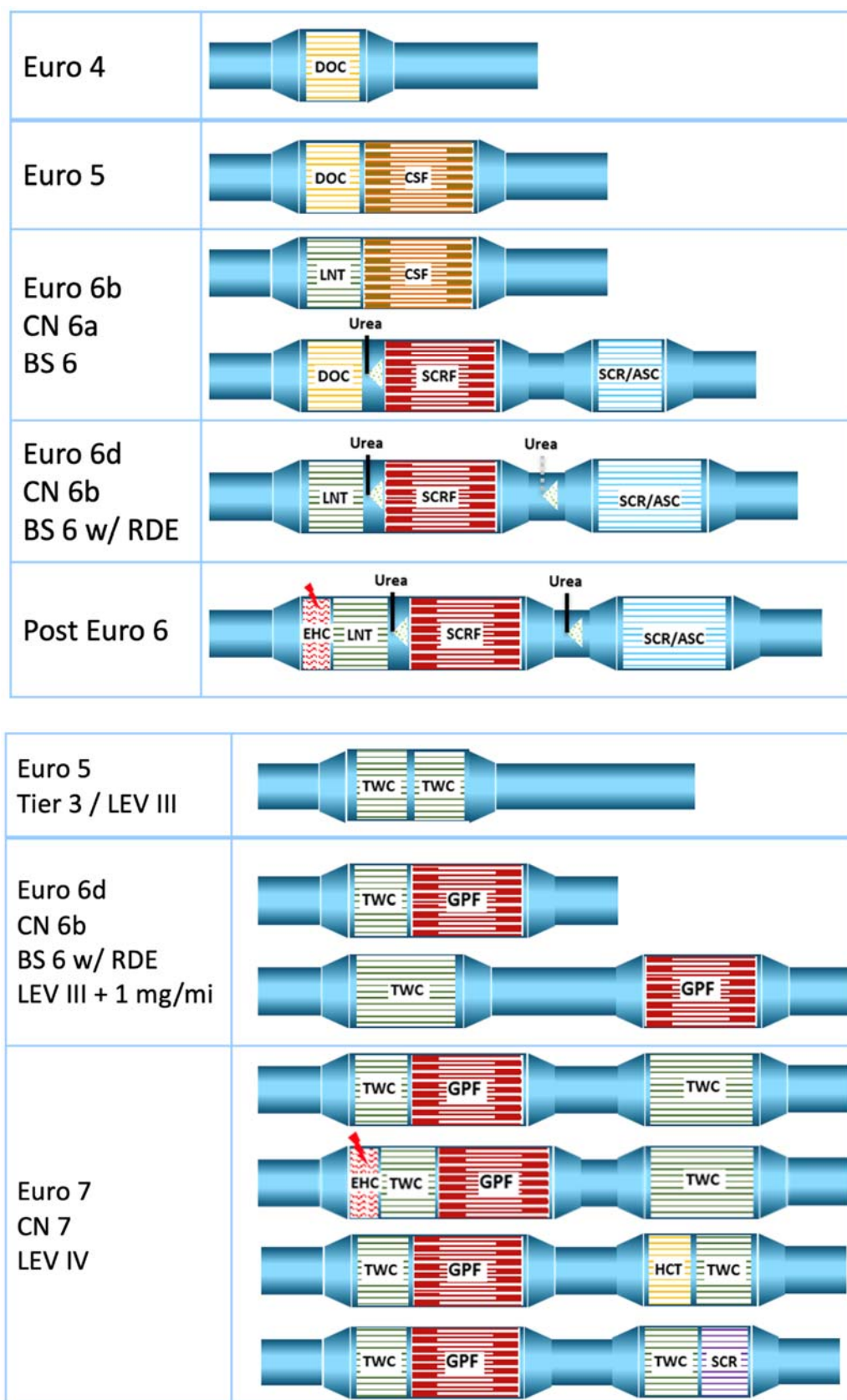
Figure 2. Evolution and newly proposed aftertreatment system (ATS) configurations for Diesel (**top panels**) and gasoline (**bottom panels**) LDVs.

3.2. Heavy Duty

Unlike LDVs, heavy-duty (HD) emissions standards are based on engine performance rather than vehicle performance. For this reason, the emission limits were defined in terms of mass per work performed over a duty cycle (g/kWh) rather than mass per distance travelled (g/km). The reason why the regulation focused on engines instead of vehicles was that the same HD engine could be used in very different applications (lorries, coaches, garbage collectors, etc.). Furthermore, even within the same application very different vehicle architectures could be used for the HD same engine. Testing all possible configurations at type-approval would have resulted in burdensome, expensive, and potentially inefficient policies.

