DERIVATION AND VALIDATION OF AN ARRHENIUS-BASED REDUCED GLOBAL MECHANISM FOR HYDROGEN-AIR FLAMES

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Abstract

A best-fitting methodology is applied in this work to derive an explicit, analytical dependence of reaction rate constant parameters on equivalence ratio, system pressure, and unburned gas temperature for an Arrhenius-based reduced one-step kinetics in the case of hydrogen-air combustion. A classic Pre-Exponential Adjustment (PEA) approach has been extended to capture both the equivalence ratio and pressure dependence of the laminar burning rate. A correction has also been introduced for temperature profile in the flame reaction region, improving the flame thermal thickness predictions. Both irreversible and reversible global reaction steps have been considered, and it has been observed that a backward path must be included to preserve the flame structure and adiabatic flame temperature near stoichiometry. Particular attention has been posed in separating the dependence on thermodynamic state and composition in the definition of the Pre-Exponential Adjustment laws, to reduce the numerical stiffness of the reduced chemistry scheme. Computations of one-dimensional unstrained/strained laminar flames have been performed for a wide range of pressures ([1; 30] atm), unburned gas temperature ([300; 800] K), and equivalence ratio ([0.4; 6.0]), showing a good agreement of the reduced mechanism with respect to detailed kinetics.

Introduction

Despite the full kinetics of hydrogen oxidation being well-known and studied, its integration into CFD calculations is challenging, with simplified chemistry mechanism becoming necessary, if not mandatory, to reduce the computational cost of simulations, especially in cases with complex geometries at high-pressure conditions. Three main pathways can be followed to reduce hydrogen kinetics. We first recall tabulated chemistry (e.g. [1]); this approach however makes strong assumptions on the combustion regime and raises multiple challenges on its applicability for multi-regime flames, often characterizing hydrogen systems (e.g., see the HYLON flame [2]). The inclusion of both premix and diffusion flames may result in tables with a size that may no longer be acceptable or require the use of expensive algorithms for storing and searching out data [3]. A second route is based on an analytical derivation of the reaction rate by means of first principles-derived approaches, as the quasi-

steady-state (QSS) approximation; in this context, we recall the model proposed in [4], based on the QSS approximation for all radicals, including H. This kind of approach, albeit formally rigorous and correct only for certain flame conditions, can nevertheless be difficult to implement in existing numerical codes, due to the non-Arrhenius-based reaction rate expression. Finally, a third approach relies on a "best-fit" targeting of reaction rate parameters to match detailed kinetics or experimental result. Some applications of this approach for hydrogen/air chemistry could be found in [5, 6], where stoichiometry-dependent Arrhenius-based reaction rate parameters for an overall irreversible reaction were defined for specific mixture conditions under unity Lewis number approach. While all mentioned works provide reasonably good descriptions of hydrogen oxidation for the specific flame conditions for which they were conceived, there is a lack in literature for an Arrhenius-based global mechanism able to capture hydrogen flames main properties in a sufficiently wide range of conditions. Based on these considerations, the present work, albeit recognizing the importance of complex chemistry and the consequent limit in accuracy of global description, aims at filling this gap, by exploiting the numerical simplicity of the best-fitting approach to define a one-step reduced mechanism describing, with sufficient accuracy, the main properties of hydrogen-air flames for several reactants' states. This may be used for preliminary calculations within CFD codes, for fast yet effective simulations prior of the introduction of detailed kinetics.

Derivation of the one-step scheme
Despite combustion being an irreversible process, hence described by a global irreversible reaction, the consequent assumption of complete combustion is not suitable to describe flame structure and temperature in the case of hydrogen combustion, especially in the near-stoichiometry region. Consequently, the global one-step reaction adopted in the proposed scheme is the reversible reaction $2\,H_2 + O_2 \rightleftharpoons 2\,H_2O$. The reaction rate constants are here expressed in the form of a modified Arrhenius equation for the forward reaction (k_f), and of a standard Arrhenius equation for the backward step (k_b), with Pre-Exponential Adjustment (PEA) laws adopted for the pre-exponential factors A_f and A_b to capture pressure- and composition-dependent behaviors. Based on [7, 8], pressure-dependent activation energies $E_{a,f}$, and $E_{a,b}$, and reaction orders n_{H2}, n_{O2} and n_{H2O} have been introduced. The temperature exponent of the forward reaction has been evaluated as $\beta = n/2 - 1$, with n being the overall reaction order. The pressure dependence for these parameters allows for a self-consistency of the reaction rate definition, and of the PEA law, at different system pressures, preserving the structure of the model over a wider range of initial conditions. For the forward Pre-Exponential Factor, the PEA is given by the product

$$A_f = A_f^*(p)f(\phi)g(\phi, p) \,, \tag{1}$$

where A_f^* represents the value of Pre-Exponential Factor matching the burning rate at stoichiometry and is linearly dependent on system pressure. The function f,

dependent only on equivalence ratio, has been defined to capture the impact of stoichiometry on the burning rate at normal temperature and pressure, and assumes the form

$$f(\phi) = \psi_0 + \psi_1 \exp\left[-\psi_2 \left(\frac{\phi - \varphi_0}{\psi_3}\right)^2\right] - \psi_4 \tanh(\phi - \varphi_1). \qquad (2)$$

