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## Modeling of nitrogen pollutants in combustion systems

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### Abstract

Nitrogen oxides (NO<sub>x</sub>) are among the main pollutants in the atmosphere. A significant amount of NO<sub>x</sub> emissions is attributable primarily to human activities, in particular the combustion of fossil fuels. This work is aimed at research and implementation of the NO<sub>x</sub> model, which is capable of modelling nitrogen-containing pollutant formation in practical combustion systems. The NO<sub>x</sub> reaction mechanisms were investigated and implemented into the CFD code FIRE. The nitrogen scheme was limited to sufficiently few homogeneous reactions to allow effective coupling with the turbulent mixing process. The effects of the turbulent fluctuations on the reaction rates when predicting NO<sub>x</sub> concentrations were modelled by using the presumed Probability Density Function (PDF) approach. The NO<sub>x</sub> model was applied and tested to the turbulent non-premixed jet diffusion flame (Sandia flame D) and the nitrogen predictions were compared to the results obtained by the Steady Laminar Flamelet Model (SLFM) and to the experimental data. The implemented NO<sub>x</sub> model was also applied for the calculation of nitrogen pollutant emission in real diesel engine configuration. The NO<sub>x</sub> predictions were compared with experimental data.

**Keywords:** Pollutants; NO<sub>x</sub>; Combustion; Modelling.

### 1. Introduction

The combustion of fossil fuels releases large quantities of pollutants into the environment. As one of the top pollutants produced by combustion, nitrogen oxides (NO<sub>x</sub>) can be formed from the molecular nitrogen (N<sub>2</sub>) carried with the air and the organic nitrogen bound in fuels (fuel-N) via different paths, which are included in detailed chemical kinetic mechanisms and account for the reactions leading to NO<sub>x</sub>. Hundreds of elementary gas-phase reactions are involved in the formation of NO<sub>x</sub>, which can be formed or destroyed by at least four separate reaction processes in the gas phase: thermal NO<sub>x</sub>; prompt NO<sub>x</sub>; fuel NO<sub>x</sub>; and nitrous-oxide (N<sub>2</sub>O). Since NO<sub>x</sub> pollutants are typically not emitted in equilibrium concentrations, finite-rate kinetics plays a role in determining the levels of emissions. Emissions of oxides of nitrogen are limited because the reactions that produce NO and NO<sub>2</sub> are much slower than the overall process of fuel oxidation. Available detailed NO<sub>x</sub> chemical kinetic mechanisms come from many researchers e.g. Miller and Bowman [1], Baulch [2], Dagaut [3] etc. However, the development of an effective NO<sub>x</sub> model requires simplification of such generalized reaction mechanisms, taking into account sufficient details to adequately describe the NO<sub>x</sub> reaction process, and to allow coupling with the turbulent mixing process in Computational Fluid Dynamics (CFD) simulation of practical combustion

systems such as boilers, furnaces, internal combustion engines etc. [4][5]. Consequently, reduced kinetic mechanisms have to be used in comprehensive combustion codes to describe the NO<sub>x</sub> reaction processes, allowing the reduction of calculation time and making this time-consuming method more attractive for industrial application. NO<sub>x</sub> pollutant modelling, by means of CFD, has been reviewed by Hill and Smoot [4], providing an overview of NO<sub>x</sub> mechanisms and modelling for the prediction of NO<sub>x</sub> in practical combustion systems.

The focus of this work was to investigate and collect the best available thermo-chemical parameters and important kinetic mechanisms using a “minimum” set of reactions to approximate the essential features of the NO<sub>x</sub> reaction process in practical combustion systems. The nitrogen scheme was limited to sufficiently few homogeneous reactions to allow effective coupling with the turbulent mixing process, but on the other hand these kinetic mechanisms must contain sufficient details to adequately describe the NO<sub>x</sub> reaction process in combustion systems. Chemistry-turbulent interactions were modelled by integration of chemical kinetic rates with respect to fluctuating temperature and appropriate Probability Density Function (PDF). NO<sub>x</sub> model was integrated into the commercial CFD code FIRE, using FIRE's user-defined functions capability. User functions, written in FORTRAN programming language, are easily linked with the AVL's FIRE code providing prediction of NO<sub>x</sub> emission in combustion systems on one hand and retaining all the usual FIRE features on the other. The NO<sub>x</sub> model was applied to Sandia National Laboratories Flame D, a piloted, turbulent, non-premixed methane-air flame for which measurements of nitric oxides concentrations exist and also to real diesel engine configuration.