3.2.1. Emission Standards (Euro I to Euro VI-E)

The Emissions Directive 88/77/EEC [158] was the first emission policy introduced for heavy-duty engines in Europe. The Euro I standards for heavy-duty engines introduced in 1992 (implemented for all vehicles in 1993) was followed by a series of amendments (Directive 91/542/EEC [159] and Directive 96/1/EEC [160]) that, in 1996, resulted in the implementation of the Euro II standard. The NOx emission limit was reduced by 37.5% with the introduction for all registered vehicles of the Euro III standard in 2000 (Directive 1999/96/EC [161]). However, it is not until the implementation of the Euro IV in 2005 (October 2006 for registered vehicles), with Directive 2005/55/EC [162], that heavy-duty Diesel engines started using SCR and/or EGR systems to comply with the further 30% reduction of the NOx limits. In 2008, the Euro V entered into force with Directive 2008/74/EC [163] (implemented for all registered vehicles in 2009) with a 42.9% NOx reduction (from 3.5 g/kWh to 2.0 g/kWh). In order to meet the more stringent NOx limit the use of SCR systems, in some cases in combination with EGR, became common for Euro V HD Diesel engines.

Euro VI emission standard was introduced by Regulation 595/2009 [14] and the implementing regulation EC/582/2011 [164]. The Euro VI introduced in 2012 the world harmonised transient cycle (WHTC) and the world harmonised stationary cycle (WHSC), implemented for all registered vehicles from December 2013. It implied a further reduction on NOx limits—400 mg/kWh for the compression ignition engines over the WHSC and 460 mg/kWh for the compression ignition engines over the WHTC and for the positive ignition engines over the WHSC. It also introduced the off-cycle in-use emission test using PEMS at type approval and the in-service conformity (ISC) tests to be performed on the road using PEMS (see 'Test Cycles and Procedures', Section 3.2.2) and a limit for particle number while keeping the limit for the mass of particle matter.

The NOx limits required by Regulation 595/2009 [14] are those currently enforced in Europe (Figure 3). Although NOx emission limits have not been changed, a series of improvements have been implemented in six steps, the last step being the Euro VI-E enforced for new vehicle types since September 2020. These steps have fine-tuned the measurement procedures and boundary conditions both at type-approval and in-service conformity tests. The changes in the procedures have often been accompanied by improvements in deNOx technologies. It should be noted that while positive ignition engines rely on TWC to meet the Euro VI-A to VI-E emission standards, compression ignition engines use different SCR systems.
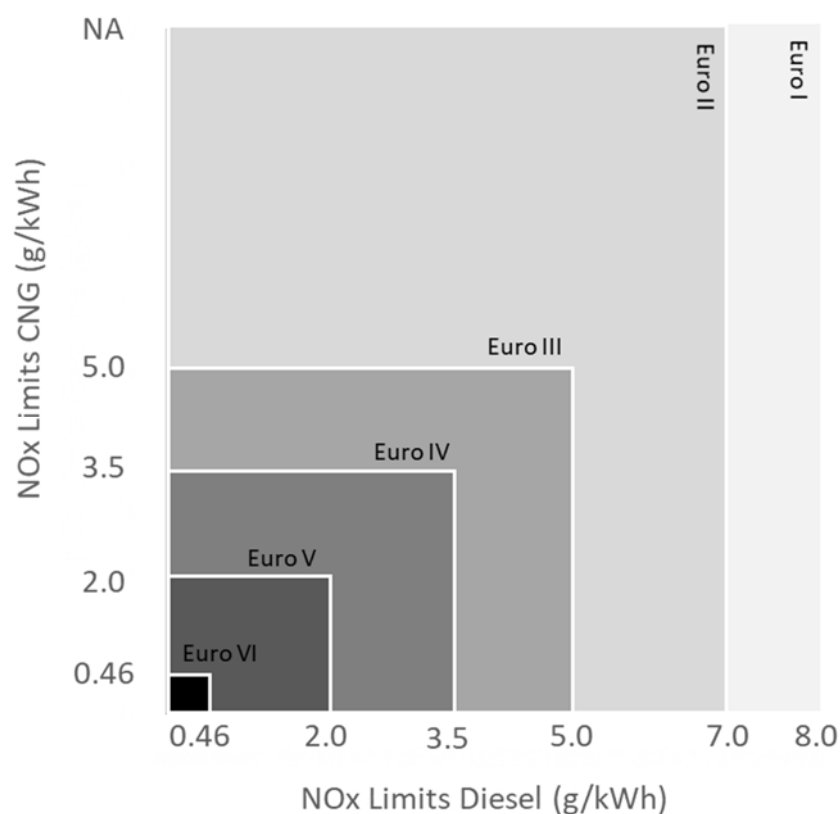
Figure 3. Evolution of NOx emissions limits enforced by EU regulation for CNG and Diesel heavy-duty vehicles (HDVs).

