

Control-Oriented Modeling of a LNT-SCR Diesel After-Treatment Architecture

2011-01-1307

Published
04/12/2011

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doi:10.4271/2011-01-1307

ABSTRACT

Lean NO_x trap (LNT) and Selective Catalytic Reduction catalysts (SCR) are two leading candidates for Diesel NO_x after-treatment. Each technology exhibits good properties to reduce efficiently Diesel NO_x emissions in order to match the forthcoming EURO 6 standards.

NO_x reduction in LNT is made through a two-step process. In normal (lean) mode, Diesel engine exhausts NO_x is stored into the NO_x trap; then when necessary the engine runs rich during limited time to treat the stored NO_x. This operating mode has the benefit of using onboard fuel as NO_x reducer. But NO_x trap solution is restrained by limited active temperature windows. On the other hand, NH₃-SCR catalysts operate in a wider range of temperature and do not contain precious metals. However, NH₃-SCR systems traditionally use urea-water solution as reducing agent, requiring thus additional infrastructure to supply the vehicles with enough reducer. These pros and cons are quite restrictive in classical LNT or NH₃-SCR architecture.

The present paper presents an after-treatment architecture combining a NO_x trap and a passive NH₃-SCR. Synergy of the two systems is possible if the SCR takes advantage of the LNT ability to produce Ammonia (NH₃). Indeed, during the rich phases (purges), small amounts of Ammonia are formed as by-product, which can be used in the downstream catalyst as the NO_x reducing agent.

A major difficulty to operate the proposed architecture is the real-time management of the NO_x purge: for future control

and diagnosis applications, it is crucial to have accurate but low-complexity models. A complete reduced model of the physicochemical phenomena involved is proposed in the present paper. Based on simplified chemical assumptions and time scale separation, the latter is suitable for on-board diagnostics and model-based control. Validation has been achieved through extensive experiments.

INTRODUCTION

After-treatment systems using various catalyst systems have been used in vehicles to convert carbon monoxide, hydrocarbons and nitrogen oxides produced during engine operations into non-polluting gases, namely, water, nitrogen and carbon dioxide. Because of the stricter fuel economy and emissions standards (Figure 1), it becomes increasingly desirable to work under lean condition, in spite of a growing difficulty to treat the NO_x. Moreover, automotive technologies are tremendously changing, becoming more restrictive. Thus, NO_x reduction in a wide range of conditions is becoming a true challenge.

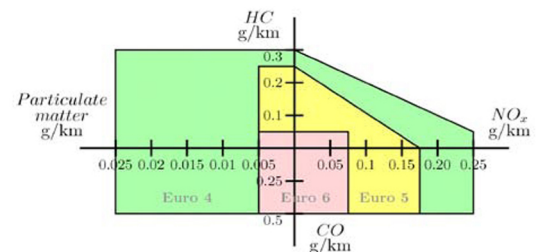


Figure 1. Evolution of the Euro standards for Diesel engine vehicles

LNT and SCR catalyst have proven to be the technologies the more competitive concerning NOx control in diesel exhaust emissions. There is a large amount of papers on chemical principles and experimental studies of hybrid catalytic systems composed of LNT and SCR (see for example [1],[2],[3],[4]). Fewer papers are on modeling and unfortunately, the available models are either incomplete or too complex for control applications.

In the LNT-SCR architecture of this study, formation of ammonia during the rich phases is considered. The ammonia formed is used over the downstream SCR catalyst to further reduce the NOx emissions through the selective reduction property. The LNT-SCR architecture improves the performance over traditional LNT systems with a good NOx and NH₃ control. Indeed this strategy permits to reduce both NOx and NH₃ at the same time. Furthermore, potential cost reduction can be obtained by elimination of the onboard urea storage and delivery system or reduction of the size of the LNT which contains precious metals. The SCR also serves as a smell filter for the H₂S emissions during regeneration periods, avoiding the need for H₂S trap.

