Simplified chemical kinetic mechanisms for hybrid rocket propulsion

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Abstract

A set of simplified chemical kinetic mechanisms for hybrid rockets applications using gaseous oxygen (GOx) and hydroxyl-terminated polybutadiene (HTPB) is proposed. The starting point is a 94-species, 614-reactions, detailed chemical kinetic mechanism for butadiene combustion, the primary HTPB pyrolysis product. The simplification is carried out systematically by means of a Computational Singular Perturbation (CSP) based algorithm. The simplification algorithm is fed with the steady-solutions of classical flamelet equations, these being representative of the non-premixed nature of the combustion processes characterizing a hybrid rocket combustion chamber. Three simplified chemical mechanisms, each comprising approximately 20 species, are obtained for three different pressure values selected in accordance with an experimental test campaign of lab-scale hybrid rocket static firings. Finally, a comprehensive simplified mechanism containing 27 species is shown to be capable of reproducing the main flame features in the whole pressure range considered.

1. Introduction

Hybrid propellant rockets have been recently proposed as a valuable choice for future-generation propulsion systems mainly because of design simplicity, safety of operations, and a relatively low development cost [1]. A number of technical challenges are still to be overcome in order to reach the standards of solid and liquid propulsion systems, such as the low regression rate as well as the reduced combustion efficiency. The Computational Fluid Dynamics (CFD) modeling of oxidizer atomization and vaporization, solid fuel pyrolysis, mixing and combustion in the gas phase, soot formation, and radiative heat release has raised a considerable interest in the scientific community. In this framework, the development of suitable simplified chemical kinetic mechanisms, capable of containing the CFD computational costs, is of fundamental importance. In the present work, the CSP-based skeletal reduction algorithm [2] is employed to simplify a detailed chemical kinetic mechanism for butadiene [3] which is the primary HTPB pyrolysis product. The simplification starting point is the creation of a dataset coherent with the current application. In this paper the dataset consists of the steady-state solutions of flamelet equations matching the pressure range and the propellants temperatures taken from the lab-scale hybrid motor tested at the University of Naples Federico II [4, 5, 6] which has been recently investigated using global mechanisms [7, 8, 9]. The flamelet equations are in fact the prototypical representation of a diffusive flame which is not encountering local extinction or autoignition phenomena, such as the case of hybrid rocket systems.

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2. Theoretical formulation

2.1. CSP reduction

The mechanism simplification is carried out by resorting to a validated numerical toolbox, CSPTk\(^1\), which relies on an analysis and reduction strategy based on computational singular perturbation (CSP) [10, 11], that has been used extensively with several models of hydrocarbon fuels [2, 12].

In the CSP-based skeletal reduction algorithm, the criterion for selecting the subset of reactions and species to be retained is based on their relevance to the fast or slow dynamics of a prescribed set of "target" species, the concentration of which is desired to be accurately reproduced by the skeletal mechanism. This algorithm is based on the ability to decompose the chemical kinetic processes into fast and slow components, as offered by CSP, and to identify the processes that produce the most significant contribution in either the fast or slow components. As a measure of the degree to which a species contributes to the fast/slow dynamics of the target species, the algorithm adopts the fast/slow CSP Importance Indices, which measure the contribution of each elementary reaction in the detailed mechanism to the fast and slow components of each species production rate. Next, a new set of active species is identified by collecting all the species participating in the selected reactions.

This approach is very useful in generating a spectrum of simplified mechanisms of different sizes, each associated with a given degree of fidelity in predicting the chosen quantities of interest, specified by a tolerance on the Importance Indices. The final choice of the simplified mechanism consists in finding a compromise between the dimensionality reduction and the required accuracy in the replication of the behavior of the species of interest.

More details on the simplification algorithm can be found in [12, 13].

For any given database of states, and considering a given set of quantities of interest - such as the set of target species - and a tolerance \(\tau\) on Importance Indices [2, 12], the CSP-based analysis and simplification strategy provides a simplified mechanism, being a subset of the starting mechanism.

