Simplified mechanism used to estimate the NO$_x$ emission of Diesel engine

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Abstract: - Chemical reactions in combustion processes is a very complicated and difficult to model, so the paper aims to describe the extension of the computer code make by author [1] to simulate nitric oxide formation. Complex kinetic mechanisms are applicable only for simple flame computations (e.g. one dimensional, laminar, etc.). For real turbulent flame calculations, their use is impractical, due to the complexity of the interacting processes (turbulence, radiation, heat transfer, etc.) which must be considered to obtain realistic results. A model derived by systematic reduction of multi-step chemistry is used in for the evaluation of the nitric oxide formation. This reduction is based on the partial equilibrium assumption of the considered elementary reactions using the extended Zeldovich mechanism describing the thermal nitrous oxide formation.

Key-Words: - NO$_x$, emissions, Zeldovich, mechanism, stoichiometric, fuel, flame.

1 Introduction

The term NO$_x$ usually includes nitric oxide (NO) and nitrogen dioxide (NO$_2$), but could also include several other oxides of nitrogen like dinitrogen oxide (N$_2$O), dinitrogen tetrooxide (N$_2$O$_4$) and dinitrogen pentooxide (N$_2$O5). In combustion the amount of NO is normally clearly dominating followed by a much smaller amount of NO$_2$. The other oxides of nitrogen occur normally in very small quantities. NO$_x$ is produced during basically all kinds of combustion and can be divided into three different types of formation.

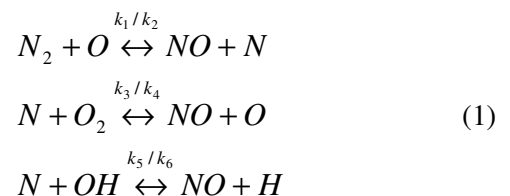In general, the nitric oxide formation stems from three principal sources:
• Thermal NO which is formed due to the dissociation of the molecular air nitrogen (Bowman; Hanson and Salimian; Polifke [2]);
• Prompt NO (Fenimore NO) formed by the "attack" of hydrocarbon fragments on the air nitrogen (Bowman; Görner);
• NO formed from nitrogen containing components in the fuel;

Fuel-NO formation can be neglected during the combustion process in internal combustion engines. Prompt NO formation can also be neglected since this process plays no dominant role in comparison to the thermal NO formation (< 5 [%] of NO is produced via this path) (Görner; Polifke [2]; Zeldovich, et al.). NO is formed in both the flame front and post-flame gases.

2 Model Formulation

In engines, the cylinder pressure rises during the combustion process, so earlier burnt gases are compressed to a higher temperature level as they have immediately after their combustion. Hence, the thermal NO formation in the burnt gases always dominates in comparison to the NO formed in the flame front and represents the main source of the nitric oxide in engines whose reaction paths are effective at high temperatures (> 1600 [K]). The reaction mechanism can be expressed in terms of the extended Zeldovich mechanism:

$$N_2 + O \overset{k_1/k_2}{\leftrightarrow} NO + N$$
$$N + O_2 \overset{k_3/k_4}{\leftrightarrow} NO + O \qquad (1)$$
$$N + OH \overset{k_5/k_6}{\leftrightarrow} NO + H$$

The first reaction represents the rate limiting step in comparison to the other reactions. A very high activation energy (or temperature) is necessary to decompose the stable triple bond of the molecular air-nitrogen. Accordingly, this reaction is significantly fast at high temperatures (hence thermal). In principal, it can be seen that the thermal nitric oxide formation is mainly determined by only five chemical species (*O, H, OH, N* and *O$_2$*) but not by the fuel being used. In order to obtain the required concentrations of the radicals, a complex reaction mechanism must be used in order to determine NO concentration. In the literature different possibilities are suggested to represent the rate law for NO (Bogensperger; Heywood; Warnatz and Maas).

In the program combustion model, an irreversible single-step reaction mechanism is used for the conversion

of fuel, involving only stable molecules such as C_nH_m (as fuel), O_2, CO_2, H_2O and N_2. Hence, an approach is implemented based on these stable molecules in order to predict thermal NO.