3.2.2. Test Cycles and Procedures

The European type-approval procedure of motor vehicles and engines with respect to emissions from heavy-duty vehicles (Euro VI) establishes a series of common technical requirements. It also sets provisions on the obligations the vehicle manufacturers have to respect when they sell or put into service their engines in the EU market. It can be argued that the most notable obligation for manufacturers may be that the technical solutions provided shall be such as 'to ensure that the tailpipe emissions are effectively limited . . . throughout the normal life of the vehicles under normal conditions of use.' [14]

In particular, in order to receive an EC type-approval, HD engines are subject to exhaust emission tests. The emissions of gaseous and particulate pollutants are determined using the WHTC and/or the WHSC test cycles. HD engines are also tested for off-cycle emissions (OCEs) and in-use emission tests (using PEMS) at type approval. The OCE and PEMS tests at type approval ensure effective control of emissions under a broad range of engine and ambient operating conditions encountered during normal in-use vehicle operation. Vehicles are successively tested under the ISC procedure, in order to ensure that the tailpipe emissions are effectively limited throughout their normal life under ordinary conditions of use. These tests are performed on-road using PEMS, in order to avoid removing the engine from the vehicle.

In contrast to compression ignition engines, which are tested with both WHTC and WHSC cycles, positive ignition engines are tested using only WHSC. The two cycles have been developed using average worldwide driving conditions. The WHTC is a transient engine dynamometer cycle. It requires the engine to be tested on the cycle under cold and hot start conditions. To calculate the engine's emission factor, the emissions obtained in the cold and hot tests are weighted as 0.14 and 0.86 fractions, respectively.

The WHSC is a hot start steady-state test cycle. The test follows a sequence of steady-state engine modes with a defined speed and torque criteria at each mode and well-defined ramps between each mode.

Both OCE and ISC tests require the measurement of NOx, THC (NMHC and CH_4 in the case of positive ignition engines), CO, and PN. A world-harmonised not-to-exceed control area and a corresponding world-harmonised not-to-exceed limits (WNTE) for gaseous and particulate exhaust emissions are defined for OCE tests. The WNTE is the sum of the WHTC limit and a WNTE component that varies for each compound that is measured (detailed information can be found in paragraph 5.2 to the Annex 10 of the UNECE (Economic Commission for Europe of the United Nations) Regulation N°49 [165]). The WNTEs are applied in randomly defined test points distributed across a WNTE control area (see paragraphs 7.1.1 through 7.1.6. of the same annex and regulation).

3.2.3. In-Service Conformity and Market Surveillance

Not-to-exceed in-use compliance standards were coined by the USA Environmental Protection Agency (EPA) in the period 2001–2003 as a result of the consent decree between the EPA and several major Diesel engine manufacturers. This stimulated the development of portable emission measurements (PEMSs) equipment. Europe followed suit by launching the EU-PEMS project in 2004 to study the feasibility of PEMS to check the conformity of heavy-duty engines. The study was followed by a pilot programme involving heavy-duty engine manufacturers, the European Commission, and national authorities in the period 2007–2008 to explore appropriate procedures. PEMSs were used for checking the conformity of in-use engines with the regulatory emission levels. The outcome of this pilot programme was the publication of the PEMS-based in-service conformity (ISC) provisions for the future EURO VI standards (also applicable for EURO V engines) in 2010 [166].

The HD ISC procedure aims at checking and demonstrating the conformity of in-service engines and vehicles with the applicable emissions limits without the need of extracting the engine from the vehicle to undergo regulatory tests at the test bench. Much similar to the case of light-duty vehicles, the HD ISC procedure includes conformity factors that take into account the larger PEMS uncertainties compared to laboratory measurement uncertainties. CF for gaseous pollutants is 1.5; from Euro VI-E engines on the PN CF is 1.63. The emission evaluation is performed by applying the moving averaging window (MAW) principle. This approach uses the reference CO_2 mass or work measured over the WHTC at engine type-approval to calculate defined sub-sets of the complete data set (the so-called moving averaging windows). Emission factors are calculated for each of the regulated pollutants in each window and consequently, the conformity factor (CF) of the window is defined as the ratio of the emission factor of the window to the regulatory limit for the pollutant in question.