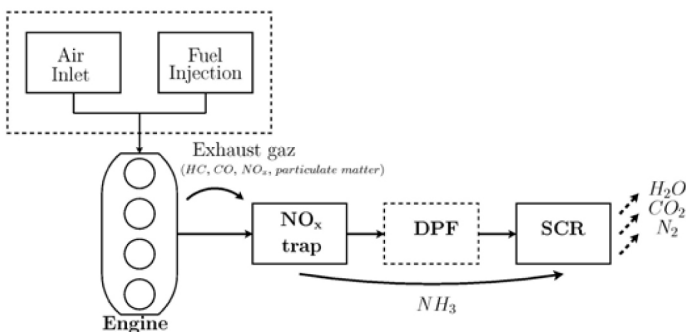


Figure 2. Principle of a combined exhaust gas after-treatment system consisting of NOx storage reduction catalyst (LNT) and selective catalytic reduction of NOx by NH₃ (SCR)

This paper describes, in a first part, a NOx after-treatment system (Figure 2) for diesel engines including (from upstream to downstream): a lean NOx trap, a Diesel Particulate Filter (DPF) to treat the particulate matter, and a SCR catalyst. In the following, the passive regeneration of the DPF ([5], [6]) is neglected. Moreover, the temperature of the inlet and outlet gas of each catalyst being measured, it is possible to take into account the thermal capacitance induced by the DPF is taken in account through the kinetic terms of the SCR, obtained from calibration. Another solution would be to give a simplified thermal model representing this effect of the DPF. So, in our modeling, only the LNT-SCR architecture as the two after-treatment subsystems in series is considered (see Figure 3).

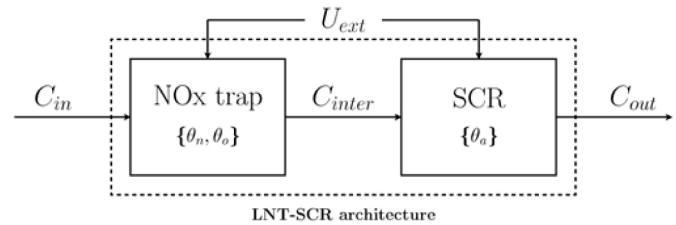


Figure 3. Scheme of the studied architecture. The subscripts “in”, “inter” and “out” refers respectively to the LNT catalyst input, the LNT output/SCR input and the SCR output; U_{ext} corresponds to the exogenous inputs, namely the inlet gas temperature and the exhaust speed.

Models of LNT and SCR have been developed independently, based on global reaction kinetics. Focus is put on model reduction for the whole system, one of the valuable features of this study. Model reduction is a need for real-time automotive applications in order to reduce the computational burden. The reduction process proposed here consists in time scale separation between the dynamics of the various state components, and use of Perturbation theory. Finally, the main model proposed herein is a system of two coupled scalar ODEs, see (32).

The model was calibrated according to experimental data obtained with catalyst samples, and validated on a standard driving cycle data, namely, the New European Driving Cycle (NEDC).

In a last stage, a single LNT model and our LNT-SCR model have been simulated separately on an ARTEMIS cycle (Assessment and Reliability of Transport Emission Models and Inventory Systems) to evaluate qualitatively the gain of the architecture as far as NOx reduction is concerned and highlight the interest of such a combination, comparatively to classical LNT architectures. The model (32) is able to reproduce with quite good accuracy the experimental behavior.

OPERATION OF A NOx TRAP

Many studies have been completed to identify and model chemical mechanisms and kinetics of NOx trap catalysts during both lean and rich operation ([7], [8], [9]). However, until now, most of the mechanisms described do not include the formation of ammonia during rich phases. Recently, ammonia formation in Lean NOx trap catalyst has gained more attention ([10], [11], [12]).

In the context of the present paper, a simplified description of the NOx trap will be considered. The NOx trap is essentially a three-way catalyst with additive metals to increase its capacity to store NOx under lean conditions. The range of temperature wherein LNT is able to provide good NOx

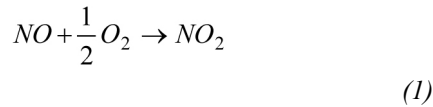
control, known as the “temperature window”, depends on many parameters but is generally situated between 250°C and 450°C. So, in spite of a good efficiency at this range of temperature, it is difficult to maintain high NOx conversion below 250°C and particularly with aged catalyst.