The maximum of NO appears at an equivalence ratio of about ~0.9, i.e. slightly fuel-lean. In most stoichiometric and fuel-lean flames, the occurring OH concentration is very small.

Using this fact, the third reaction of the Zeldovich mechanism can be neglected. In addition, the characteristic times (Heywood) for the formation of thermal NO is several orders of magnitude slower than those characteristic times of the combustion process. Hence, the combustion and the NO formation processes can be assumed to be decoupled and therefore, the concentrations of O_2, N, O, OH and H can be approximated by an equilibrium assumption. If the assumption is made that the thermal nitric oxide formation starts at considerably high temperatures (due to the decomposition of the stable triple-bond of N_2) a partial equilibrium of the first two reactions can be assumed.

An analysis of experiments and simulations indicates that at high temperatures (T > 1600 [K]) the reaction rates of the forward and reverse reactions are equal (Warnatz and Maas). The state of the considered reaction is said to be in partial equilibrium where the reaction couples are in equilibrium. Using this assumption, the concentrations of radicals can be expressed in terms of the concentrations of stable molecules (since they are easier to measure). These are present in much larger concentrations than the radicals. The assumption of partial equilibrium provides satisfactory results only at considerably high temperatures, since at temperatures less than 1600 [K] a partial equilibrium is not established.

For the formation of thermal NO, the partial equilibrium approach can be used and so the equilibrium of the first two reactions can be expressed as follows by:

$$k_1[N_2][O] = k_2[NO][N]$$
$$k_3[N][O_2] = k_4[NO][O]$$

(2)

Using these expressions, the equation system can be solved and results in a global reaction approach for the thermal nitric oxide formation which can be expressed as:

$$N_2 + O_2 = 2NO \qquad (3)$$

with $kf = k1 \cdot k3$ as the forward and $kb = k2 \cdot k4$ as reverse reaction rate. The chemical species appearing in this global reaction is also used in the given single-step

fuel conversion equation. Hence, the source term in the conservation equation for NO is obtained via:

$$\frac{d[NO]}{dt} = 2kf[N_2][O_2] \qquad (4)$$

where only the formation (therefore, only the forward reaction) is considered. The reaction rate of the forward reaction is given as:

$$kf = \frac{A}{\sqrt{T}}\exp\left(-\frac{E_a}{RT}\right) \qquad (5)$$

where A pre-exponential factor and Ea activation energy.

3 Computational Program

The presented simplified mechanism for NOx formation is implemented in on computational cod. The developed program is of multi-dimensional type and it solves the specific combined equation systems of:
Turbulent compressible flow by using:
-SGS (Sub grid scale turbulent viscosity) model for turbulence;
- wall logarithm law for the turbulent boundary layer;
- altered Reynolds formula for the caloric boundary layer;
- approximating the fluid as Newtonian to compute its viscosity
-Chemical reactions of fuel combustion by using:
- a kinetic equation of fuel combustion (decal);
- splitting equations of combustion products treated on equilibrium;
- extended Zeldovich mechanism simplified for NOx formation.
-The flow and evaporation of liquid jet of particles by using:
- the general equation of jet simplified in stochastic approach ;
- the equation of drops' evaporation as deducted by O'Rouke;

The formula is bi-dimensional in space and thus allows a plane and axial symmetrical approach of the geometry of the combustion chamber. The axial symmetrical formula, the most often case met in practice, allows us to take into account the swirl movement as well, enhancing thus the spatial resolution and partially implementing the third geometric dimension.

The temporal differentiate is based on ICE (Implicit Continuous-fluid Eulerian) algorithm which is a partial implicit method. This iterative technique joins the continuity and moment equations and solves them simultaneously by using the state equation; the energy equation is solved explicit apart from the other two. To

move forward in time some values several steps in time are needed. For this reason each cycle is achieved in three temporal sub-steps or phases. This approach is in direct connection to the spatial digitization based on ALE (Alternate Lagrangean Eulerian Method) method.