2.2. Choice of a proper dataset - The flamelet equations

The dataset to be fed in the simplification algorithm should be selected in accordance with the specific physical problem of interest. The combustion processes typical of a hybrid rocket combustion chamber consist in diffusive flames located where the mixing between the gaseous fuel emanated by the pyrolysis solid propellant and the injected oxidizer takes place. The laminar flamelet is the simplest prototypical system representing a diffusive flame and therefore was chosen to generate the numerical datasets. Defining the mixture fraction according to Bilger [14], the steady state flamelet equations describe the balance of reactive and diffusive processes in a non-premixed system. Using unity Lewis number assumption [15], they read:

\[
\dot{\omega}_\alpha = -\frac{1}{2}\rho\chi \frac{\partial^2 Y_\alpha}{\partial \xi^2} , \quad \dot{\omega}_T = -\frac{1}{2}\rho\chi \left[ \frac{\partial^2 h}{\partial \xi^2} + \sum_{\alpha=1}^{n_s} h_\alpha \frac{\partial^2 Y_\alpha}{\partial \xi^2} \right] ,
\]

where \(\rho\) is the mixture density, \(Y_\alpha\) are the species mass fractions, \(h\) and \(h_\alpha\) are the mixture and \(\alpha\)–th species sensible enthalpies respectively. These equations are derived assuming the pressure \(p\) being constant in the mixture fraction space. While the scalar dissipation \(\chi = \left(\frac{\partial^2}{\partial \xi^2}\right)^2\) regulates the diffusive processes. Although in the CFD context the scalar dissipation is computed from the physical mixture fraction field, in this case it is a user-provided handling parameter.

\(^1\)CSPTk - A Software Toolkit for the CSP and TSR Analysis of Kinetic Models and the Simplification and Reduction of Chemical Kinetics Mechanisms, 2015. The software can be obtained upon request from M. Valorani (mauro.valorani@uniroma1.it).
2.3. Choice of the simplified mechanism - Error definitions

The CSP-based simplification procedure does not allow to enforce an a-priori error requirement on the simplified mechanisms, due to the highly non linear character of the system of interest. For a given generated mechanism, an a-posteriori error estimation needs to be carried out to assess its quality in replicating the steady-state solution of the species of interest. The discrepancies between the steady-state solutions \( Y_{\alpha}^{d}(z) \) and \( Y_{\alpha}(z) \), \( \alpha = 1, ..., ns + 1 \), generated with the detailed and simplified mechanism respectively, can be computed as an integral measure of their distance in the mixture fraction space. For the \( \alpha \)-th species, it reads:

\[
E_{\alpha} = \int_{0}^{1} |Y_{\alpha}^{d}(z) - Y_{\alpha}(z)| \, dz
\]

We define the mechanism error as the average of the errors associated to the target species. This error is expected to be much lower than the error averaged over all the species since, by construction, the skeletal mechanisms are tailored over the target species only.

3. Results and Discussion

The CSP-based simplification algorithm has been employed on 3 distinct datasets, namely the steady-state solutions of 3 laminar flamelets at the pressure values of 3, 17 and 36 bar respectively, spanning the pressure range of the aforementioned experiments and numerical campaign [7]. The scalar dissipation \( \chi \) has been assigned the value of 100 Hz for all the test cases, this being representative of an hybrid combustion chamber [7].

Each analysis allowed to generate a set of simplified mechanisms of different sizes, following the specification of a number of increasing tolerances on the importance indices and the selection of a set of target species, namely: CO\(_2\), H\(_2\)O, CO, H\(_2\), OH and C\(_2\)H\(_2\).

![Graph showing error as a function of number of species](image)

Figure 1: Integral flamelet shape %error as a function of the number of active species in the simplified mechanisms for the three representative pressure considered (p = 3bar, 17bar, 36bar).

While the first four species are important to recover the right equilibrium temperature along the flamelet profile, the two latter are chosen for this particular application. The hydroxyl radical OH is selected since...
it is the primary species which accelerate throat erosion. On the other hand, acetylene $\text{C}_2\text{H}_2$ is selected being an important polycyclic aromatic hydrocarbon (PAH) precursor which can be correctly represented by steady state flamelet solutions because of its relatively fast chemistry [16, 17]. Nevertheless, semi-empirical soot models use acetylene-based chemistry for soot inception and growth [18].