Lean NOx trap need to be operated in two operation conditions: *storage* and *regeneration*, which is now presented.

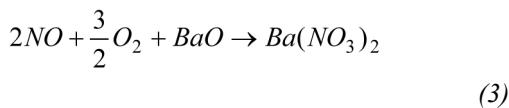
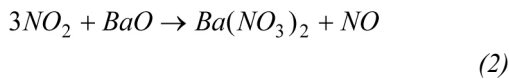
STORAGE

During the lean (or loading) mode, NOx is stored on the catalyst in form of nitrate through a two-step process. Firstly, NO is oxidized on Pt sites to form NO₂ and then adsorbed on metal (Barium) oxide sites. The mechanism is described by the following equations:

Oxidation of NO to NO₂

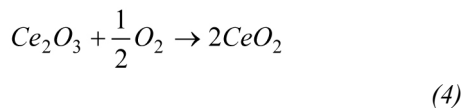


NO and NO₂ Storage During the Lean Time



Adding of Cerium Oxides onto the catalyst gives the catalyst the ability to store Oxygen, and this is taken into account in this process:

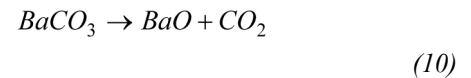
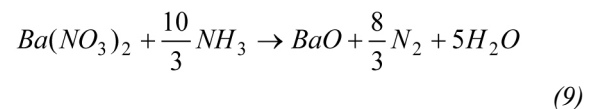
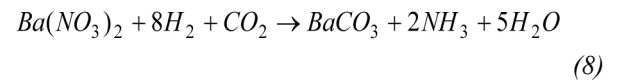
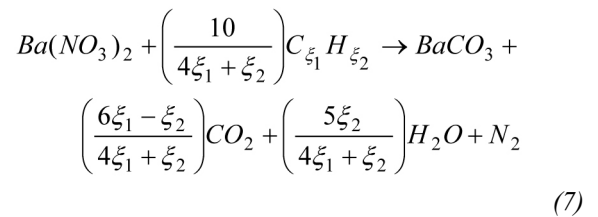
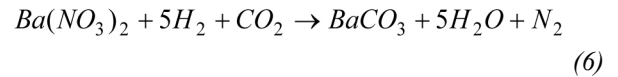
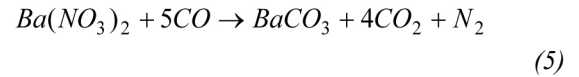
Oxygen Storage



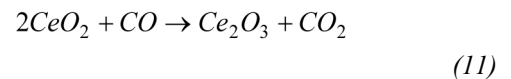
REGENERATION

During the rich (or regeneration) mode, the Air Fuel Ratio (AFR) is driven rich to achieve reducing conditions (introduction of HC, CO and H₂). The stored NOx and Oxygen are treated by the reducing species according to the following reactions:

Decomposition of the Stored NOx During Rich Time with the Reducer



Oxygen Reduction



The focus of this study is that we take in consideration the formation of small amount of ammonia as byproducts during the regeneration mode (equation (8)). The so-called NH₃ slip efficiently supplies the downstream SCR to further reduce the stock of NOx. Ammonia formation only takes place at the end of long rich periods, when most of the NOx has been reduced to N₂ or desorbed. This points out two interesting features about ammonia during the regeneration period: Ammonia formation is delayed compared to the NOx desorption and has a characteristic shape during rich period, which will be discussed in more detail later. This phenomenon was also reported in [17] and [18].