## 2. Mechanisms for NO<sub>x</sub> Formation in Combustion Systems

The generic designation NO<sub>x</sub> refers to the summation of all oxides of nitrogen, namely NO, NO<sub>2</sub>, N<sub>2</sub>O, N<sub>2</sub>O<sub>2</sub>, N<sub>2</sub>O<sub>3</sub>, N<sub>2</sub>O<sub>4</sub> and N<sub>2</sub>O<sub>5</sub>. The most damaging of the hazardous nitrogen compounds formed during combustion are nitrogen monoxide, or nitric oxide (NO), and nitrogen dioxide (NO<sub>2</sub>). However, combustion sources emit NO<sub>x</sub> mostly in the form of nitric oxide with NO representing 90 to 95 percent of the total NO<sub>x</sub> emissions. Considering that most of the NO<sub>x</sub> emitted by combustion sources is NO with only a small fraction appearing as NO<sub>2</sub>, and that other nitrogen oxides are emitted in negligible concentrations, the presence and effects of NO<sub>2</sub>, N<sub>2</sub>O, N<sub>2</sub>O<sub>2</sub>, N<sub>2</sub>O<sub>3</sub>, N<sub>2</sub>O<sub>4</sub> and N<sub>2</sub>O<sub>5</sub> during combustion processes are ignored in this work.

The formation of NO from a specific combustion device is determined by the interaction of chemical and physical processes occurring within the combustion chamber. In practical combustion systems, NO can be formed from two different sources: the molecular nitrogen (N<sub>2</sub>) present in the combustion air and the nitrogen bound in a fuel. There are three fundamentally different chemical mechanisms of NO formation: the thermal NO mechanism, the prompt NO mechanism and the fuel NO mechanism. The thermal NO mechanism arises from the thermal dissociation and the subsequent reaction of nitrogen and oxygen molecules in combustion air at relatively high temperatures in a fuel-lean environment. This process is described by a set of chemical reactions known as the extended Zeldovich mechanism.



This mechanism is extended to more accurately describe thermal NO formation under fuel-rich conditions by including an additional elementary reaction:



From these reactions a following expression can be derived to approximate the rate of thermal NO formation:

$$\frac{dc_{\text{NO}}}{dt} = k_{1f}c_{\text{O}}c_{\text{N}_2} + k_{2f}c_{\text{N}}c_{\text{O}_2} + k_{3f}c_{\text{N}}c_{\text{OH}} - k_{1b}c_{\text{NO}}c_{\text{N}} - k_{2b}c_{\text{NO}}c_{\text{O}} - k_{3b}c_{\text{NO}}c_{\text{H}} \quad (4)$$

The reaction rate coefficients  $k_{1f}$ ,  $k_{1b}$ ,  $k_{2f}$ ,  $k_{2b}$ ,  $k_{3f}$ ,  $k_{3b}$  for the forward reactions and the corresponding backward reactions can be expressed according to the Arrhenius law:

$$k = AT^\beta \exp\left(-\frac{E_\beta}{RT}\right) \quad (5)$$

where  $A$  is the pre-exponential factor,  $\beta$  indicates the order for the temperature dependence of the pre-exponential factor,  $E_\beta$  is the activation energy,  $T$  is the temperature, and  $R$  is the universal gas constant. The concentration of O atoms and the free radical OH is calculated from empirical relations [6] or based upon the radical concentration of the combustion model.

The prompt NO mechanism forms NO from nitrogen much earlier in the flame than the thermal NO mechanism. This mechanism, only significant in fuel-rich regions of flames, involves the intermediate formation of hydrogen cyanide (HCN), followed by the oxidation of HCN to NO. The following reactions are the most likely initiating steps for prompt NO:



The model used in this work to predict prompt NO concentration is calculated as:

$$\frac{dc_{\text{NO}}}{dt} = kc_{\text{O}_2}^b c_{\text{N}_2} c_{\text{fuel}} \exp\left(-\frac{E}{RT}\right) \quad (9)$$

where  $c$  denotes the concentration,  $k$  is the pre-exponential factor,  $b$  is the order of reaction for molecular oxygen and  $E$  is the activation energy.

