

A Novel Methodology for Chemical Time Scale Evaluation with Detailed Chemical Reaction Kinetics

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Abstract

Interaction between turbulent mixing and chemical kinetics is the key parameter which determines the combustion regime: only understanding such interaction may provide insight into the physics of the flame and support the choice and/or development of modeling tools. Turbulence/chemistry interaction may be evaluated through the analysis of the Damköhler number distribution, which represents the flow to chemical time-scale ratio. Large Damköhler values indicate mixing controlled flames. On the other hand, low Damköhler values corresponds to slow chemical reactions: reactants and products are quickly mixed by turbulence so the system behaves like a perfect stirred reactor. The calculation of the Damköhler number requires the definition of proper flow and chemical time-scales. For turbulent conditions, the flow time-scale can be evaluated as the integral time-scale, even though in literature other mixing scales

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are used (e.g. Taylor scales, Kolmogorov). Chemical time-scale calculation poses some issues. In literature several examples of Damköhler calculation are reported, but in most cases just a single global chemical reaction is taken into account to describe the oxidation process. A method for considering more complex kinetic schemes is proposed by Fox¹ who defines the chemical time-scale in terms of the inverse of the eigenvalues from the decomposition of the chemical source term Jacobian matrix. The present work aims at developing a procedure for the calculation of the chemical time-scale (and thus of the Damköhler number) with complex kinetics starting from the analysis of the Jacobian matrix of the chemical species source terms. Emphasis is made on the dimension of the Jacobian matrix, as it is not fully understood how the species for the time-scale calculation have to be chosen. In other words, one can refer to the full set of species (thus all species will have the same “weight”), but also to a sub-set of them. The main idea is to perform a preliminary analysis, based on Principal Variables (PV) to determine the relative importance of the chemical species, in order to select an optimal sub-set for the chemical time-scale calculation. Moreover the knowledge of chemical time-scale may help the choice of a proper time discretization for transient numerical models, such as those based on Large Eddy Simulations techniques. The procedure is illustrated and applied for the Moderate and Intense Low-oxygen Dilution (MILD) combustion as this kind of regime shows a strong coupling between turbulence and chemistry, mainly because of slower reaction rates (due to the dilution of reactants) in comparison with conventional combustion. The methodology is further validated on a DNS data set modeling a CO/H_2 jet flame.

Introduction

Interaction between turbulent mixing and chemical kinetics is the key aspect in combustion modeling as it determines the combustion regime. Therefore, a fundamental understanding of turbulence/chemistry interactions in reacting systems may provide the needed insight into the physics of the flame, allowing an appropriate selection or development of physical models. The Damköhler (Da) number characterizes the behavior between mixing and reaction in a system, given by the ratio of a mixing or flow time scale to a chemical time scale (τ_f/τ_c). The decision of the most

relevant flow and chemical time scales which control the flame structure is important in obtaining meaningful parameters which describe the system. When defining the Damköhler number for pre-mixed flames the flow time scale is generally defined by the ratio of the turbulent length scale to the turbulent intensity (l/v'), which is proportional to the integral time scale ($\tau_I = k/\varepsilon$) being the largest turbulent time scales in the system. The chemical time scale τ_c , is calculated from the ratio of the flame thickness to the laminar flame speed (δ/s_L),^{2,3} leaving a definition for the Damköhler number as:

$$Da_I = \frac{kv'}{\varepsilon l} \quad (1)$$

Another useful non-dimensional number used in pre-mixed flames is the Karlovits number (Ka), defined for premixed flames as the ratio of the representative chemical time scale to the Kolmogorov mixing scale, leaving $Ka = l_F^2/\eta^2$, where η is the Kolmogorov length scale, and l_F is the flame thickness. This dimensionless number is relevant when looking at the ability of the mixing to alter the flame physics. For pre-mixed flames the following general combustion regimes⁴ are found:

- *Laminar Flames* ($Re < 1$) - simple diffusion flames with no turbulent structures effecting the physics of the system.
- *Thickened Flame* ($Re > 1, Da_I \ll 1, Ka > 100$) - A turbulent regime where the reaction time scales of the system are much slower than the mixing time scales. Here reactants and products are quickly mixed by turbulence as the mixing scales are small enough to enter the inner reaction layer, accordingly the system behaves like a perfect stirred reactor leaving a system governed by the reaction scales.
- *Thin reaction zones* ($Re > 1, 100 > Ka > 1$) - A turbulent regime where the reaction scales of the system are larger than the smallest mixing scales, and the smallest mixing scales are not sufficiently small to enter the inner reaction layer where radicals begin to react with the fuel, but large enough to perturb the inert pre-heat zone thus distorting the laminar flame

structure.

