HIGH PRESSURE METHANE-OXYGEN COMBUSTION KINETIC ANALYSIS

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Abstract
Kinetic assessment of high pressure methane-oxygen ignition and combustion was performed as preliminary step towards Liquid Rocket Engine (LRE) on-ground technological demonstrator design, manufacturing, development, experimentation and optimization. Ignition delay times were calculated using a commercial zero-dimensional software (ANSYS ChemkinPro 17.0) and literature available both detailed and reduced kinetic schemes of methane oxidation at temperatures, pressures and mixture ratios generally experienced in LRE combustion chamber. Comparison of kinetic parameters, among the various investigated kinetic schemes, allows the identification of the most suitable mechanism for analysing, by means of a computational approach, the reacting flow dynamics of methane-oxygen mixtures with in a high pressure LRE and build up a numerical method for improving the predictive capacity of Computational Fluid Dynamics (CFD) simulations used for design criteria.

Introduction
At the moment, the access to space is primarily guaranteed by rocket engines driven by means of exothermic, high pressure, chemical reactions i.e., combustion processes. Among the family of rocket engines, for many mission profiles liquid propellants rockets offer several advantages e.g., high specific impulse, throttability, shutdown and restart operations. In recent years, considerable efforts were devoted to design, manufacture and realize a LRE fuelled by methane. Indeed, that simplest hydrocarbon possesses many advantages in comparison with more conventional hydrogen e.g., easier to store, higher density, more elevated boiling temperature, therefore simplifying the tank thermal protection devices, not requiring helium to drain and pressurize, etc. [1].

Investigation and optimization of combustion phenomena occurring within a LOx/LCH₄ LRE is useful for designing and realizing more efficient and high performing space propulsion systems i.e., able to generate more elevated specific impulses with lower costs and reduced thrust chamber sizes, therefore increasing the payload capacity.
A first well-consolidated approach is based on Computational Fluid Dynamics (CFD) simulations of multiphase, high pressure, reacting turbulent, multi-species, unsteady flows of propellants ignition and combustion using commercial and in-house codes.

Nevertheless, the ever-increasing Central Processing Unit (CPU) power and availability of clusters of super-computers, CFD simulations of full-scale thrust chambers require millions of mesh nodes and therefore a simplified kinetic mechanism is often used for achieving a preliminary solution in a reasonable time. For this reason, the use of a suitable kinetic scheme, capable of both gathering the main aspects of the combustion process and at the same time reducing the computational cost is much appreciated.

A valuable criterion for discerning among various kinetic mechanisms is based on calculation of ignition time delay by means of zero-dimensional kinetic software e.g., ANSYS ChemkinPro, Cantera, Kintecus, etc.

In this investigation, the commercial software ANSYS ChemkinPro 17.0 was used and a parametric study, of several detailed, skeletal and reduced schemes was performed aimed to develop a deeper understanding of methane-oxygen, high-pressure ignition and combustion and to identify the most suitable kinetic mechanism to implement into commercial an in-house CFD codes for LRE combustion simulations.

**Kinetic Mechanisms**

In literature, many reduced kinetic mechanisms for methane oxidation are available ranging from one-step global reactions up to skeletal mechanisms. Among the various usable kinetic schemes, the following five mechanisms have been selected and preliminary tested in different operative conditions (temperatures, pressures, equivalence ratios) by means of calculation of the ignition delay time $\tau_{\text{ign}}$ predicted in zero-dimensional simulations:

1. ANSYS FLUENT one-step [2];
2. Jones & Lindstedt [3];
3. Revised Jones & Lindstedt or Frassoldati [4];
4. Li & Williams [5];
5. REDRAM [6].

1. The ANSYS FLUENT one-step is the global reaction, proposed by the company ANSYS, owner of the CFD commercial code FLUENT for simulations of the methane-oxygen combustion, in which the kinetic parameters are optimized using a special procedure for reproducing, in the most accurate way, the experimental ignition time delay data. The advantage of this mechanism is its simplicity. Indeed, it represents the most compact way of modelling the methane oxidation with the minimum number of species and reactions. Therefore, the CPU power required for CFD
simulations using that scheme is the lowest possible. However the main disadvantage of all one-step global reaction mechanisms is the noticeable over-prediction of the adiabatic flame temperature, due to the absence into that scheme, of endothermic dissociation reactions of CO$_2$ and H$_2$O spontaneously occurring at elevated temperatures.

2. The Jones & Lindstedt kinetic scheme is a very popular reduced mechanism consisting of 6 chemical species (plus the optional inert component) involved in 4 reactions. It represents an extension of the one-step global reaction mechanism that is capable of reproduce more accurately the peak temperature.

3. The Revised Jones & Lindstedt kinetic scheme is an optimization of the previous mechanism, specifically conceived for oxy-fuel combustion systems, including also the endothermic dissociation reactions of H$_2$O and CO$_2$ and considering the significant impact in limiting the heat release of the radical pool, therefore able to predict correctly the adiabatic flame temperature of the methane-oxygen reacting mixture.

