

## Modelling of a Lean NO<sub>x</sub>-Trap system with NO/NO<sub>2</sub> differentiation and sulfur poisoning

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### ABSTRACT

One of the challenges in the automotive industry is to develop new vehicles and new technologies with minimal costs. In this context, modeling becomes an important tool for the design of future technologies by reducing the number of tests needed to develop a new exhaust system. With the emergence of future European standards [ 1 ], which are more restrictive on NO<sub>x</sub> and takes account of the differentiation between NO and NO<sub>2</sub> emissions, European manufacturers have to describe precisely the formation and the behavior of NO<sub>2</sub> in the after-treatment systems.

The aim of this study is to improve the one dimensional after-treatment models developed by Renault by introducing the NO<sub>2</sub> contribution from the engine to the tail pipe. The first part of this study focuses on the adaptation of after-treatment systems models in order to differentiate NO and NO<sub>2</sub>. Thus different global kinetics models for the Lean NO<sub>x</sub>-Trap System were studied. Different runs were carried out either at Renault or at the “Laboratoire de Réactivité de Surface”, for understand the phenomena involved in NO<sub>2</sub> formation and consumption's. Then, the calibration of the model has been performed. Part of this paper focuses on the choice of an automated optimization method for this calibration step. By the end, the final model was validated versus engine bench tests performed on full size monoliths. The second part of the study describes more precisely the integration of the sulfur poisoning effect in the Lean NO<sub>x</sub>-Trap Model including the integration of NO<sub>2</sub> in the model.

### INTRODUCTION

This paper introduces the modelling method in order to help the development of future vehicles of the Renault group. These models are used for the development of the future after-treatment line for the EURO 6 vehicles [2].

One of the challenges of the EURO 6 standards is the reduction of NO<sub>x</sub> and the NO/NO<sub>2</sub> differentiation. These changes demand a better understanding of the catalytic components of the exhaust line, including Diesel oxidation catalysts, Diesel particulate filters, Lean NO<sub>x</sub>-Trap and Selective Reduction Catalysts. For this study, we focused on the Lean NO<sub>x</sub>-Trap System. A special attention was paid on sulfur poisoning effects; on the NO<sub>x</sub> storage capacity and on the behavior of NO / NO<sub>2</sub> in the trap. The first part of this manuscript introduces the mathematical description of the lean NO<sub>x</sub>-trap model and the introduction of the new features. The second part deals about the tests used for the calibration and validation of the model. In the third part a comparison is made using different calibration methods for each feature. In the last part, the results of the best calibration will be introduced.

### AFTER TREATMENT MODELLING

In this first part, the principle of modelling of an LNT is presented. All the one dimension models (1D) are developed using a Matlab/Simulink platform.

## OVERARCHING PRINCIPLE

The model is written in a Matlab S-Function with C-Language and solved by Simulink using a discrete solver and a fixed time step. For computational time concerns, the following assumptions are made:

- Homogeneous temperature, concentration and gas velocity distributions in front of the monolith (monolith behavior is 1D), this assumption can be useless using Multi 1D models (with several reactors at the entrance of the catalyst)
- Multi 0D modeling is used to describe the 1D behavior of a channel
- Gas are considered like perfect gas
- Conduction and radiation are neglected
- No pressure loss through the monolith (pressure is the same all along a channel)
- Quasi-steady state approximation (QSSA) for the gaseous concentrations mass balance: [Eq.1](#)

$$\frac{dC}{dt} \ll \frac{dT}{dt}, \frac{dC^*}{dt} \quad (1)$$

As a consequence of these assumptions, only one channel is considered, the behavior of this channel being representative of the behavior of the entire monolith. The channel is also considered like a sequence of Perfect Stirred Reactor (PSR), the exit of one PSR being the entrance of the next PSR. In one reactor and for each step time, the following equations are computed:

- Reactions rates : [Eq.2](#)

$$r_j(z, t) = k_j^0 \exp\left(\frac{-Ea_j}{RT_g(z, t)}\right) \dots \prod_{i=products} (C_{i,j}(z, t))^{n_{i,j}} \quad (2)$$

- Mass balance on pollutants: the basic mass balance equation is described on [Eq.3](#) but as the QSSA on [Eq.1](#) is applied, the set of [Eq.3](#) is equal to zero. The resolution of this equations system allows the computing of the gaseous concentrations at the exit of every PSR. As a consequence, from a computational point of view, gaseous concentrations are no more considered as state variables but as scalars.

$$\frac{d}{dt}(C_i(z, t)) = -\rho_u \sum_{j=reactions} n_{i,j} r_j(z, y) - \frac{V_e C_i(z, t) - V_e C_i(z - dz, t)}{dz} \quad (3)$$

- Mass balance on adsorbed species: [Eq.4](#)

$$\frac{d}{dt}(C_i^*(z, t)) = -\rho_u \sum_{j=reactions} n_{i,j} r_j(z, y) \quad (4)$$