- *Flamelets* ($Re > 1, Ka < 1, Da_I > 1$) - the system is governed by the mixing as the reaction times are all smaller than the smallest mixing scales, this is the case where the flame preserves a laminar flamelet shape within the smallest turbulent structures.

In contrast to premixed flames distinct regime definition for non-premixed combustion is difficult. The definition of a characteristic flame velocity such as that of pre-mixed combustion is not available,⁵ thus complicating the calculation of a reaction time scale. Non-premixed flames exhibit multiple flow scales which may evolve temporally as well as have dependence on spatial coordinates, and burner flow conditions,⁶ this results in multiple choices for definition of the flow scales. Many authors suggest the use of the inverse of the stoichiometric scalar dissipation rate for the definition of a local mixing time τ_χ .^{5,6} The local mixing time is calculated as $\tau_\chi = 1/\chi_{st} = \left(2D \overline{|\nabla Z''_{st}|^2}\right)^{-1}$, where Z''_{st} is the mixture fraction fluctuation and D is the thermal diffusivity.⁷ Additionally literature shows the non-premixed Damköhler number being calculated using τ_I , and τ_η the Kolmogorov mixing time which is the scale of the smallest eddies in the system where energy is dissipated to heat.⁷ For gases the Batchelor scale τ_B is equal to the Kolmogorov scale τ_η , which is associated to the largest scales at which non-premixed streams remain segregated.¹ This length scale defines a mixing scale that is interesting for the Damköhler analysis of non-premixed flames. The definition of the Batchelor length scale comes from the assumption that τ_η and the Batchelor time scale (τ_B) are equal for a gaseous mixture $\left(\frac{\lambda_B^2}{\Gamma} = \left(\frac{\nu}{\varepsilon}\right)^{1/2}\right)$. Four definitions of the Damköhler number for non-premixed combustion can be modeled depending on the choice of the mixing time: the integral Damköhler number (Da_I), the local mixing Damköhler number (Da_χ), which uses the local mixing time τ_χ , the Kolmogorov (Da_η) and Batchelor Damköhler number (Da_B), which are equivalent for gases. Several authors have attempted to characterize non-premixed combustion regimes. An example of one was demonstrated by Poinso, where Da_I and the turbulent Reynolds (Re_t) number, defined as $\frac{\tau_I}{\tau_\eta} = \frac{k/\varepsilon}{(\nu/\varepsilon)^{1/2}} = \sqrt{\left(\frac{k^2}{\nu\varepsilon}\right)} = \sqrt{Re_t}$ are used to characterize the regimes. When the Damköhler number is large enough the laminar flamelet assumption (LFA) applies, leaving a transitional Damköhler number (Da_I^{LFA}) at which point the combustion regime changes. Given a

sufficiently small Damköhler number extinction occurs, here the transitional Damköhler number Da_I^{EXT} is defined. The following non-premixed combustion regimes are generally described in terms of the Damköhler number.

- *Laminar* ($Re_t < 1$) - simple diffusion flames with no turbulent structures effecting the diffusion of fuel and oxidizers.
- *Flamelet* ($Re_t > 1, Da_I \geq Da_I^{LFA}$) - a turbulent regime where mixing scales are larger than reaction scales thus preserving the steady laminar flamelet.
- *Unsteady* ($Re_t > 1, Da_I^{LFA} > Da_I > Da_I^{EXT}$) - a regime where mixing scales produce instability in the flame front.