A not-to-exceed (NTE) conformity factor that takes into account the measurement uncertainty of the PEMS equipment as compared with laboratory standard analytical instruments is prescribed. An engine/vehicle is conforming if the CF at the 90th cumulative percentile of all the valid windows is below or equal to the NTE CF. The NTE CF is 1.5 for gaseous pollutants and 1.63 for particle number (PN) in Euro VI-E engines.

The procedure includes a series of boundary conditions to be fulfilled during the PEMS test, including vehicle payload, ambient conditions, engine coolant temperature, and the specifications for the lubricating oil, fuel, and reagent. It also prescribes the trip and operational requirements, in addition to the availability and conformity of the ECU data stream information which is required for ISC testing.

Through the implementation of the different Euro VI steps, some of the requirements of the ISC procedure have been changed. Hence, for Euro VI-C vehicles or earlier, windows with an average power of 20% or less of the maximum engine power were excluded (i.e., considered as invalid windows). This power threshold was modified to 10% from Euro VI-D vehicles onwards to include low-power operations. These are normally related to urban operations of vehicles, thus expanding the fraction of the engine map assessed by the test. Moreover, until Euro VI-D the ISC of HDVs was carried out using a 50–60% payload, while Euro VI-D and VI-E HDVs can be tested with any payload between 10% and 100%. Finally, the ISC of Euro VI-D and Euro VI-E HDVs requires the engine coolant temperature

to be below 30 °C when the test starts, whereas Euro VI-E includes cold-start emissions in the data evaluation, and also PN emissions, further increasing the representativeness of the procedure.

3.2.4. Post-Euro VI

Figure 4 shows some of the most common ATS applications and architectures used by HD Diesel vehicles since the introduction of the Euro IV standard. As in the case of the LDVs, the ATSs have increased in number and complexity to be able to meet the more stringent limits required with the different Euro standards discussed in the previous section. The figure also illustrates two examples of ATSs that could potentially be used by post-Euro VI Diesel HD applications. Once again, the experts indicate that SCR may be an important component also for the ATS in Diesel vehicles in the near future to cover both cold-start and running emissions. The former can be covered by using the close coupling of the catalytic units in order to speed up their warm-up, later by using a second SCR unit, with the possibility to use it on filter. This approach will also see the introduction of multiple DEF dosing points to increase overall deNOx performance and ensure additional flexibility in the control of the system. More detailed information is presented in Section 2.4.1, 'Advanced Configurations'.
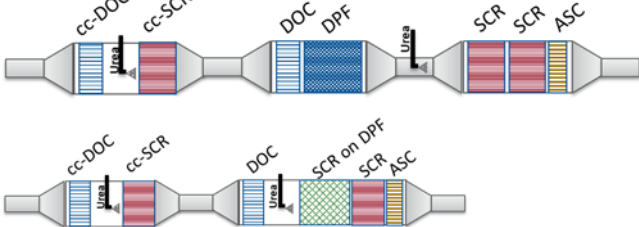
Regulation	After-treatment System
Euro IV **Euro V**	
Euro VI	
Post Euro VI (example configurations)	

Figure 4. Evolution and newly proposed ATS configurations for Diesel HDV.

4. Results and Effects of Regulation Adoption

4.1. NOx Emission Trends

The previous sections summarise how the NOx emission standards have changed over the years in Europe. This evolution has led to a reduction of the emission limits and more comprehensive and robust testing procedures.

Figure 5 presents data measured at the Joint Research Centre of the European Commission on laboratory and on-road tests for NOx emissions from Euro 4 to Euro 6d-TEMP vehicles. The appropriate regulatory procedures were used for the tests performed in the laboratory according to the emission standard step, i.e., the NEDC was used for vehicles up to Euro 6b and the WLTP for Euro 6d-TEMP vehicles. Details of the on-road tests can be found in the literature [167–170]. The tested gasoline vehicles resulted in low NOx emission factors already in the Euro 4 standard step. Since then, their NOx emissions have not shown any particular trend. This is true for both the laboratory and the on-road tests

performed with these vehicles. The vehicles tested reached such NOx emissions levels by a combination of engine calibration strategies and the use of TWC.