- Thermal balance for gas: [Eq.5](#)

$$\frac{dT_g}{dt} = -\frac{1}{\varepsilon_m C_{p_g} \rho_g} \dots \left[ -\frac{V_e \rho_g}{dz} (T_g(z) C_{p_g}(z) - T_g(z - dz) C_{p_g}(z - dz) + h_m \frac{dS}{dV} (T_g(z) - T_s(z))) \right] \quad (5)$$

- Thermal balance for solid: [Eq.6](#)

$$\frac{dT_s}{dt} = -\frac{h_m dS(T_g(z) - T_s(z)) + h_{ext} dS_{ext}(T_{ext} - T_s(z)) - \rho_u \sum_{i=species} r_i \Delta H_i dV}{(1 - \varepsilon_m) C_{p_{app}} \rho_{app} dV} \quad (6)$$

## LEAN NO<sub>x</sub>-TRAP KINETIC MECHANISM

The kinetic mechanism used for the model is a global mechanism that is able to take account of the different phenomena occurring in the LNT, but also permits a low simulation time. This type of mechanisms can be compared with those already presented in the literature [3,4,5]. In this part, the presentation of the mechanism only takes account of the equations of the model without NO<sub>x</sub> adsorption and sulfur poisoning.

See [Table 1](#) after last section of paper

For each equation of [Table 1](#), a reaction rate is then coded. Thus, for the lean burn conditions, ten couples of kinetic parameters are required for calibration. Also, each equation was previously calibrated for one type of catalyst and ageing.

See [Table 2](#) after last section of paper

The equations of the [Table 2](#) represent the adsorption and desorption equations implanted in the model. For each equation, two reactions rates are coded and four couples of kinetic parameters are then required. For this type of equation, a calculation of free adsorption site was done. Generally, the adsorption rate has an inhibition term that depends on the loading of the free adsorption sites.

See [Table 3](#) after last section of paper

For the Rich conditions, the hydrocarbons are equivalent to CH<sub>2</sub>.

For the equations of the [Table 3](#), for each equation, a reaction rate is coded and a couple of kinetic parameter is required for the new calibration.

## NO/NO<sub>2</sub> DIFFERENTIATION

The first study of this paper is the NO/NO<sub>2</sub> differentiation. For this study, the work of [5,6] was a valuable information source. The study is focused on the adsorption of NO and NO<sub>2</sub> on the barium sites and the oxidation of NO to NO<sub>2</sub>. Two schemes were coded and tested for the study.

One scheme consists of one NO adsorption equation and one NO<sub>2</sub> adsorption equation and with an inhibition term which depends on the filling of the NO<sub>x</sub>-Trap. The second scheme is based on the work of L.Cao et al. [6] and is coded with an equation for NO adsorption and two equations for NO<sub>2</sub> adsorption, one for the behavior of NO<sub>2</sub> on barium sites near to a Platinum or Palladium and one for the rest of barium. The free adsorptions sites for all the equations are the same.

The first scheme with the associated reaction rates is given in the [Table 4](#) and the differences between both schemes are given in [Table 5](#).

See [Table 4](#) after last section of paper

BaCO<sub>3</sub> : oxycarbonate of barium is considered as the principal free adsorption sites for NO<sub>x</sub> storage.

See [Table 5](#) after last section of paper

Both schemes were calibrated. The calibration methods and the results will be presented thereafter.

## SULFUR POISONING EFFECT

Our study also focuses on the modelling of sulfur poisoning effect on NO<sub>x</sub> adsorption. A number of paper show the possibility to understand and predict the effect of the sulfur on NO<sub>x</sub> adsorption [7,8].

For this study, the method is to calculate for each step of time and each PSR the number of sites that can be poisoned by the sulfur. Usually, the simulation is performed on regulated driving cycles, which take less than thirty minutes. The amount of sulfur that the LNT can absorb during this period is then insignificant.

Furthermore, for the modelling of the sulfur effect, the amount of sulfur during the simulation does not often change.

Consequently, the amount of sulfur adsorbed on the LNT is a parameter of the model and can be used in g/Lcatalyst. [Eq.40](#) shows how the total free adsorption sites in mol/m<sup>3</sup> for NO<sub>x</sub> are calculated and the [Eq.41](#) shows how the numbers of sites poisoned by sulfur in mol/m<sup>3</sup> are calculated.

$$siteN_{tot} = \frac{NSC_{max} * 1e3}{M_{NOx} * \left(1 - \frac{\rho_m}{\rho_{app}}\right)} \quad (40)$$

$$SOx_{tot} = \frac{SOx_{ads}(PSR) * \frac{Max_{PTS}}{V_{cata}}}{M_{SOx} * \left(1 - \frac{\rho_m}{\rho_{app}}\right)} * EqSOx_{NOx} \quad (41)$$

In these equations, the total free adsorption sites for NO<sub>x</sub> are calculated for each PSR and the sites occupied by sulfur are calculated with an amount of sulfur that can be different for each PSR. Consequently, a repartition of the sulfur over the catalyst is possible and then is applied. Moreover, one can define an equivalence term between SO<sub>x</sub> and NO<sub>x</sub>, which fix the amount of free adsorption sites occupied by one SO<sub>x</sub>.

