PREDICTING NO FORMATION IN FLAMELESS COMBUSTION REGIME

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Abstract The direct implementation of large kinetic mechanisms for the prediction of pollutant emissions into CFD codes is still unfeasible, due to computer time limitations which become particularly relevant when considering the typical scale of the industrial applications. Therefore, simplified modeling approaches are generally adopted, as they allow reducing the computational effort associated with the numerical simulations. With regard to NO formation, simple one-step rates are used to describe each of the relevant routes contributing to the overall generation of NO, i.e. thermal, prompt, etc... The main drawback associated to a simplified NO formation approach lies, however, in the extreme sensitivity of the lumped rates on the thermo chemical state which characterize the combustion system of interest. Then, a proper description of turbulence-chemistry interactions must be performed in the CFD model, to provide a realistic background for the estimation of NO emissions. This becomes particularly important in flameless combustion regime, which generally requires an accurate description of the gas-phase oxidation, due to the kinetic control on the overall combustion process. The present paper discusses main key aspects and requisite for predicting NO formation in flameless combustion regime. The approach is based on the direct coupling of simplified NO mechanisms to the CFD calculation and is applied to different flameless conditions. An a priori analysis for the selection of the best available CFD model for the system of interest is also proposed. In particular, Principal Component Analysis (PCA) is employed for the extraction of the parameters controlling the thermo-chemical state of the system and to identify the CFD modelling requirements, from the point of view of turbulence/chemistry interaction models.

Keywords MILD combustion, Computational Fluid Dynamics

INTRODUCTION

The numerical simulation of turbulent reacting flows remains a primary challenge due to the wide range of time and length scales associated with practical combustion systems. In some circumstances, a certain degree of decoupling between the combustion process and the system fluid dynamics can be achieved, due to the partial separation of the inherent time scales of fluid flow and chemical kinetics. This allows, for example, to effectively exploit the so-called fast-chemistry combustion models for the description of systems where the combustion process is intimately fast and the overall process is controlled by mixing. However, combustion regimes exist where the oxidation kinetics have to be taken explicitly into account, as it happens in flameless combustion [1], also known as MILD [2] or HITAC [3]. Such combustion regime is characterized by a strong overlap of chemistry and fluid dynamic time scales and requires combustion models able to take into account the effects of finite rate chemistry on the oxidation process. Nevertheless, some degree of decoupling can be still accomplished with respect to the pollutant chemistry, being the latter characterized by timescales much larger than those of the main oxidation process. Moreover, the small concentration
levels of the pollutant species are such that the main species distribution is barely affected by the pollutant formation process.

Our interest is mainly focused on NOx, being such pollutants the main adverse products when operating with “clean” fuels, such as methane and hydrogen. Two options are generally available for the prediction of NOx emissions, namely the direct coupling of simplified global rates into a CFD code (i.e. thermal mechanism, prompt route, etc ...) and the kinetic post-processing of CFD results. The first option generally requires the use of more complex kinetic mechanisms within the CFD simulation for the main oxidation process, whereas simpler kinetic schemes may be adopted in the second case, being the detailed kinetic calculation carried out in a post-processing step. In the present paper, the primary interest is represented by the determination of a simplified modelling approach for NOx formation, through the validation of global kinetic rates (i.e. thermal, prompt, N2O and NNH) relevant at the investigated operating conditions.

The present paper shows a numerical and experimental investigation of a burner, i.e. FLOX®, operating in flameless combustion regime and fed with hydrogen enriched fuels. Further details regarding the burner and its operations can be found in [4]. A primary challenge related to the numerical simulation of such system lies in the limited availability of experimental data, due to its industrial characteristics. For instance, no measurements regarding the flame structure inside the combustion chamber are taken, being the system silicon carbide made, thus not providing any access to the burner interior. Therefore, efforts have been spent to derive information as reliable as possible, by means of the so-called Verification and Validation methodology (V&V) [5]. V&V helps quantifying the uncertainty inherently related to the numerical simulations, providing a measure of the level of confidence associated to the computations. This is a crucial step for an actual validation of computer models, to really help decision making in new design and regulation. The validation of the numerical simulations is carried out using the experimental data available for the temperature profiles on the combustion chamber walls and for the NO emissions in the exhaust stream leaving the burner.

METHODOLOGY

The numerical simulations are carried out using a commercial CFD code FLUENT 6.3 by Ansys Inc, for a set of experimental runs performed on the FLOX® burner varying the hydrogen content of the fuel stream from 0 up to 50% by wt. Additional details regarding the experimental campaign may be found in [4]. However, it should be recalled here that the investigated runs refer to ultra-lean oxidation conditions. This has a direct impact on the approach adopted for modelling NO formation as the conventional formation routes generally available in the commercial codes, i.e. thermal and prompt, do not completely explain the observed pollutant emissions and alternative routes, such as the N2O intermediate and the NNH routes, should be taken into account.