In the case of Diesel vehicles, there is a clear trend towards lower NOx emissions with the tightening of the NOx standards. For Euro 4 to Euro 6b (pre-RDE and WLTP), the decreasing trend is more pronounced for laboratory tests. As widely discussed in the literature [169] NOx emission factors from Diesel vehicles up to Euro 6b are higher during on-road tests than during laboratory tests. This has often been explained by the activation of the EGR system, employed to control NOx emissions in the tests performed in the laboratory and not during on-road investigations. While a limited NOx reduction was observed from Euro 4 to Euro 5, on-road NOx emissions were substantially reduced from Euro 5 to Euro 6b. This reduction was possible by using LNT or SCR systems. Still, NOx emissions from Diesel vehicles were on average high when compared to gasoline vehicles. With the introduction of the WLTP and the RDE regulations, which for the first time included on-road NTE limits (see Section 3.1.3, 'Real-Driving Emissions (RDE) Test Procedure'), the use of SCR became almost ubiquitous. Some of the deNOx after-treatment architectures include SCR, LNT + SCR, dual-SCR, and SCR on filter. The implementation of these systems has led to low NOx emissions from Diesel vehicles, reaching levels that are comparable, and in some cases even lower, than those measured from gasoline vehicles.
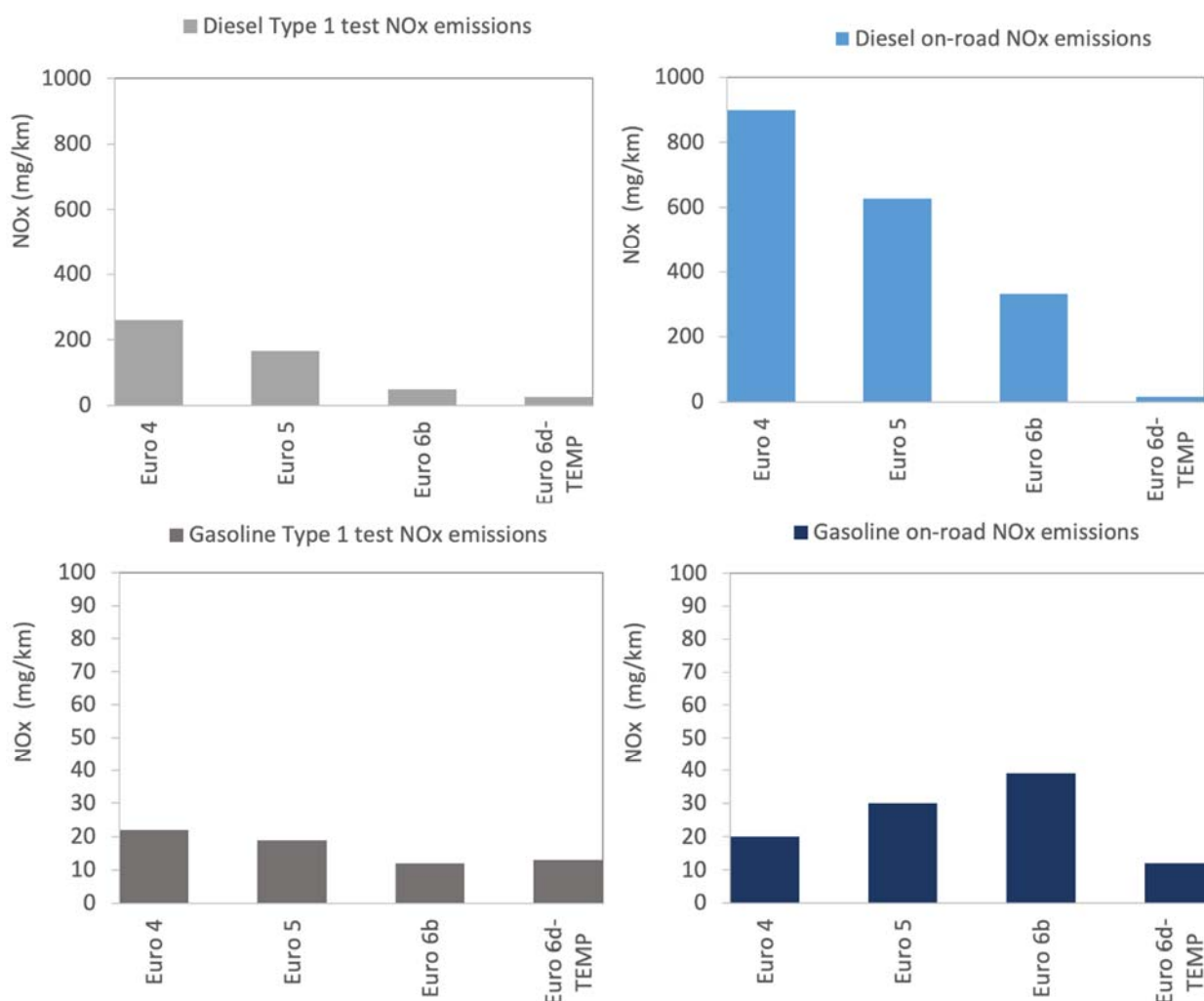

Figure 5. NOx emission factors from Diesel (**top panels**) and gasoline (**bottom panels**) light-duty vehicles tested over the Type 1 test (**left panels**) and on the road (**right panels**). Note that y-axes for gasoline vehicles are one order of magnitude lower than that of Diesel vehicles.