Finally, if the fuel contains organically bound nitrogen, as for example in the case of heavy oil or coal, then the fuel NO is formed during the combustion process. The nitrogen that is bound into fuel molecules is released in the flame region, and some is oxidized to form fuel NO. Natural gas and most distillate oils have no chemically bound fuel nitrogen and essentially all NO formed from the combustion of these fuels is thermal NO and prompt NO. Therefore, only these two mechanisms are used for calculation procedure.

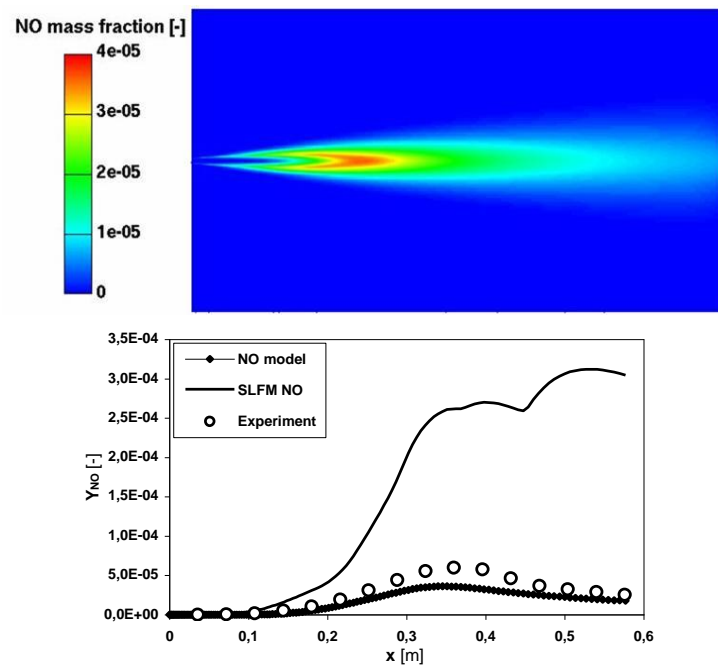
### 3. Numerical simulations and results

The NO<sub>x</sub> model was tested, investigated and validated for the turbulent methane-air jet diffusion flame (Sandia flame D), experimentally investigated by Barlow & Frank [7] In addition, the NO<sub>x</sub> model was applied for simulation of the real internal combustion engine. The 3D steady-state simulations were performed using the AVL's CFD code FIRE, which uses conventional numerical methods, and differencing schemes for completely arbitrary mesh, and can solve large computational meshes which are

required for simulating practical combustion devices [8]. A 3D steady-state incompressible solution for governing the equation was performed by the iterative procedure to obtain the solution.

### 3.1. Turbulent methane-air jet diffusion flame simulation

In the case of Sandia flame D the fuel is a mixture of 25% methane ( $\text{CH}_4$ ) and 75% air by volume. The methane-air reaction mechanism was taken into account via the SLFM model [9]. A detailed chemical reaction mechanism GRI Mech 3.0 for methane, which consists of 53 species and 325 elemental reactions and contains nitrogen chemistry, was used for the calculation of flamelet profiles in the pre-processor step. The radiative heat transfer was calculated using the discrete transfer method, where the radiative properties are modelled as the weighted sum of grey gases. Turbulent flows were modelled using the standard  $k$ - $\epsilon$  turbulence mode.



**Figure 1.**  $\text{NO}_x$  mass fraction distribution along the flame axis and axial profiles of  $\text{NO}_x$

Figure 1 shows temperature distribution and  $\text{NO}_x$  distribution, obtained by  $\text{NO}_x$  model, in a vertical plane along the flame axis. The trends in the results show that  $\text{NO}_x$  distribution is well characterized by the temperature distribution. It is also shown comparison of the  $\text{NO}_x$  mass fraction profiles with experimental data along axis symmetry of the burner for Sandia flame D. The predicted  $\text{NO}_x$  mass fraction profile calculated by  $\text{NO}_x$  model is in fairly good agreement with the experimental data, while NO mass fraction profile calculated by SLFM is over-predicted. The calculated  $\text{NO}_x$  mass fraction profiles show similar trends with the calculated temperature profile, where the temperature maximum corresponds to the peak of the  $\text{NO}_x$  concentration.