The grid is adjustable and is made up of generalised quadrangles whose corners are specified by co-ordinates dependent on time and are reported to the inferior position of the piston, which allows us to approach the problem Eulerian or Lagrangean as necessity should arise.

4 Numerical simulations

The model presented is used for numerical simulation on T684 engine manufactured by „Tractorul" Plant Braşov, for which author have experimental data.

For evaluation, author is use comparators white measuring data and results obtained whit Wave 5 code produce by Ricardo.

Program calibration is make for indicating diagram uses measuring data, and results of Wave 5 code, for the tow important speed 2400 rpm (speed of max. power) and 1440 rpm (speed of max. torque) the speed of engine emission test cycle Euro 2. The results are present in figures 1 and 2.
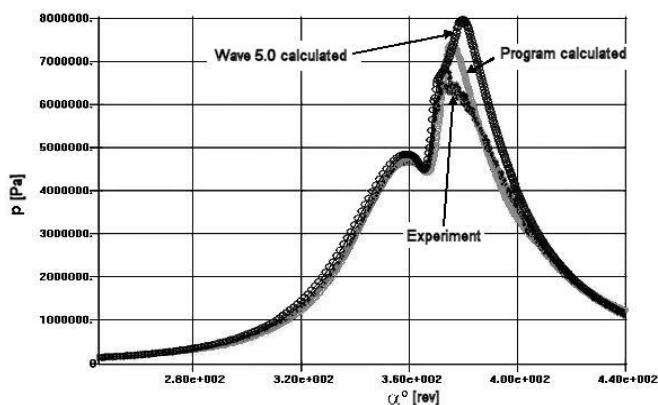

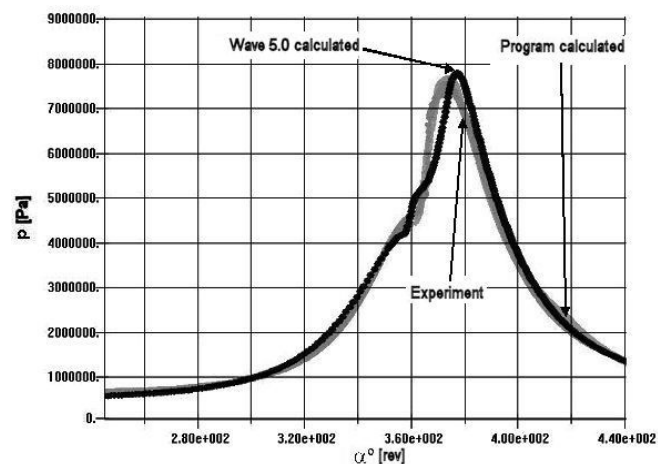Fig.1. Indicating pressure at 2400 rpm speed and 100% load

Fig.2. Indicating pressure at 1440 rpm speed and 100% load

The next step is to compare the measuring data for NOx emission (the medium value) whit the calculated data by program and Wave 5.0 for a cycle. Unfortunately the available measuring data is medium for a cycle.
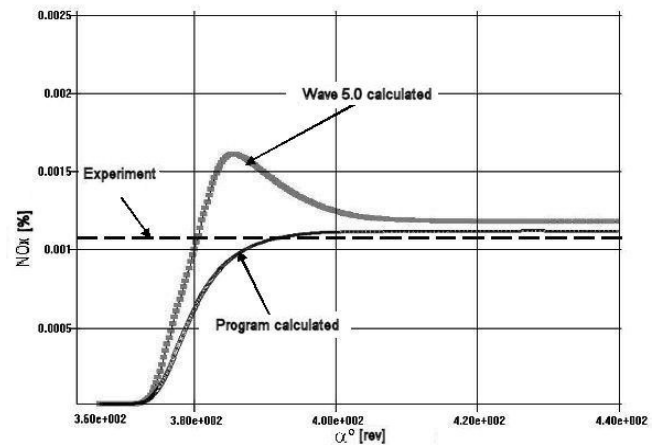