Figure 6 summarises the trend on NOx emissions from Diesel HDVs starting from Euro IV to Euro VI-C stage. Experimental data for all these vehicle categories are very scarce in the literature. Here, we present average NOx emissions factors for vehicles from different emission standards tested on the road during ISC-like (Euro IV and Euro V vehicles) and ISC tests (Euro VI vehicles) [166,171]. The figure clearly illustrates that NOx emissions from Diesel HDVs have substantially decreased following the introduction of new emissions standards. Moreover, the gap between the NOx emissions from the engine and from the vehicle with respect to the emissions limits has been drastically reduced with the introduction of the Euro VI standard. In fact, the figure shows that a substantial reduction in NOx emissions was achieved after the introduction of the Euro VI standard, which requires vehicle testing and ISC (see 'Heavy-Duty' in Section 3). For what regards the deNOx ATS, the Euro VI standard saw the introduction of a generation of SCR systems that, compared to those used in Euro V vehicles, are able to better control some critical elements such as the NOx control loop with more efficient DEF dosing and better thermal management.
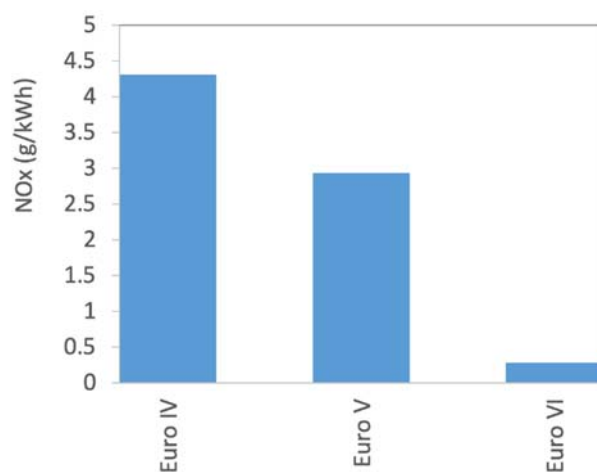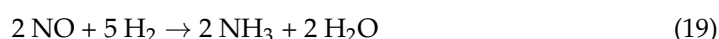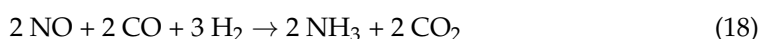

Figure 6. Evolution of NOx emission factors from Diesel heavy-duty vehicles.

4.2. Trends in the Chemical Composition of Vehicles' Exhaust
N_2O and NH_3

Following the introduction of the catalysed aftertreatment systems, and some changes in the engine operating strategies, a series of compounds have appeared in the vehicles' exhaust. These include NH_3, N_2O, and nitrates.

NH_3 emissions from spark-ignition vehicles are mainly linked to two-reaction mechanisms that take place on the TWC after the catalyst light-off and during engine rich-operation, namely, the water–gas shift reaction between CO and water (Equation (17)) [172,173], and the reaction of NO and H_2 (Equations (18) and (19)) [174] as follows:

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (17)$$

$$2\,NO + 2\,CO + 3\,H_2 \rightarrow 2\,NH_3 + 2\,CO_2 \qquad (18)$$

$$2\,NO + 5\,H_2 \rightarrow 2\,NH_3 + 2\,H_2O \qquad (19)$$

NH_3 emission factors reported in our previous studies for Euro 4 and Euro 5 vehicles, tested over the NEDC and Euro 6 vehicles over the WLTC and measured using FTIR [8,175–177], show a rising trend of these emissions going from Euro 4 to Euro 6b gasoline vehicles. More recently, a decrease of NH_3 on Euro 6d-TEMP vehicles has been observed in JRC experiments. It should be noted that tested Euro 6d-TEMP vehicles presented substantially lower mileage than the vehicles from previous standards, and high NH_3 emissions have been linked to high vehicle mileage in gasoline vehicles [178].