Indeed much work is yet required for a more detailed description of the non-premixed combustion regimes. The determination of chemical time scales for turbulent combustion systems is particularly difficult as detailed reaction mechanisms are often required for adequate description of the combustion process. A definition of the laminar flame velocity s_L , used for the calculation of τ_c (δ/s_L) doesn't exist for non-premixed combustion. The chemical time (τ_c) is determined from several different methods including activation energy asymptotics,⁸ global chemistry assumption,⁹ or the critical scalar dissipation rate at quenching $\tau_q = 1/\chi_q$ has been used for estimation of τ_c with complex chemistry cases.⁷ At this time a clear definition for τ_c for complex chemistry systems involving detailed kinetic mechanisms is needed, and it is the focus of this work. In most cases a global chemistry assumption is made to simplify the estimation of τ_c . An example of this is given by Kuo¹⁰ where the following definition is used:

$$Da_I = \left(\frac{\nu K_r^2}{\varepsilon} \right) \quad (2)$$

where ν is the kinematic viscosity, ε is the dissipation of turbulent kinetic energy, and K_r is the kinetic constant of the global reaction. On the other hand, Fox¹ provides a method for considering more complex kinetic schemes, suggesting that the chemical time-scale can be defined in terms of the eigenvalues of the $N \times N$ Jacobian matrix \mathbf{J} of the chemical source terms, whose elements J_{ij} are given by (for an isothermal case):

$$J_{ij} = \frac{\partial R_i}{\partial Y_j} \quad (3)$$

Chemical time-scales can then be associated to each eigenvalues as:

$$\tau_a = \frac{1}{|\lambda_a|} \quad (4)$$

where λ_a is the eigenvalue vector from the eigenvalue decomposition of \mathbf{J} . In a complex kinetic scheme, for which the time-scales can range over several orders of magnitude, the slowest chemical time-scale should be chosen for the estimation of the Damköhler number:

$$\tau_c = \max(\tau_a) \quad (5)$$

Such an approach was recently applied by Rehm et. al.¹¹ who calculated the Damköhler number for a gasification system using the most abundant species (i.e. $N = 5$) to define the Jacobian matrix. Retaining all the species of the kinetic mechanism may lead to the determination of non-meaningful time-scales, due to the complete inactivity of some species in specific regions of the flame. The choice of the species to be retained is not to date established and is generally made by looking at the major species as done in the work by Rehm et. al. The selection of species to be retained is addressed and a newly proposed method is presented in the subsequent section. Upon determination of an appropriate expression for τ_c and τ_f the evaluation of the Damköhler number can easily allow one to identify the predominant combustion regime which allows for appropriate turbulent combustion model selection as well as development. Turbulent combustion models are generally well suited for (1) high Damköhler numbers where mixing dominates the process or (2) low Damköhler numbers where chemistry dominates the physics and finite rate chemistry models are required. An example of a high Damköhler number model is the Steady Laminar Flamelets Model (SLFM),^{12,13} which uses the mixture fraction variable as well as the mixture fraction variance to describe the flame as an ensemble of steady laminar diffusion flames under going various strain rates which are all well characterized by the two transported variables. In lower Damköhler flows turbulent structures can enter the flame pre-heating zone and further mix and distort the flame front, these unsteady effects require a modeling approach with higher coupling between the chemical reactions and the turbulent mixing. A model such as Eddy Dissipation

Concept (EDC)^{14–17} transports the species involved in a detailed reaction mechanism, and treats the flame as an ensemble of perfectly stirred reactors (PSR) where the PSR residence time is a function of the local mixing time scales. This allows for a more complex chemistry tracking approach, while coupling the turbulent structures to the chemistry physics.

A particular combustion regime of interest in terms of the Damköhler analysis is the Flameless (or MILD) combustion regime. This regime is characterized by a strong coupling between turbulence and chemistry, because of slower reaction rates (due to the dilution of reactants) with respect to conventional combustion.⁹ It is a generalized opinion that for such combustion regime the Damköhler number approaches unity.¹⁸ Indeed many modeling investigations have shown that high Damköhler number approaches such as SLFM are not suited for this combustion regime due to the slow chemistry.¹⁹ Encouraging results have been obtained through the EDC model,^{17,20–24} especially for its capability of handling detailed kinetic schemes.²⁵ However, some discrepancies are still observed when using EDC and model modifications have been proposed in the literature for better capturing flameless conditions.^{26,27} The objective of the present paper is that of defining a methodology for the determination of the principal variables of a reacting system, to allow the determination of a chemical time-scale τ_c based on complex reaction schemes, so that a meaningful Damköhler number maybe calculated. Such a formulation is interesting for combustion process where detailed kinetics need to be taken into account like in flameless combustion. The proposed choice of the size of the Jacobian matrix and of the variables that should be involved in the chemical time-scale calculation becomes fundamental. The present paper proposes a methodology based on Principal Variable Analysis for the selection of the variables carrying most of the relevant information. In the following, the methodology is first presented with an introduction to Principal Component Analysis (PCA) and Principal Variables (PV). Then a discussion on the size of the Jacobian follows, to rigorously determine the minimum number of species which should be included in the Jacobian calculation. Finally, results are presented for a flameless combustion data set,²⁸ and for consistency the approach is demonstrated on a DNS data set for non-premixed syngas combustion.