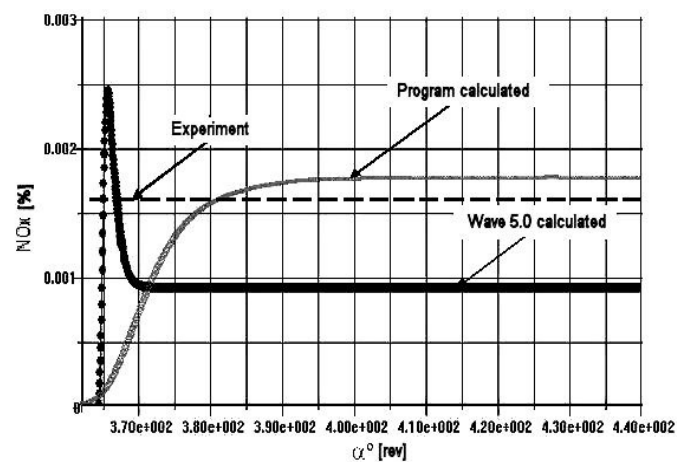Fig.3. NO$_x$ concentration at 2400 rpm speed and 100% load

Fig.4. NO$_x$ concentration at 1440 rpm speed and 100% load

Final we test the program for other load different from that of calibration and present the results in figures 5 and 6.
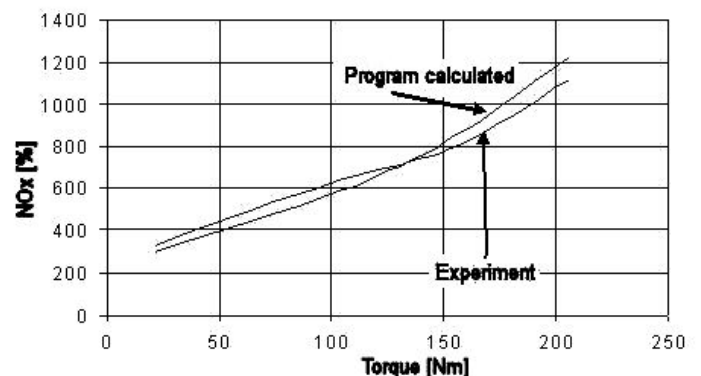
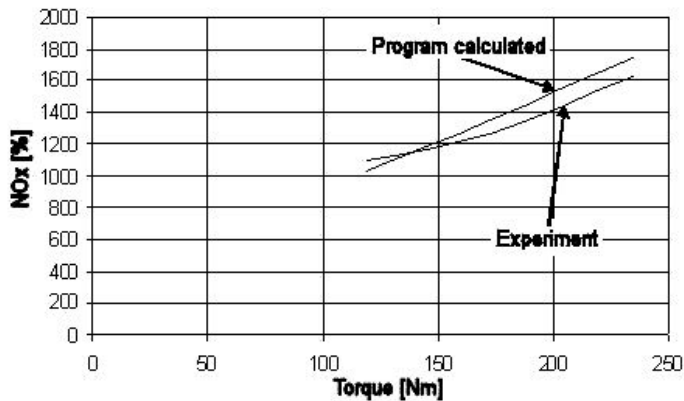Fig.5. NO$_x$ emission, for load curve at 2400 rpm speed

Fig.6. NO$_x$ emission, for load curve at 1440 rpm speed

4 Conclusion

1. The programme is able to estimate *NOx* emissions of Diesel engines;
2. Results are in compliance with experimental data, especially for calibration and load regimes;
3. Under given and well defined conditions the programme is predictive enough to be used to analyse particular cases;
4. If well calibrated the programme can be used to analyse the combustion process in order to improve technical and economic performances and cut *NOx* emissions of diesel engines; this can be achieved mainly by optimizing:
   a. the injection lead;
   b. the shape of the combustion chamber;
   c. the organized or erratic movements in the cylinder.
5. Results largely depend on the constants of the models and for this reason they have to be closely analysed and carefully interpreted as they may carry a subtle mistake and this would lead to wrong conclusions;
6. The performances of the programme are limited by the models used and for this reason the cases and values studied must be carefully selected so that we do not surpass their applicability range.

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