Being the impact of pressure different on lean and rich flames, the function g has been introduced, to extend the model on a wider range of pressure:

$$g(\phi, p) = [\xi_0 + \xi_1 \tanh(\phi - \varphi_2)]^{[\xi_2 \ln(p/p^0)]}. \qquad (3)$$

The pressure exponent allows for the scalability of the model, at least in the range of system pressures tested in the present study. Being it a logarithmic term, the condition $g(\phi, p) \equiv 1$ for $p = p^0 = 1$ atm is automatically imposed. For the backward reaction, the Pre-Exponential Factor is computed from the one of the forward reaction by taking into account equilibrium. These explicit functions allow, at least in the considered range of states, a computationally cheap prediction of laminar burning velocity of premixed hydrogen flames.

Together with flame speed, flame thermal thickness is another important parameter for CFD codes since it defines mesh resolution constraints. Under the assumption of constant non-unity Lewis number [9, 10], an additional function has been introduced to adjust the diffusion parameters, so that flame thickness is properly predicted. In particular, Prandtl and Schmidt numbers, as well as A_f and A_b, are divided by a Flame Thickness Adjustment (FTA) term:

$$FTA(\phi) = \frac{\sigma_1}{1 + \exp\left(-\frac{\phi + \sigma_2 - \sigma_3/2}{\sigma_4}\right)} \left[1 - \frac{1}{1 + \exp\left(-\frac{\phi + \sigma_2 + \sigma_3/2}{\sigma_5}\right)}\right] - \sigma_6. \qquad (4)$$

Validation of the one-step scheme

The validity of the reduced one-step scheme 1S_H2AIR_REV_FGS has been assessed by performing flamelet calculations involving hydrogen-air mixtures and comparing with experimental results or reference calculations based on the San Diego (UCSD) [11], the Konnov [12], and the H2_NOX_15_94_TC [10] mechanisms. A comparison of the laminar flame speeds predicted by the reduced mechanism with the reference schemes and experimental data is shown in Fig. 1. It can be observed that the proposed scheme is able to capture with elevated accuracy the burning rate at all system pressures of interest, with a maximum relative percentage error with respect to the UCSD scheme of 6% in the whole range of pressures considered.
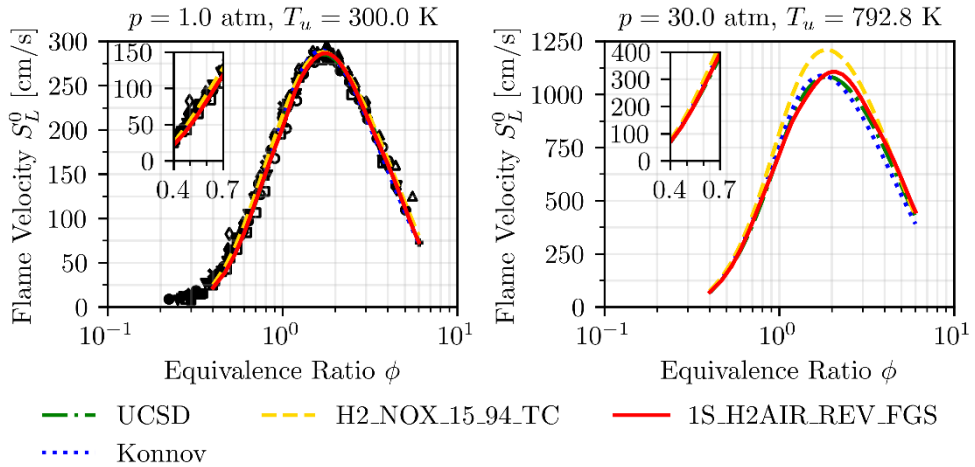
Figure 1. Laminar flame speed of H_2/air at 1 atm (left) and 30 atm (right) versus equivalence ratio, with a focus on the lean regime for $0.4 \leq \phi \leq 0.7$. Comparison between experimental measurements (symbols) taken from [3] and references therein, and numerical integrations with reduced and reference schemes.

The importance of the *FTA* function is proved in Fig. 2, where flame thickness results are shown, with the modification of diffusion coefficients allowing to adjust the temperature gradient of the reduced scheme. Interestingly, although the thickness value range varies significantly with pressure, the scaling factor between the detailed chemistry and the reduced scheme remains almost unaffected.