Methodology

Principal Components Analysis. Principal Components Analysis^{29,30} is a statistical technique employed in the analysis of multivariate data-sets, for detecting the directions that carry most of the data variability, thus providing an optimal low-dimensional projection of the system. For a data set, \mathbf{X} , consisting of n observations of Q variables, the sample covariance matrix, \mathbf{S} , of \mathbf{X} can be defined as $\mathbf{S} = 1/(n-1)\mathbf{X}^T\mathbf{X}$. Recalling the eigenvector decomposition of a symmetric, non singular matrix, \mathbf{S} can be decomposed as $\mathbf{S} = \mathbf{A}\mathbf{L}\mathbf{A}^T$, where \mathbf{A} is the $(Q \times Q)$ matrix whose columns are the eigenvectors of \mathbf{S} , and \mathbf{L} is a $(Q \times Q)$ diagonal matrix containing the eigenvalues of \mathbf{S} in descending order, $l_1 > l_2 > \dots > l_p$. The covariance matrix indicates, therefore, the level of correlation between the non-dimensional variables. Values close to zero denote uncorrelated variables whereas correlations close to one indicate strongly correlated variables. Based on the correlation values, the redundant, less important information contained in the original data-sets can be easily removed. Once the decomposition of the covariance matrix is performed, the Principal Components (PC), \mathbf{Z} , are defined by the projection of the original data onto the eigenvectors, \mathbf{A} , of the covariance matrix, \mathbf{S} , $\mathbf{Z} = \mathbf{X}\mathbf{A}$. Then, the original variables can be stated as a function of the PC as $\mathbf{X} = \mathbf{Z}\mathbf{A}^T$, being \mathbf{A} orthonormal and, hence, $\mathbf{A}^{-1} = \mathbf{A}^T$. Nevertheless, the main objective of PCA is to replace the p elements of \mathbf{X} with a much smaller number, q , of PC, preserving at the same time the amount of information originally contained in the data. If a subset of size $q \ll Q$ is used, the truncated subset of PC is $\mathbf{Z}_q = \mathbf{X}\mathbf{A}_q$. This relation can be inverted to obtain:

$$\mathbf{X}_q = \mathbf{Z}_q\mathbf{A}'_q \quad (6)$$

where \mathbf{A}_q is the matrix obtained by retaining only the first q columns of \mathbf{A} . The linear transformation provided by 6 ensures that the new coordinate axes identified by PCA are orthogonal and they provide independent and decreasing contributions to the amount of original variance explained by the PC. Thus, if only the subset \mathbf{A}_q of \mathbf{A} is retained, \mathbf{X}_q represents the best q -dimensional approximation of \mathbf{X} in terms of squared prediction error. Variables are generally centered before PCA is

carried out, to convert observations to fluctuations on the mean; moreover, scaling is applied when the elements of \mathbf{X} have different units or when they have different variances, as it is the case for this investigation. A centered and scaled variable can be defined as:^{31,32}

$$x_j = \frac{x_j - \bar{x}_j}{d_j}. \quad (7)$$

where d_j is the scaling parameter adopted for variable x_j . Several scaling options are available, including normalization by the variable range, standard deviation, maximum and average values. The present paper uses the standard deviation as scaling parameter. This ensures that all the elements of the scaled \mathbf{X} matrix have a standard deviation equal to one, giving them similar relevance.