As already been shown by Choi et al. [9], the repartition of the sulfur over the catalyst is heterogeneous, therefore a specific calculation of the occupation of the adsorption sites available for NO<sub>x</sub> adsorption has to be made. The principle of this calculation is to fill the adsorption sites of the first PSR with sulfur, and if the amount of sulfur in the catalyst is higher than the free adsorption sites of the first PSR, the remaining amount of sulfur is then included in the second PSR like in the first PSR, and again and again with the next reactor if there are available sulfur.

So before running the model, the total amount of sulfur is distributed in all the PSR, with the priority of the first part of the LNT. For the study, a homogeneous distribution of the sulfur all over the catalyst will be tested for comparison with the heterogeneous distribution.

## PERFORMED TESTS

In this part, the different tests used for the calibration of the model are presented. We focus first on the NO<sub>x</sub> adsorption capabilities of the LNT. We tried to calibrate the models exclusively with laboratory tests on catalyst carot of monolith (1 inch length, 1 inch diameter), one of the challenges of this study being to obtain a predictive model on real condition tests with the only use of lab tests for calibration.

## LABORATORY TESTS

For the calibration of the model, a synthetic gas test bench was used. This type of bench can make stationary tests and so NO<sub>x</sub> Storage Capacity (NSC) tests. NSC tests are adsorption of NO<sub>x</sub> on stabilized point for different temperatures for 150°C to 450°C. The gas used for these tests are near to a real condition tests: N<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>O, CO<sub>2</sub>, CO, C<sub>3</sub>H<sub>6</sub>, NO<sub>2</sub> and NO.

The Laboratory bench scale runs are stabilized tests under specific composition and different temperatures. The catalyst used is a 0.16 L sample catalyst of Pt/Pd/Ba commercial Lean NO<sub>x</sub>-Trap.

For the calibration of the NO/NO<sub>2</sub> differentiation, the catalyst is aged in an oven in presence of water but not poisoned with sulfur. A chemiluminescence NO / NO<sub>x</sub> analyzer is used at the outlet of the LNT sample.

For the calibration of the sulfur poisoning, the same aged catalyst is poisoned with two levels of poisoning: 1 gram per monolith liter (g/L) and 2g/L of sulfur. For these tests, only NO<sub>x</sub> measurement is available, so the calibration would be only with total amount of NO<sub>x</sub>.

The [Table 6](#) describes the conditions for each test. These conditions are representative of Gas Hour Space Velocity (GHSV) and pollutants for each temperature in comparison of real conditions.

See [Table 6](#) after last section of paper

## REAL CONDITIONS TEST

For this study, only one real condition test is used. The interesting part of this method is it's possible to validate both modifications of the model with this one. The test was made on an engine test bench using a New European Driving Cycle (NEDC), who is the homologation cycle for European vehicle. The [Fig.1](#) represents the velocity profile of an NEDC.

The engine used for the test is a 2L Turbo Diesel Common Rail. The catalyst used is the same as used for the laboratory tests, same ageing, with a volume of 2.2L and 3g of sulfur adsorbed. The pollutants are analyzed before and after the catalyst simultaneously, with a frequency of 1 Hz. Both analyzers can measure total amount of NO<sub>x</sub> and NO simultaneously.

See [Figure 1](#) after last section of paper

## CALIBRATION METHODS

This part will present the methods used for model calibration. For both models, different methods of calibration were used because of the complexity of calibration parameters.

### CALIBRATION FOR NO/NO<sub>2</sub> DIFFERENTIATION

The calibration of the NO/NO<sub>2</sub> model is based on the “lsqnonlin” function of Matlab. This function is an optimization tool that permits to find the minimum of a user defined function. This algorithm is a subspace trust region method and is based on the interior-reflective Newton method described in [10,11].

The first part of the calibration is to write the user defined function. This function has for inlet parameter the kinetic parameters. The function's content is like following:

- Modification of the model parameters with the new kinetic parameters
- Running of the model
- Analysis of the relevant output of the model
- Comparison between experimental and computed values and calculation of the optimization target

So with this function, the optimization function will try to reduce the gap between simulation and experience. Two methods of comparison have been tested: comparison between instantaneous values and comparison between cumulative values.

Because the optimization algorithm is not powerful enough to make huge gaps on parameters, a modification of the method has been applied. Indeed only the pre-exponential factors have been optimized, the five energies of activation were fixed before the optimization. The modified methodology i:

- All the activation energy “Ea” are fixed before the optimization
- The optimization method optimizes the 5 “k” in the same time
- The best solution is kept for the previous “Ea”
- “Ea” values are modified
- The 10 fitted parameters cannot be <0