



Explicit formulation of the reactivity of hydrogen, methane and decane



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ABSTRACT

Explicit expressions for chemical times relative to ignition, as functions of pressure, temperature and reactants concentrations are derived for hydrogen, methane and decane. They stem from an eigenvalue analysis, similar to that used in the Computational Singular Perturbation method among others. Significant simplification arises from neglecting high-order terms in the characteristic polynomial, allowing direct analytical resolution. Such expressions find many applications: they can serve to readily identify the most reacting areas in a complex flow simulation, in runtime or as a post-processing; or provide a simple way to assess a general activation energy of the chemical process. They may also provide a suitable alternative to the tabulated chemical times required in certain turbulent combustion models.

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1. Introduction

In the past decades, the number of challenges of the combustion science community has increased: to the initial goal of obtaining a high power output were progressively appended the objectives of obtaining more efficient energy production, and reducing contaminants emissions. This motivated extensive studies of the fuel's flammability characteristics [1–6], pollutants emission being tightly bound to the fuels kinetics. These studies are of the utmost importance for the community, and the kinetic rates are being continuously improved.

Unfortunately for the engineer, the number of elementary reactions to consider is quite intimidating: from 21 for the H₂ elementary fuel [3], to several thousands for kerosene [2,6]. Each of these reactions have a rate of progress which may be associated to a kinetic time. It is therefore useful to develop techniques able to identify the governing scales in the combustion process, a first step in reducing the chemistry complexity.

In this paper we present a derivation of explicit expressions for the characteristic chemical times related to the ignition process, as a function of the mixture composition, pressure and temperature conditions. The first section relates the characteristic autoignition times to an eigenvalue problem, a well-known property at the base of various reduction techniques [7,8].

In the second section it is shown, in the case of hydrogen, that under high temperature conditions this problem can be considerably simplified, leading to explicit expressions of the eigenvalue. This peculiarity allowed us in the past to develop reduced chemistry models for both hydrogen and syngas, able to reproduce most combustion processes, including autoignition [9–12].

An extension of the formulation is proposed in the last section, in order to cope with methane and decane under high-temperature conditions, where chain-branched reactions are predominant.

2. Association of the chemical time scale to an eigenvalue problem

The evolution of the *i*th species molar concentration C_i in an isobaric spatially homogeneous reactor can be described by the integration of the differential equation

$$\frac{dC_i}{dt} = \dot{\omega}_i(C_i), \quad (1)$$

where $\dot{\omega}_i$ is the chemical source term for species *i*, which stems from the kinetics mechanism involved.

Some techniques determine the times of kinetics processes as the inverse eigenvalues of the Jacobian, a matrix **J** with terms

$$J_{ij} = \frac{\partial \dot{\omega}_i}{\partial C_j}. \quad (2)$$

For instance, the Computational Singular Perturbation (CSP) method [7], as well as the Intrinsic Low-Dimensional Manifold (ILDm) method [8] are two important contributions that lead to

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recent systematically reduced chemistry models [13–15]. The study of the Jacobian's eigenvalues is also key to the Chemical Explosive Mode Analysis (CEMA), developed as a diagnostic to identify flame and ignition structure in complex flows [16,17].

Applying the aforementioned techniques to H₂–O₂ for instance would *a priori* require the resolution of an 8 × 8 eigenvalue problem, since there are 8 reactive species involved in the detailed chemistry [3]. Application to more complex fuels becomes rapidly very expensive as methane and kerosene require consideration of respectively 52 [18] and thousands of reactive species [6].

The procedure we follow in this paper is very similar to these methods in essence. However, by systematically simplifying the characteristic polynomial, we are able to offer a simple analytical expression for the eigenvalue of interest to ignition – the positive eigenvalue, characteristic of the explosive mode, for the three fuels considered here: hydrogen, methane and decane.

3. The hydrogen reactivity

In hydrogen combustion, the three shuffle reactions have long been known to be central to ignition processes [1]. These shuffle reactions, triggering an exponential growth of the radicals H, O and OH, are in competition with the third-body reaction H + O₂ + M → HO₂ + M, which acts as a sink for the radical H. This competition, described by Lewis and von Elbe [19], defines the second explosion limit. In our approach, we consider the four reactions listed in Table 1. The reported rates are issued from the well-validated San Diego mechanism [3].

The production of each radical through these four reactions may be written as follows:

$$\frac{d\bar{C}}{dt} = \mathbf{A} \cdot \bar{C} \quad \text{where} \quad \bar{C} = \begin{bmatrix} C_H \\ C_O \\ C_{OH} \end{bmatrix} \quad (3)$$

The components of the 3 × 3 matrix

$$\mathbf{A} = \begin{bmatrix} -(1/\tau_1 + 1/\tau_4) & 1/\tau_2 & 1/\tau_3 \\ 1/\tau_1 & -1/\tau_2 & 0 \\ 1/\tau_1 & 1/\tau_2 & -1/\tau_3 \end{bmatrix} \quad (4)$$

represent the reciprocal of the kinetic times τ_i associated with reactions 1–4: $1/\tau_1 = k_1 C_{O_2}$, $1/\tau_2 = k_2 C_{H_2}$, $1/\tau_3 = k_3 C_{H_2}$ and $1/\tau_4 = k_4 C_{O_2} C_M$. These quantities are assumed to be constant during the ignition process, so that \mathbf{A} only depends on the reactants concentrations (thus on the pressure and mixture fraction), and on the Arrhenius rates (thus on the temperature). It corresponds exactly to the Jacobian as defined in Eq. (2), restricted to the three major radicals H, O and OH.