Principal Variables. Principal variables (PV) represent an attempt to help the physical understanding of Principal Components. PV algorithms try to link the PC back to a subset of the original variables, which satisfies one or more optimal properties of PCA. A number of methods exist for selecting a subset q of Q original variables which preserve most of the variation in \mathbf{X} . We can then suppose to partition the set of variables into $\mathbf{X}(1)$ and $\mathbf{X}(2)$. We can, therefore, express the sample covariance matrix as:

$$\mathbf{S} = \begin{bmatrix} \mathbf{S}_{11} & \mathbf{S}_{12} \\ \mathbf{S}_{21} & \mathbf{S}_{22} \end{bmatrix} \quad (8)$$

Then, the partial covariance for $\mathbf{X}(2)$ given $\mathbf{X}(1)$ can be expressed as:

$$\mathbf{S}_{22,1} = \mathbf{S}_{22} - \mathbf{S}_{21}\mathbf{S}_{11}^{-1}\mathbf{S}_{12}. \quad (9)$$

With respect to Eq. (9), PV techniques attempt to minimize the information carried by the covariance matrix $\mathbf{S}_{22,1}$, by only considering the most important variables within the dataset.

Several PV methods exist in the literature.²⁹ In the present work, the method considered is the so-called B2 backward method. In the B2 method, PCA is performed on the original matrix of Q variables and n observations. The eigenvalues of the covariance/correlation matrix are then com-

puted and a criterion is chosen to retain q of them, leaving $S_{22,1}$ as a $(Q - q) \times (Q - q)$ dimensional matrix. The criterion that determines q is then given by the trace of $S_{22,1}$ as:

$$\frac{\text{trace}(S_{22,1}(q))}{\text{trace}(S)} \lesssim \gamma \quad \text{for } q = 1, 2, \dots, Q \quad (10)$$

here q begins at $q = 1$ and is incremented by 1 until the criterion is met. The term $\frac{\text{trace}(S_{22,1}(q))}{\text{trace}(S)}$ can be interpreted as the lost variance of \mathbf{X} by selecting the subset q . Selecting a value of $\gamma = 0.01$ (which is done in this study) would leave a retention of 99% of the variance in the system. This will lead to discarding $Q - q$ variables, which are evaluated starting from the last component, looking for the variables corresponding to highest eigenvector coefficient. Those variables are then discarded, as they are highly correlated with a component not carrying any useful information.

Jacobian matrix down-sizing. The variables extracted with the principal variable algorithms are used to compute a subset of the full Jacobian matrix, only including the derivatives with respect to the selected principal variables. This allows the determination of the modes to be compared with the ones provided by the full Jacobian matrix, including all the species involved in the original detailed kinetic mechanism. In all cases, the determination of the Jacobian matrix is performed with an *in house* MATLAB® code JACOBEN. The code is particularly interesting as it formulates the chemical source term equations as symbolic expressions and then uses the symbolic differentiation function in MATLAB® to form the analytical expressions for the derivatives of the chemical source terms with respect to chemical species. The code requires the chemical mechanism to be in CHEMKIN format, as well as all thermodynamic state space parameters describing the turbulent combustion, including the species mass fractions and Temperature. A Jacobian matrix is then evaluated for every grid point provided in the thermodynamic state space input file. Figure 1 summarizes the process used in order to calculate the Damköhler number.