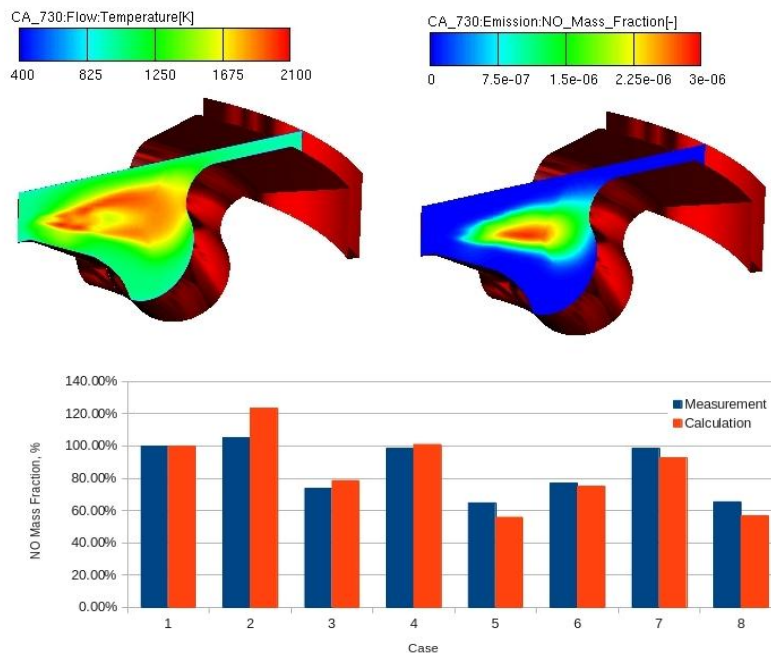
### 3.2. Internal combustion engine simulation

The internal combustion engine used as second case of simulation is a single research engine with electro hydraulic valve actuation and three intake ports with swirl flaps.

**Table 1.** Engine specification

Stroke	0.094 [m]
Bore	0.085[m]
Spray angle	158 [deg]
Compression ratio	16:1 [-]
Number of injection holes	8
Speed	3000 [rpm]

The main engine specifications are summarized in Table 1.



**Figure 2.** Temperature and NO<sub>x</sub> distribution at 730 crank angle and comparison of calculated relative NO<sub>x</sub> mass fraction with experimental data

Since the combustion chamber geometry and the 8 hole injector configuration are symmetrical, the calculated engine domain is only 1/8 of the cylinder/piston bowl arrangement with one nozzle in order to save computational time. Turbulence was modelled by the standard k-epsilon model. The diesel combustion was represented by the Extended Coherent Flame Model (ECFM-3Z) model [10]. The NO<sub>x</sub> model was integrated into FIRE code via user functions, and an additional NO transport equation

was solved as active scalar. Combustion and  $\text{NO}_x$  formation were calculated for 8 combustion system variation, changing the parameters such as start of injection 1-10 deg, residual gas amount 12-20%, swirl level 0-74 % and injection pressure 1200-1600 bar. Figure 2 shows the gas temperature distribution and  $\text{NO}_x$  mass fraction distribution, indicating that  $\text{NO}_x$  occurs wherever there is high temperature. It is also shown comparison of  $\text{NO}_x$  formation trends with corresponding measured data. As can be seen, calculated  $\text{NO}_x$  concentrations and measured data exhibit similar trends and also absolute values are in fairly good agreement.

#### 4. Conclusion

In this paper, the formation of nitrogen pollutants in computational fluid dynamics simulations of turbulent non-premixed jet flame and also internal combustion engine was modelled by coupling a reduced  $\text{NO}_x$  chemical reaction mechanisms with combustion model. The reduced nitrogen scheme was based on thermal  $\text{NO}_x$  formed by oxidation of atmospheric nitrogen and prompt  $\text{NO}_x$  formed by reactions of atmospheric nitrogen with hydrocarbons radicals in fuel-rich regions of the flame. The effects of the turbulent fluctuations on the  $\text{NO}_x$  reaction rates were accounted for by integrating the kinetic rates with respect to fluctuating temperatures over presumed probability density function. The overall agreement between predictions of the nitrogen pollutant formation, in both cases jet flame and internal combustion engine flame, and measurements was good.

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