Figure 1 shows the $a$-posteriori error estimation for all the generated mechanisms.

Figure 2: Comparison between the detailed and selected simplified mechanisms for the three pressure considered ($p = 3\text{bar}$, $17\text{bar}$, $36\text{bar}$). Results are shown in terms of temperature, major species (fuel $\text{C}_4\text{H}_8$, oxidizer $\text{O}_2$ and products expressed as a progress variable $C = \text{CO}_2+\text{CO}+\text{H}_2+\text{H}_2\text{O}$) and target species (hydroxyl radical $\text{OH}$ and acetylene $\text{C}_2\text{H}_2$).

One mechanism for each pressure has been chosen based on what we consider an acceptable trade-off between mechanism size and solution accuracy. In particular, a 19-species mechanisms has been selected for the $3\text{bar}$ case, a 19-species mechanisms for the $17\text{bar}$ case and a 20-species for the $36\text{bar}$ case. All of them are able to deliver a steady-state solution whose percent-error with respect to the detailed one is

\[ \text{VII. 4} \]
Figure 2 shows the comparison between the detailed and the select simplified mechanisms for the three pressure considered in terms of the steady-state solutions of temperature, major species (fuel \( \text{C}_4\text{H}_6 \), oxidizer \( \text{O}_2 \) and products \( \text{CO}_2, \text{CO}, \text{H}_2, \text{H}_2\text{O} \)) and other species of interest (hydroxyl radical \( \text{OH} \) and acetylene \( \text{C}_2\text{H}_2 \)).

The simplification algorithm has then been employed comprehensively on the whole pressure range. The adopted database of states comprised the steady-state solutions of the detailed mechanism computed at 11 pressures evenly selected between 3 bar and 36 bar, in order to provide one simplified mechanism with good accuracy over all the pressure range. The select simplified mechanism, consisting of 27 species and 212 reactions, exhibits an error below 10% when employed at the three test pressures of 3, 17 and 36 bar. Its performance at the three different pressures in terms of the accuracy in replicating the species of interest at steady-state are shown in figure 3. A good agreement between the simplified mechanism and the detailed one can be observed for the temperature profile as already seen in the previous cases. A better representation of the acetylene is also provided with respect to the previous, single-pressure, simplified mechanisms. Moreover, although not presented here, all the resulting simplified mechanisms proved to be in agreement with the reference solutions up to \( \chi =10^5 \) Hz.

Figure 3: Steady-state solutions obtained with the comprehensive 27-species simplified mechanism at the three representative pressure values considered (\( p = 3 \text{bar}, 17 \text{bar}, 36 \text{bar} \)) in terms of temperature and target species (hydroxyl radical \( \text{OH} \) and acetylene \( \text{C}_2\text{H}_2 \)).

4. Conclusion and perspective

A set of simplified chemical kinetic mechanisms for hybrid rockets applications using gaseous oxygen (GOx) and hydroxyl-terminated polybutadiene (HTPB) have been proposed using a Computational Singular Perturbation (CSP) based algorithm operating on steady-state flamelet solutions datasets. The present set is summarized in Table 1.

The simplified mechanisms show reasonable agreement with the detailed mechanism results in the pressure range and propellants temperature considered. The set of simplified chemical kinetic mechanisms for hybrid rockets applications using gaseous oxygen (GOx) and hydroxyl-terminated polybutadiene (HTPB) are made available to the combustion and propulsion communities and may be obtained from the authors.
<table>
<thead>
<tr>
<th>Pressure [bar]</th>
<th># of species</th>
<th># of reactions</th>
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<tbody>
<tr>
<td>3</td>
<td>19</td>
<td>104</td>
</tr>
<tr>
<td>17</td>
<td>19</td>
<td>148</td>
</tr>
<tr>
<td>36</td>
<td>20</td>
<td>150</td>
</tr>
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<td>3-36</td>
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Table 1: Summary of simplified mechanisms

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References


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