Modelling and speciation of nitrogen oxides in engines

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Available online 2 July 2012

Abstract

The present study extends the Nitrogen Oxide Relaxation Approach (NORA [Vervisch et al., *Combust. Flame* 158 (2011) 1480–1490]) for NO_x modelling in engines by introducing alternative chemical routes to the thermal pathway as well as a speciation of nitrogen oxides into nitrogen monoxide (NO), nitrogen dioxide (NO_2) and nitrous oxide (N_2O). Perturbations of equilibrium state are considered to identify nitrogen oxide reactivity in various mixture and thermodynamic conditions. A common Intrinsic Low-Dimensional Manifold (ILDM) is identified for NO and NO_2, while nitrous oxides appear to stay in near-equilibrium state for any in-cylinder conditions. The relaxations back towards the equilibrium state after the perturbations are analysed to extract the characteristic times of relaxation, an image of the species reactivity. Tabulation of equilibrium mass fractions and characteristic relaxation times as a function of mixture and thermodynamic conditions allows nitrogen oxide modelling to be performed for internal combustion engines at very low computational cost through idealised ILDMs that are independent of the combustion ones. Results show the accuracy of the modelling approach for nitrogen oxide emissions of a Diesel engine at part and full load.
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Keywords: Nitric oxide; Nitrogen dioxide; Nitrous oxide; ILDM; Tabulated chemistry

1. Introduction

Nitrogen oxides are combustion by-products that are toxic to humans, induce acid rains and smog, conduct to ozone depletion and favour greenhouse gas effect, so that their emissions from vehicles are legislated worldwide. Legislations generally refer to NO_x which are the sum of NO (90–95% of emissions) and NO_2 (5–10%). Since NO and NO_2 have a lifetime of 4 days, emissions from ground vehicles do not reach the stratosphere where ozone layer depletion takes place. On the other hand, N_2O has a lifetime of 150 years allowing the emissions at ground level to diffuse to the stratosphere and to integrate the ozone destruction cycle. N_2O is also a major greenhouse gas with a global warming potential about 300 times larger than that of CO_2 over a period of 100 years. Therefore, N_2O is presently under consideration for inclusion in future legislations.

Among the numerous existing tools, CFD modelling is a growing source of information for combustion device optimisation. The most precise description of nitrogen oxide formation and reduction would be obtained through the solving of a detailed chemistry scheme including the combustion-related and nitrogen-oxide-related reactions. Nevertheless, such an approach is not reachable today for industrial purposes because of the excessive CPU time consumption. Therefore, models are introduced both for combustion and nitrogen oxide description.

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The most common approach for NO_x modelling relies on the direct solving of a detailed kinetic mechanism [1] for the prediction of thermal NO emissions. Alternatively, Löffler et al. [2] have proposed a simplified model which is a post-processing tool over combustion calculation results. Both approaches are very sensitive to the radical concentrations [2]. For the radicals specific to NO_x kinetics, the accuracy could be ensured through a quasi-steady-state hypothesis but, for combustion-related radicals, the influence of the combustion model is central. Such NO_x models are therefore highly sensitive to the combustion modelling hypotheses if anything but a very detailed chemistry scheme is solved.

Another approach is the decoupling of nitrogen oxide modelling from combustion modelling to avoid the addition of errors. By introducing idealised Intrinsic Low-Dimensional Manifolds (ILDMs) that are independent of the combustion ILDM, the present study considers this approach as a continuation of the works of Nafe and Maas [3], Vervisch et al. [4] and Zoller et al. [5].

The chemical routes for nitrogen oxide formation and reduction included in the identification process of such ILDMs are first detailed in the next section in conjunction with the choice of the reference detailed chemistry. Then, the concept of ILDM is detailed for combustion and for the specific chemistry of nitrogen oxides. The identification of idealised ILDMs for all three considered nitrogen oxides and their use to build a tabulation approach are explained. Eventually, the model is validated through a direct comparison with detailed chemistry in constant-enthalpy and engine-like homogeneous reactors as well as through comparison of 3D CFD results with experiment for an actual Diesel engine.

2. Kinetics of nitrogen oxides

The most abundant nitrogen oxide is NO, which formation from air nitrogen can occur through four routes: thermal NO, prompt NO, N_2O route and NNH route. The thermal (Zeldovitch) route [1] involves breaking-up N_2 triple-bond by O atoms and is the main NO formation pathway at higher temperatures [2]. The prompt (Fenimore) route [6] is initiated by reactions between N_2 and CH radicals [7,8] and is less dependent on temperature. The N_2O route [9,10] is initiated by the N_2O adduct formation. The subsequent reaction of N_2O with H or O radicals yields NO. The NNH route [11] due to the reaction of H radical with N_2 is only of minor importance in most hydrocarbon flames but can have a significant contribution in hydrogen flames [12].

NO_2 and N_2O are the other two major nitrogen oxides that are formed and oxidised as part of the NO kinetics. N_2O mainly originates from the eponymous N_2O route leading to NO as a partial oxidation product. On the contrary, NO_2 is mainly formed through the oxidation of NO [13].

In the present study, the focus is on the inclusion of all these routes in engine calculations for large hydrocarbon fuels. Among the numerous detailed chemistry schemes describing NO_x formation, only a few are coupled with such fuels [14–16], notably because few published data are available to validate the influence of large hydrocarbon fuels on the predicted emissions. Therefore, Diesel is here emulated with *n*-heptane and the detailed kinetic mechanism of Anderlohr et al. [16], validated against experimental NO_x profiles for small [17–19] and large [20] hydrocarbon fuels, is selected as the reference mechanism. Its NO_x subset derives from GRI Mech 3.0 [21] for high temperature NO_x chemistry and from Glaude et al. [22] for low temperature NO_x chemistry. Accordingly, prompt NO is described through the HCN rather than the NCN pathway unlike in more recent mechanisms. This point is acceptable here because only undiluted mixtures are considered but will need reconsideration in a near future for low temperature combustions with diluted mixtures.

3. Intrinsic Low-Dimensional Manifolds

The concept of ILDM has been introduced by Maas and Pope [23] to reduce detailed chemistry schemes without explicitly choosing species in quasi-steady-state or reactions in partial equilibrium. It relies on the identification of the local characteristic times of chemistry through a mathematical analysis of the kinetics in a homogeneous, closed-volume, constant-enthalpy reactor. The evolution of such a system is described by the set of equations:

$$\begin{cases} \frac{\partial h}{\partial t} = 0 \\ \frac{\partial p}{\partial t} = 0 \\ \frac{\partial Y_i}{\partial t} = \dot{\omega}_i(h, p, Y_1, \dots, Y_N) \quad i = 1 \dots N \end{cases} \quad (1)$$

where h and p are the system total enthalpy and pressure, respectively, while Y_i and $\dot{\omega}_i$ are the mass fraction and mass rate of reaction of species i, respectively, and N is the number of species.

For a given atomic balance, whatever the initial chemical composition described by vector Y_i $(i = 1 \dots N)$, the system evolves towards a unique equilibrium state Y_i^{eq} $(i = 1 \dots N)$. Maas and Pope [23] have demonstrated the existence of preferential chemical pathways for the progress towards the equilibrium that are governed by the slowest chemical processes. These processes can be locally identified through a mathematical analysis. The chemistry evolution written as $\frac{\partial Y_i}{\partial t} = F(Y_i)$ may be locally linearised to extract the system Jacobian $J(Y_i) = F_{Y_i}$. The eigenvalues of F_{Y_i} with the