In the case of Diesel vehicles, NH_3 emissions are related to the use of SCR and LNT deNOx systems. In fact, as illustrated in Figure 7, NH_3 only appears in Diesel vehicles' exhaust at the Euro 6 stage, when LNT and SCR systems were introduced [176,177]. In contrast to the formation of NH_3 in the LNT, which follows a similar path to that of the TWC, NH_3 emissions from vehicles equipped with SCR take place flowing the processes described above. Average NH_3 emissions from Diesel vehicles have decreased from Euro 6b to Euro 6d-TEMP. The lower NH_3 emissions from the Euro 6d-TEMP are explained by the introduction of ASC systems, which were not commonly used in Euro 6b vehicles.

Even though the introduction of ASC catalysts has led to the reduction of NH_3 emissions, the use of these systems has also caused an increase in N_2O emissions [8]. As illustrated in Figure 7, N_2O emissions appear in the Diesel exhaust of Euro 5 vehicles. It first appeared as a by-product of the DOC which intended to increase the NO_2 fraction in the exhaust to promote passive regeneration of the DPF. Later, with the introduction of LNT and SCR, the emissions of this molecule would further increase. In the first case, because N_2O is formed during the rich regeneration of the catalyst. In the second, due to the increasingly intensive use of the DOC, aimed at reaching a 1:1 NO_2 to NO ratio that would improve the deNOx activity on the SCR. As described in Section 2.1, 'Basic Principles', N_2O is also formed as a by-product of the SCR. Finally, the introduction of the latest catalyst, the ASC, will further contribute to the formation of N_2O via unselective oxidation of unreacted NH_3.

N_2O is also produced during the TWC light-off. However, the thermal window for the formation of this molecule is more limited, and for that reason, N_2O emissions from gasoline vehicles are relatively low, as shown in Figure 7. Our experimental data show no particular trend for the N_2O emissions from gasoline vehicles.
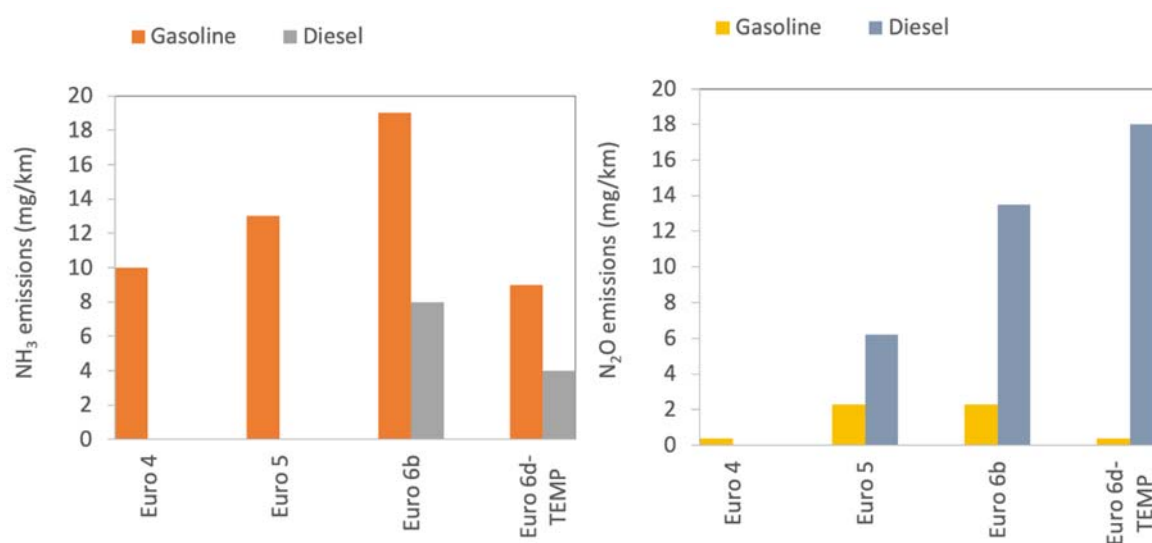

Figure 7. Emission factors of NH_3 (**left panel**) and N_2O (**right panel**) from Diesel and gasoline light-duty vehicles.