Figure 1 shows the conceptual scheme followed in the experimental and numerical investigation of the system. Experimental data are first used to validate the general fluid-dynamic simulation by comparing the measured and simulated temperatures at the burner walls. Then, the NO calculation
can be carried out with two different approaches, as outlined in Section 1, namely the direct coupling of simplified global formation routes into the main CFD calculation and the kinetic post-processing of simplified CFD simulations, such as through Reactor Network Analysis (RNA) techniques. In the present paper only the results obtained using the direct coupling approach will be presented. Therefore, the CFD simulations are carried out with detailed kinetics for gas-phase oxidation, to base the successive NO calculation on a reliable temperature distribution inside the combustion chamber. This represents a crucial requisite for modeling flameless combustion, as it is acknowledged in the literature [6]. Moreover, an analysis of flameless combustion based on Principal Component Analysis (PCA) indicated the inadequacy of fast-chemistry models, such as the two-parameters flamelet model, for the description of flameless operations [4], thus confirming the need of turbulence/chemistry approaches able to provide an adequate description of finite-rate chemistry effects, via the incorporation of detailed kinetic mechanisms.

**CFD simulations**

Favre-averaged Navier-Stokes equations are solved using the standard k-ε turbulence model. The Eddy Dissipation Concept (EDC) by Magnussen [7, 8] is used for turbulence/chemistry interactions and to include detailed chemistry in the numerical simulation. Two different kinetic mechanisms are adopted to describe the oxidation of methane/hydrogen mixtures, the KEE58 [9] and the DRM-19 [10]. Thermal NO formation is modeled using a Finite Rate (FR) approach and a simplified one-step kinetic mechanism, available in the code [11] and obtained from the Zeldovich scheme by assuming a steady state for the N radicals and relating the O radical concentration to that of oxygen by means of the dissociation reaction [12]. Similarly, prompt NO formation from methane is modeled following De Soete [13]. The N₂O intermediate [14] and NNH [15] routes are also included in the computer model, to account for low-temperature formation mechanisms and for the presence of H₂ fractions in the fuel. The NNH route is not directly available in the code; therefore, it has been implemented by means of a user defined subroutine (UDF) following [16]. The kinetic rates are integrated over a probability density function (PDF) for temperature in order to take into account the effect of turbulent fluctuations on the mean reaction rates [11].
Additional details regarding the modeling approach (i.e. radiative model, spectral properties, ...) can be found in [4]. As far as the boundary conditions are concerned, two user defined functions have been coupled with the code in order to make the burner model self-sufficient. The air inlet temperature is evaluated as a function of the exhaust gases temperature, using an empirical correlation available from the burner supplier. Moreover, particular attention is paid to the boundary condition at the wall delimiting the combustion chamber (radiant tube). The burner under investigation is designed for heating-up applications, in environment where the oxidizing atmosphere must be kept separated from the process atmosphere (e.g. reducing), as it happens in the steel industry for annealing processes. Therefore, a subroutine for the evaluation of the radiative heat transfer from the radiant tube has been developed on purpose [17].

Validation criteria

As outlined in the Introduction, the level of agreement between experiments and numerical simulations needs to be assessed by means of quantitative metrics [18]. These allow estimating the error associated to a numerical simulation, given the availability of experimental data, and provide also a confidence associated to the quantification of such error estimate.

The definition of such metrics requires the determination of the statistical confidence interval for the observed experimental mean, $\bar{y}_e$, together with the definition of a true, $E$, and estimated error, $\tilde{E}$:

$$\mu \sim \left(\bar{y}_e - t_{\alpha/2,\nu} \frac{s}{\sqrt{n}} \right) \bar{y}_e + t_{\alpha/2,\nu} \frac{s}{\sqrt{n}} \right)$$  \hspace{1cm} (1)

$$E = y_m - \mu$$ \hspace{1cm} (2)

$$\tilde{E} = y_m - \bar{y}_e.$$ \hspace{1cm} (3)

In Eq. (1), $\mu$ is the true mean of the observed population, $s$ is the population standard deviation, $n$ represents the number of experiments and $t_{\alpha/2,\nu}$ is the $t$-
\( a/2 \) quantile of the experimental data distribution with \( v = n - 1 \) the degrees of freedom. In Eqs. (2-3) \( y_m \) represents the output of the numerical simulations.

Combining Eqs. (1-3), it is possible to derive an expression for the interval containing the true error associated with the numerical simulations within a prescribed confidence level:

\[
E = \left[ \bar{E} - t_{\alpha/2,\nu} \frac{s}{\sqrt{n}}, \bar{E} + t_{\alpha/2,\nu} \frac{s}{\sqrt{n}} \right]
\]

(4)

where the confidence in the estimation of \( E \) is given by \( C = 100(1 - \alpha)\% \).