Finally, stretch response has been analyzed by considering consumption speeds in a counterflow premixed flame configuration, with this quantity defined as in [9]:

$$S_c = -\frac{1}{\rho_u \left(Y_F^u - Y_F^b\right)} \int_{-\infty}^{+\infty} \dot{\omega}_F \, d\mathbf{n} \tag{5}$$

As shown in Fig. 3, a very good agreement can be observed for lean flames, which are of the utmost interest for industrial applications. Reasonable results are found also for rich flames, while the most significant differences are obtained for a stoichiometric flame. In this case, the imposition of a constant value for Lewis numbers, which directly impact stretch response, in the simplified transport model adopted for the reduced schemes, can be at the origin of such limitation. In future work, the *FTA* function may be adapted to dynamically vary the Lewis number, so that a better prediction of such behavior can be obtained for all flames of interest.
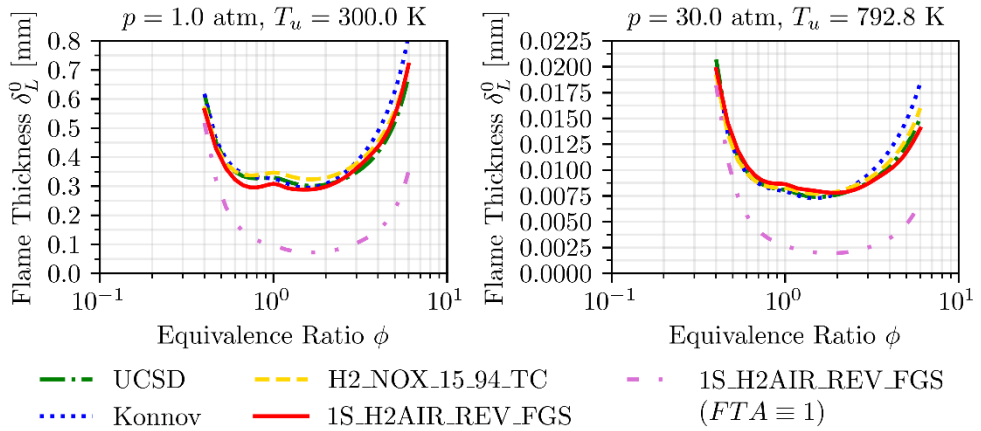
Figure 2. Thermal flame thickness of H_2/air at 1 atm (left) and 30 atm (right) versus equivalence ratio. Comparison between numerical integration with reduced schemes and reference mechanisms.
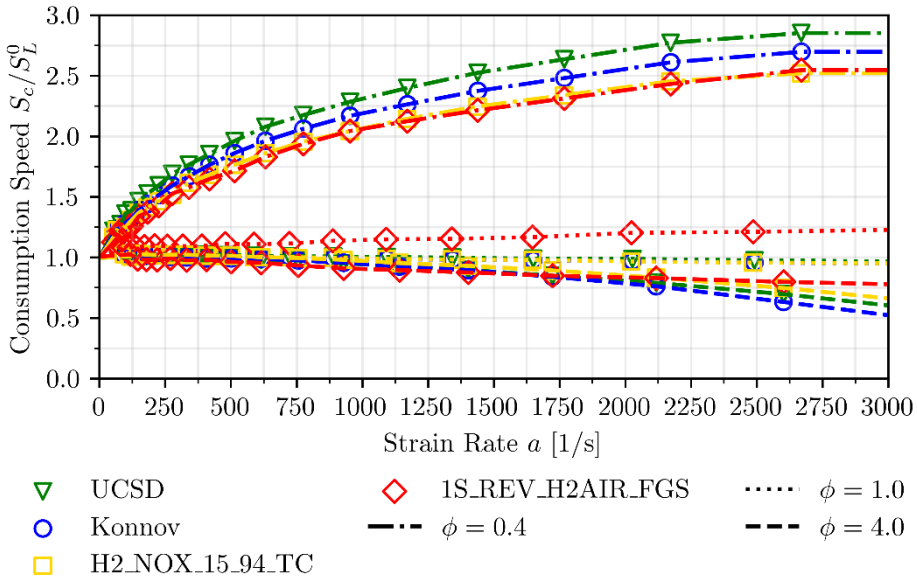

Figure 3. Normalized consumption speed versus global strain rate at different values of equivalence ratio. Comparison between numerical integration with reduced and reference schemes.

Conclusions

In this work, the derivation of a global one-step reduced scheme, based on an Arrhenius formulation, was presented. The mechanism is based on an analytical modelling of hydrogen oxidation to reduce the number of species, hence of transport equations

to solve, in CFD codes, with a significant gain in computational efficiency. The proposed model has been validated by comparison with reference schemes for canonical flamelet configurations, showing an overall good agreement in the prediction of main flame properties. Some limits have been found in the prediction of stretch response for stoichiometric flames, indicating potential for further optimization.

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