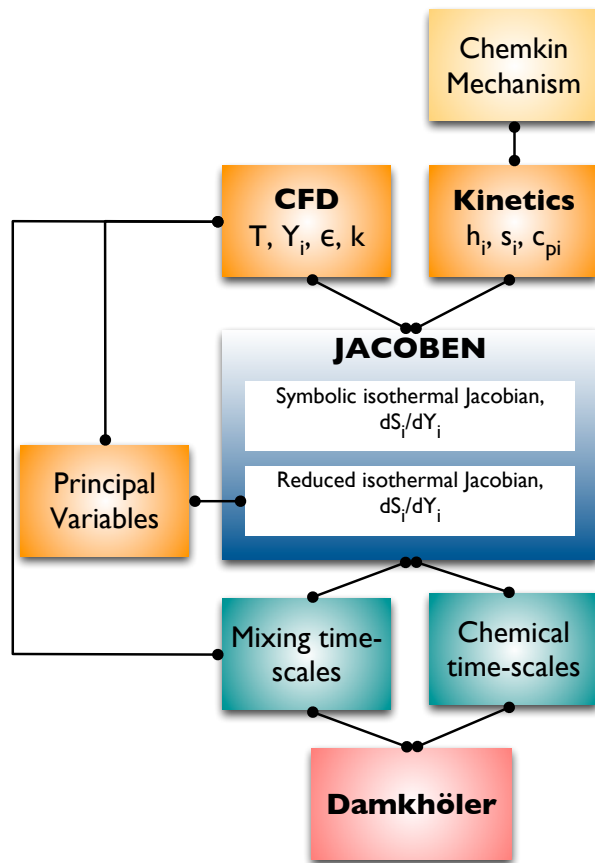


Figure 1: Flow Diagram describing the process of analysis used to obtain the Damköhler number.

Test Cases

First a demonstration of the Principal Variable approach for the Damköhler number calculation is given based on a flameless combustion data set where a unity Damköhler number is expected. The data used in the present work refers to the jet in hot co-flow (JHC) burner designed by Dally²⁸ to emulate flameless combustion conditions. It consists of a jet of a CH_4/H_2 mixture (inner diameter of 4.25 mm) within an annulus co-flow (inner diameter of 8.2 mm) of hot oxidizer gases from a porous bed burner mounted upstream of the exit plane. The entire burner is placed inside a wind tunnel feeding air at the same velocity as the hot co-flow. The datasets used in the present work refer to a jet Reynolds number of around 10,000 and different oxygen mass fraction, i.e. 3% (HM1), 6% (HM2) and 9% (HM3) in the co-flow. The jet Reynolds number is around 10,000 for all flames. The available data consists of the mean and root mean square (RMS) of temperature and concentration of major (CH_4 , H_2 , H_2O , CO_2 , N_2 , and O_2) and minor species (NO , CO , and OH) at different locations. A detailed description of the systems and tests can be found in the work by Christo.²⁰ The JHC was modeled with the Fluent 6.3 software by Ansys Inc. A 2D axisymmetric domain was chosen with a structured grid made of 25,000 cells. The steady-state Reynolds-Averaged Navier-Stokes (RANS) equations were solved with a modified version of the k- ϵ turbulence model (i.e. imposing $C_{\epsilon 1} = 1.6$ for round jets.^{23,33} The KEE-58 mechanism³⁴ consisting of 17 species and 58 reversible reactions was employed for the oxidation process. Turbulence/chemistry interactions were modeled with the EDC model. The constant of the residence time in the fine structures was set to 1.5 as this was found to improve substantially the predictions of temperature and chemical species in flameless conditions.²⁷ For the boundary conditions, velocity inlet conditions were given to the unmixed fuel jet, co-flow oxidizer and tunnel air, paying particular attention to turbulent intensity.²³ The discretization was made with a second-order upwind scheme, whereas the pressure-velocity coupling was handled with the SIMPLE algorithm. Residuals for all equations were kept lower than 10^{-6} as a convergence criterion. The temperature and CO mass fraction were also monitored at the exit plane as another convergence criterion. The numerical simulation results obtained from the simulation of the JHC burner have been successfully validated²⁷ against the

available experimental data and they represent an ideal data-set for testing the proposed methodology for chemical time-scale calculation in case of complex kinetic mechanisms. Figure 2 shows