Figure 4 gives an illustration of the previous mechanisms:

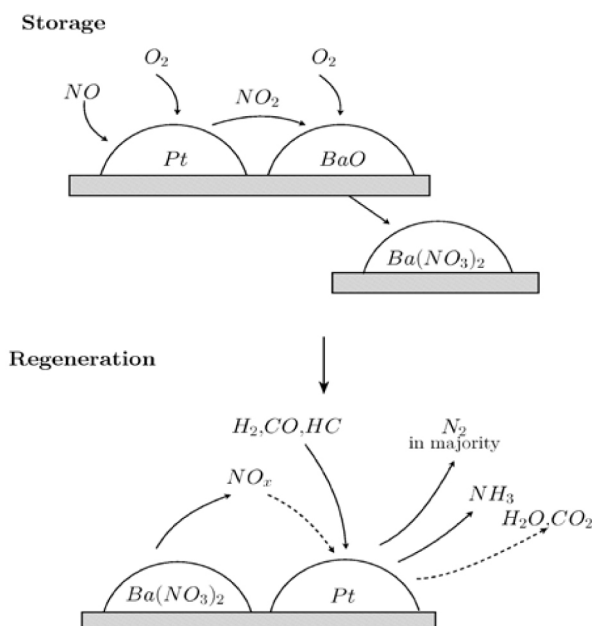


Figure 4. Operation of a NO_x trap

During the purges, high temperatures result in the release of some SO₂ but also large quantities of H₂S. Though it is not a regulated pollutant, it is a source of consumer dissatisfaction and must be diminished, and in fact eliminated. This requires an additional catalyst that is not considered in this work. This point will be discussed further in the sequel.

OPERATION OF A SCR

The Selective catalytic Reduction with urea as the reducing agent, has become an efficient technology for NO_x emission reduction of diesel heavy-duty vehicles and has allowed many others to meet European standards ([13], [14]).

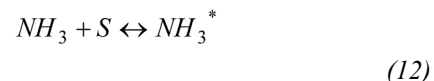
In standard configuration, the NH₃-SCR technology needs an additional reducing agent (ammonia) along with a dosing system to meter the desired amount of reductant. Ammonia is generated from urea solution injected in a controlled way in the exhaust line. Ammonia then reacts selectively with NO_x under lean conditions, giving mostly N₂ as a final product. The ability of SCR catalysts to reduce NO_x even below 200°C makes them particularly suitable for NO_x control on diesel engines. Although not limited by the legislation yet, ammonia emissions are undesirable, notably because of their toxicity. Therefore, the ability of the SCR catalyst to store NH₃ could help prevent NH₃ slip from upstream LNT catalyst and limit its emission.

Automotive applications led to a fundamental investigation of SCR reaction mechanisms ([15]). The three main SCR reactions used in the model are shown from equations (14), (15), (16). NH₃ adsorption (denoted by *) and desorption on a

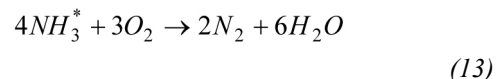
free active site denoted S (equation (12)) have been included, as well as oxidation of NH₃, only into N₂ (equation (13)).

AMMONIA STORAGE

Adsorption/Desorption Process



Oxidation Process



SELECTIVE REDUCTION PRINCIPLE

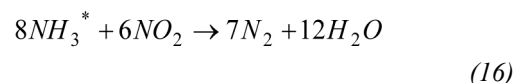
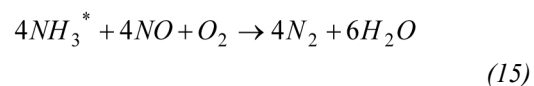
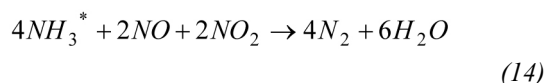


Figure 5 illustrates this principle:



Figure 5. Principle of the Selective catalytic reduction of NO_x by NH₃

AFTER-TREATMENT MODELING

In this part, the principle of modeling respectively for a LNT and a SCR catalyst is described. All models are 0D and developed using a Matlab/Simulink platform. The different steps of simplification of the LNT and SCR models for on-line control application are detailed. Being further reduced, the LNT model is more detailed than the SCR, which corresponds to classical model for control application (without taking in account NO/NO₂ ratio). Firstly, the physicochemical laws governing the main phenomena are provided. Then, under few assumptions and mathematical technique, this leads to ODE-based models. They are next submitted to reduction, identified and validated.