Similar to the situation of light-duty vehicles, NH_3 emissions appeared in Diesel heavy-duty vehicles' exhaust with the introduction of the SCR system (Figure 8). Our experimental data show that only SCR-equipped Diesel HDVs presented NH_3 emissions during ETC (European Transient Cycle) and ISC tests performed on a chassis-dynamometer. Our data show that with the introduction of the Euro VI standard, which included a 10 ppm limit for NH_3 emissions, these decreased. The reduction of NH_3 emissions was achieved using ASC catalysts, which in turn led to higher N_2O emissions compared to previous Euro standards in which this system was not commonly used (Figure 8). The N_2O emissions from HDVs followed the same trend as the light-duty Diesel vehicles, i.e., (i) negligible N_2O emissions until the introduction of DPF and consequently intensive use of DOC; (ii)

increase of N_2O emissions following the introduction of SCR; and (iii) further increase following the introduction of ASC systems.
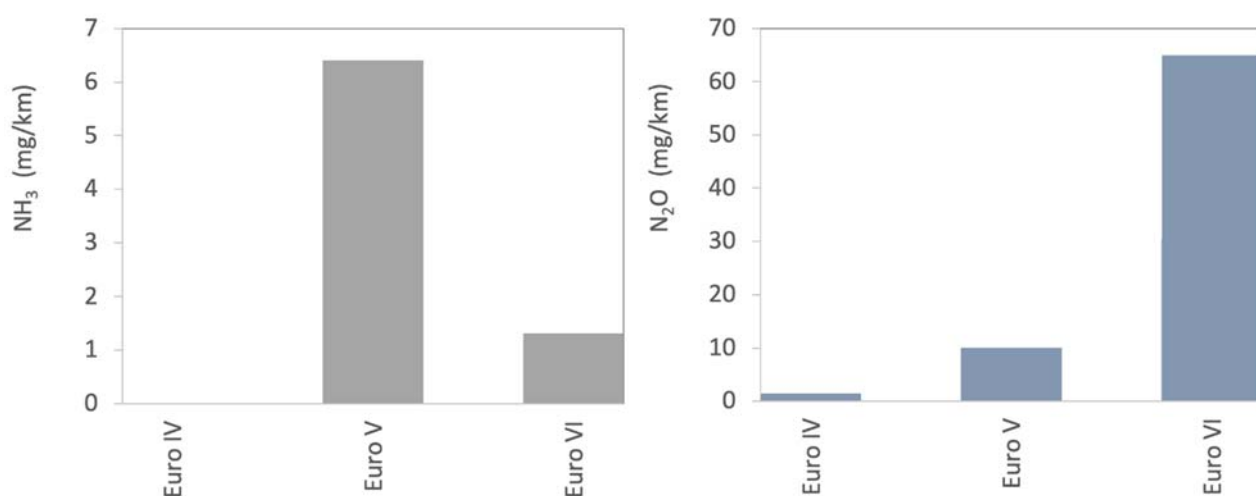

Figure 8. Emission factors of NH_3 (**left panel**) and N_2O (**right panel**) from Diesel heavy-duty vehicles.

5. Summary and Final Remarks

The Euro vehicle emissions standards have seen a long evolution (Euro 1 to Euro 6d for LDVs and Euro I to Euro VI-E for HDV) since their first implementations in the early 1990s. As summarised in the dedicated sections, over these years, the NOx emissions limits have been substantially decreased for both LDVs and HDVs from 0.97 gNOx + THC/km to 0.08–0.06 gNOx/km and from 8 gNOx/kWh to 0.46 gNOx/kWh, respectively. A similar trend has been observed for other regulated pollutant emissions. These reductions were accompanied by improved and more representative procedures to assess the emission performance of vehicles, ensuring that tailpipe emissions are effectively limited throughout the actual use and normal life of the vehicles. Diesel vehicles were able to meet the first series of requirements (Euro 1 to Euro 5 and Euro I to Euro IV) by means of engine calibration and the use of techniques such as EGR. However, with the more demanding requirements of the latest regulations, vehicle manufacturers have equipped their Diesel products, both LD and HD, with increasingly more complex and sophisticated ATS that, in the most recent models, always include SCR deNOx systems. On the other hand, the use of these systems has generated growing concerns for the emissions of previously irrelevant pollutants such as N_2O and NH_3, two compounds until now not regulated for LDVs, whereas NH_3 was regulated for HDVs only.

A general assessment has started in view of the implementation of the next European emission standard. It appears that the SCR technology will clearly play an important role in reducing NOx emissions in particular in lean-burn vehicles. While the research on this field continues, some common trends could be identified for near-future applications, namely, (i) close-coupling of the catalytic units in order to speed up their warm-up; (ii) need for some active heating strategies in order to dose DEF at an early stage or to accelerate TWC light-off; and (iii) introduction of multiple DEF dosing points to increase overall deNOx performance and ensure additional flexibility in the system control. More than ever, this growing complexity must be adequately supported by advances in system modelling and control strategies, while the scientific community continues to push the boundaries towards the improvement of catalytic materials and supports.

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