4. The Li & Williams nine-step reduced mechanism is a kinetic scheme especially formulated for predicting the ignition characteristics of methane-oxygen reacting mixtures at low temperature (T < 1300 K) and equivalence ratio below 1.5. It consists of 11 chemical species interacting through 9 reactions, eight of which are linearly independent differential equations containing non-vanishing chemical source terms and the seventh step is not linearly independent, although its rate, of course, is present in the systems of equations [5].

5. The REDRAM or REDuced Ram Accelerator Mechanism is a skeletal kinetic scheme, containing 34 reactions and 22 species, derived from the RAMEC mechanism [7] by means of a detailed reduction procedure, consisting in retaining the elementary-reaction format used in the full mechanism and eliminating reactions and species with no influence on the induction time and/or concentration of the key molecules and products final temperature. Also, a sensitivity analysis has been performed for driving the elimination process [6]. The REDRAM was proved to predict ignition delay times $\tau_{ign}$ to better than 5% and post-combustion temperatures to within 10 K of the full mechanism over a wide range of operating conditions.

Finally, Table 1 summarizes the available information about the investigated kinetic schemes, in terms of number of chemical species and reactions, and operative conditions validity range.
Table 1. Summary of the validity range for the investigated kinetic schemes.

<table>
<thead>
<tr>
<th>Kinetic schemes</th>
<th>Species</th>
<th>Reactions</th>
<th>T [K]</th>
<th>P [atm]</th>
<th>φ</th>
</tr>
</thead>
<tbody>
<tr>
<td>ANSYS FLUENT one-step</td>
<td>4</td>
<td>1</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>Jones &amp; Lindstedt</td>
<td>6</td>
<td>4</td>
<td>n.a.</td>
<td>1</td>
<td>n.a.</td>
</tr>
<tr>
<td>Revised Jones &amp; Lindstedt</td>
<td>9</td>
<td>6</td>
<td>n.a.</td>
<td>1</td>
<td>n.a.</td>
</tr>
<tr>
<td>Li &amp; Williams</td>
<td>11</td>
<td>9</td>
<td>&lt;1300</td>
<td>1-150</td>
<td>&lt;1.5</td>
</tr>
<tr>
<td>REDRAM</td>
<td>22</td>
<td>34</td>
<td>1000-1500</td>
<td>40-260</td>
<td>0.4-6</td>
</tr>
</tbody>
</table>

Zero-Dimensional Kinetic Model
In order to test the five-selected skeletal and/or reduced kinetic schemes and to identify the best mechanism to implement in fully turbulent 3D, high pressure, and steady or unsteady CFD simulations, zero-dimensional, homogeneous, adiabatic, isobaric, batch reactor calculations were carried out, at different operative conditions: temperatures (T), pressures (P), equivalence ratios (φ) using ANSYS ChemkinPro (release 17.0) commercial software.

Results and Discussion
In the present study methane-oxygen, combustion at elevated pressure was investigated. Therefore 3 very high pressures of 50, 100 and 150 bar, 3 typical equivalence ratios of 0.5 (fuel-lean), 1 (stoichiometric) and 2 (fuel-rich) and two initial temperatures of 800 (less below the auto-ignition temperature of the methane-air mixtures equal to 813 K) and 1000 K (above the auto-ignition temperature) were selected as input data.

The output of every zero-dimensional simulation is the temperature-time profiles, from which a preliminary evaluation of the ignition delay times τ_{ign} can be calculated as the time corresponding to the abrupt increase of the temperature up to the adiabatic flame level.

As an example, Figure 1 shows a comparison of temperature profiles at the three different pressures, among the various kinetic schemes investigated, at the fixed initial temperature of 1000 K and at constant equivalence ratio equal to 1.
Conclusions
As expected, the best agreement of ignition delay time and peak temperature results, calculated using the detailed RAMEC kinetic mechanism was achieved by the REDRAM skeletal scheme. It is not surprising because the REDRAM is the reduced version of the RAMEC, especially conceived for predicting the combustion of methane at elevated pressures and intermediate temperatures. In particular, at every pressure and equivalence ratio investigated, the agreement, between the two kinetic schemes is very satisfactory, setting 1000 K as initial temperature, but it is less appealing at 800 K. In fact, 800 K is beyond the range of operating conditions of the REDRAM mechanism (1040 - 1600 K).

In addition, the ignition delay times calculated by the Li & Williams mechanism are of the same order of magnitude of the induction times obtained using the full RAMEC kinetic scheme. However, the peak temperatures are not always similar. This is justifiable, because the Li & Williams mechanism is designed to model only the methane-oxygen ignition, but not the whole combustion; and therefore, the endothermic dissociation reactions of CO$\textsubscript{2}$ and H$\textsubscript{2}$O are not considered.

It is interesting to notice the strong lack of accuracy of the Jones & Lindstedt and the Revised Jones & Lindstedt reduced mechanisms, at least in the operative envelope of the present work, especially in terms of ignition delay times, that is underpredicted by about three orders of magnitude. Instead, the adiabatic flame temperatures are more correctly calculated.
Finally the ANSYS FLUENT one-step global reaction, although over-predict the ignition delay times by about two order of magnitude, and underrate the peak temperatures by about 25%, on the basis of these data, is anyway more suitable than the Jones & Lindstedt and Revised Jones & Lindstedt kinetic schemes.

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References