Eqs. (2-4) can be easily extended to the case of a system quantity response monitored over a range of the input variable. Moreover, in some applications, it is desirable to provide global metrics, able to summarize the level of agreement for a large number of computational models and experimental data. In particular, an average error metric can be defined as:

\[
E_{\text{avg}} = \frac{1}{x_u - x_l} \int_{x_l}^{x_u} \left( y_m(x) - \bar{y}_e(x) \right) dx
\]

(5)

where \( x_u \) and \( x_l \) define the upper and lower limit of the input variable. The confidence interval to be associated with this average relative error is the average confidence interval normalized by the value of the estimated experimental mean over the range of the data:

\[
\left| \frac{CI}{\bar{y}_e_{\text{avg}}} \right| = \frac{t_{\alpha/2,\nu}}{(x_u - x_l)\sqrt{n}} \int_{x_l}^{x_u} \left| \frac{s(x)}{\bar{y}_e(x)} \right| dx
\]

(6)

**RESULTS**

The present Section describes the results of the validation activity carried out on the system outlined in the Introduction. Following the conceptual description provided in the Methodology Section, the validation of the energy balance inside the combustion chamber is first presented, through the comparison of measured and computed temperatures at the burner walls. Then, the validation of the NO modelling approached is assessed, through the quantification of the error associated to the numerical predictions.

Figure 2 shows a comparison between the calculated and measured average temperatures on the radiant tube, over the range of fuel composition fed to the burner. The computed average temperatures have been obtained from the experimental campaign [4]. It can be observed how the numerical results are very close to the experimental mean for the 10% and 20% cases, while the proposed model underpredict the average radiant tube temperature for all the other cases, although the calculated values are always within the experimental confidence interval. The maximum departure is observed for the 70% \( \text{H} \) thermal input and is around 23 K. This slight under prediction is actually expected, due to the geometric simplification and the choice of a 2D model for the burner, instead of a 3D grid, which determines an over prediction of the recirculation degree [17].
Figure 3 shows the confidence intervals for the average NO emissions from the burner, together with the comparison between experiments and model predictions. Different variants of the model including NNH have been tested, due to an uncertainty in the activation energy for the NO formation reaction via NNH [19]. It can be observed that NO formation is very sensible to such parameter, especially at high H$_2$ concentrations. Figure 3 shows that an impressive range of solutions are obtained by simply acting on the possible source of NO emissions. This represents a strong input towards the development of methodologies for the constructive comparison between numerical results and experimental data, to effectively assess the reliability of the model predictions.

Figure 2 - 95% confidence intervals for the average temperature of the radiant tube and comparison with the numerical results
Figure 3 - 95% confidence intervals for the average NO emission from the burner and comparison with the numerical results.

Figure 3 indicates that the role of the NNH route is critical to explain the NO emissions. Without considering such route the resulting error would be very large. A considerable improvement in the prediction is also obtained by varying the activation energy for the NNH route within the uncertainty range (30±5 kJ/mol) indicated by [19]. The value of 2.5 kJ/mol seems the one providing, in all cases better agreement with the experimental data. Moreover, the KEE-58 mechanism appears to provide always better results than the DRM-19 mechanism. Such results are quantitatively confirmed by the metrics shown in Table 1, following the definition provided in the Methodology Section.

Table 1 - Average and maximum global validation metrics for the average NO emissions from the burner. All average metrics are ±2.1%, with 95% confidence.

<table>
<thead>
<tr>
<th>Model</th>
<th>$\frac{\tilde{E}}{\tilde{y}_{\text{avg}}}$</th>
<th>$\frac{\tilde{E}}{\tilde{y}_{\text{max}}}$</th>
<th>$\frac{\tilde{C}}{\tilde{y}_{\text{max}}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>KEE - Th+Pr</td>
<td>0.992</td>
<td>0.996</td>
<td>±0.022</td>
</tr>
<tr>
<td>KEE - Th+Pr+N₂O</td>
<td>0.635</td>
<td>0.740</td>
<td>±0.022</td>
</tr>
<tr>
<td>KEE - Th+Pr+N₂O+NNH</td>
<td>0.181</td>
<td>0.291</td>
<td>±0.022</td>
</tr>
<tr>
<td>KEE - Th+Pr+N₂O+NNH (Eₐ±2.5 kJ/mol)</td>
<td>0.089</td>
<td>0.191</td>
<td>±0.040</td>
</tr>
<tr>
<td>KEE - Th+Pr+N₂O+NNH (Eₐ±2.5 kJ/mol)</td>
<td>0.138</td>
<td>0.276</td>
<td>±0.040</td>
</tr>
</tbody>
</table>

CONCLUSIONS
A numerical investigation of NO formation in flameless combustion has been carried out. Results from CFD computations have been validated against experimental campaigns carried out on semi-industrial flameless burner. The Verification and Validation (V&V) methodology has been
applied to quantitatively assess the reliability of simplified global NO mechanisms directly coupled to the CFD code. Results show that it is possible to achieve a reasonable agreement between simulations and experiments only by taking into account detailed kinetic schemes for gas-phase combustion and including, with simplified one-step mechanisms, all the relevant sources of NO at the investigated operating conditions. In particular, the role of the so-called NNH route appears determinant, representing the main source of NO at the investigated operating conditions.

REFERENCES