The matrix \mathbf{A} becomes singular when $\tau_1 = 2\tau_4$ which corresponds to the second explosion limit, where the temperature equals the crossover temperature $T = T_c$. When $T > T_c$, $2k_1 > k_4 C_M$ and the chain-branched explosion characteristic of hydrogen

Table 1

Rate coefficients in Arrhenius form $k = AT^n \exp(-E/RT)$, for the computation of the H₂ reactivity.

	Reaction	A ^a	n	E ^a
1	H + O ₂ → OH + O	3.52 · 10 ¹⁶	−0.7	71.42
2	H ₂ +O → OH + H	5.06 · 10 ⁴	2.67	26.32
3	H ₂ +OH → H ₂ O + H	1.17 · 10 ⁹	1.3	15.21
4	H + O ₂ +M → HO ₂ +M ^b	5.75 · 10 ¹⁹	−1.4	0.0
	k _∞	4.65 · 10 ¹²	0.44	0.0

^a Units are mol, s, cm³, kJ, and K.

^b Chaperon efficiencies are 2.5 for H₂, 16.0 for H₂O, and 1.0 for all other species; Troe falloff with $F_c = 0.5$.

combustion occurs. Reciprocally, below crossover, the chain-branching remains “frozen” by the termination step which consumes the H radical. The reaction path is then fundamentally different, and consideration of HO₂ and H₂O₂ becomes necessary [20,21].

The characteristic polynomial of matrix \mathbf{A} reads:

$$\det(\lambda \mathbf{I} - \mathbf{A}) = l_3 \lambda^3 + l_2 \lambda^2 + l_1 \lambda - l_0 = 0, \quad (5)$$

where

$$\begin{aligned} l_3 &= \tau_1 \tau_2 \tau_3, \\ l_2 &= \tau_1 \tau_2 + \tau_1 \tau_3 + \tau_2 \tau_3 (1 + \alpha), \\ l_1 &= \tau_1 + \alpha(\tau_2 + \tau_3), \\ l_0 &= 2 - \alpha, \quad \text{with} \quad \alpha = \tau_1/\tau_4. \end{aligned} \quad (6)$$

One can show that the system admits only one positive real eigenvalue λ when $T > T_c$ (or $l_0 > 0$), thus representing the explosive mode of the chemistry [22]. Incidentally, the cubic term is negligible in Eq. (5), as shown in [9,10], so that the explosive mode eigenvalue can be approximated as a simple quadratic expression:

$$\tau^{-1} = \lambda = \left((l_1^2 + 4l_0 l_2)^{1/2} - l_1 \right) / (2l_2). \quad (7)$$

Additional comments concerning this systematic simplification – central to this study – are provided in the last section of the paper.

Figure 1 shows the evolution of the quadratic expression obtained above with time in a spatially homogeneous isobaric reactor initially containing a stoichiometric mixture of H₂ and air, at 1200 K and 1 atm. Also plotted is the exact resolution of the maximum real eigenvalue of the 8 × 8 Jacobian as defined in (2), for the 21-step detailed San Diego mechanism for hydrogen combustion [23]. In this figure is also superimposed the temperature evolution of the homogeneous reactor, showing that during most of the induction period, when the temperature has not yet risen, Eq. (7) provides an approximation which compares very well to the detailed eigenvalue problem.

The quadratic expression (7) suffices for the assessment of H₂–O₂ mixtures characteristic chemical time [10]. This expression has been used in [10–12,24] to correct departures from steady-states of O and OH during autoignition processes, in explicit reduced chemistry formulations. The same expression has been also used in [22], to offer a post-processing solution for lifted flames, by readily identifying the most reacting zones, where autoignition occurs – a method very similar to CEMA [16]. A beneficial feature of this formulation is that a cold flow simulation

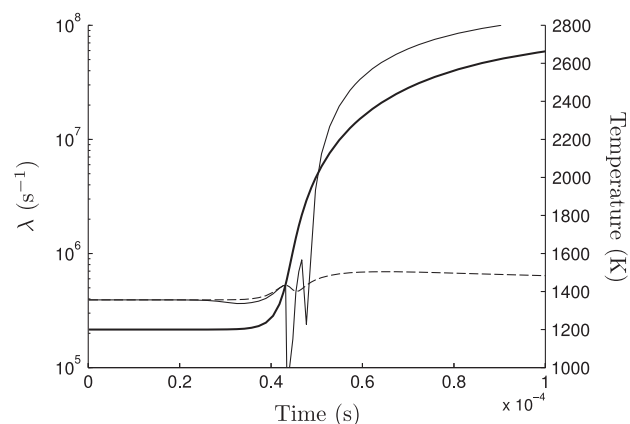


Fig. 1. Comparison of the exact solution for the maximum real positive eigenvalue of the Jacobian (solid curve), and the quadratic expression (dashed curve), during an H₂–air isobaric autoignition process, for initial conditions of 1 atm and 1200 K. The thick solid curve represents the temperature evolution of the homogeneous reactor.

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