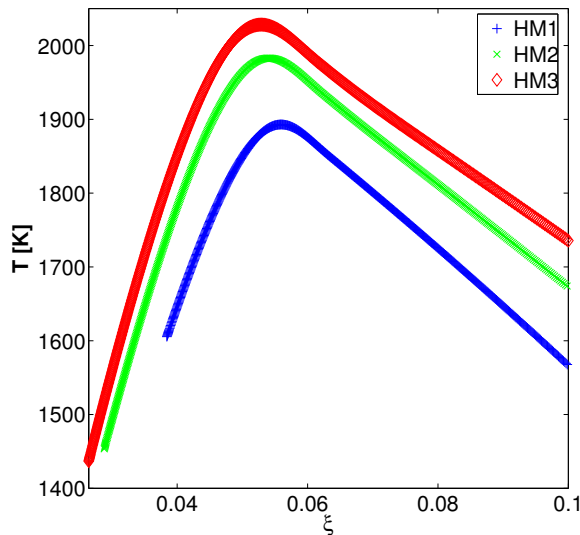


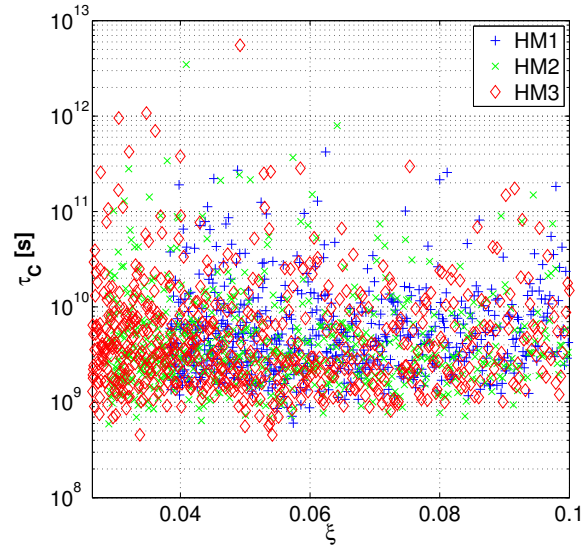
Figure 2: Temperature as a function of mixture fraction ξ for cases HM1, HM2 and HM3 along the axis of the burner.

the temperature T for cases HM1, HM2, HM3 along the axes of burner.

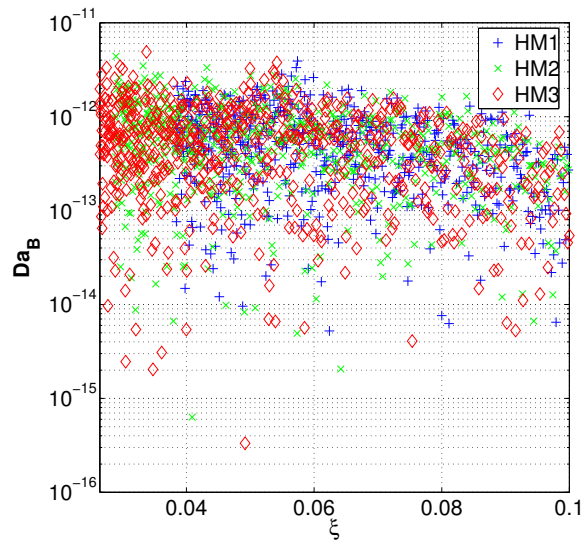
Second, in order to demonstrate consistency for the chemical time scale approach an additional analysis on Direct Navier Stokes (DNS) data, created by Sutherland³⁵ using Sandia National Laboratories S3D³⁶ code is shown. The code uses 8th order explicit finite difference derivatives, and 4th order, six-stage explicit Runge-Kutta time integrator. Here a case with $Re = 4478$, an inlet fuel stream containing 50% CO , 10% H_2 , and 40% N_2 (by volume), and an oxidizer stream containing air are simulated. The domain comprises of a 2D rectangular mesh containing 2160 by 720 grid points evenly spaced. A skeletal CO/H_2 mechanism was developed from the detailed CO/H_2 mechanism by Li,³⁷ without modifying the reaction rate parameters while only removing species which were not pertinent for adequate description of chemistry. The skeletal mechanism contained 12 species: H , O_2 , O , OH , H_2 , H_2O , CO , CO_2 , HO_2 , H_2O_2 , HCO , and N_2 .

Results and Discussion

First we analyze the flameless combustion data set. Figure 3a shows the chemical time-scale τ_c , and Figure 3b the Damköhler number Da_B , all as a function of mixture fraction ξ . The plotted data comes from the axis of the cylindrical burner for all three systems (HM1-HM3). In Figure 3 the results for τ_c and the Damköhler number are calculated using the full Jacobian matrix for the chemical time scales (Equations 3-5) and the Batchelor mixing scale. From the analysis it is clear that keeping all of the variables in the Jacobian matrix does not help in identifying the relevant processes for the system under investigation. In particular, if no filtering is applied to the original thermo-chemical state variables, the analysis will point out the existence of the extremely slow time-scales of the non-reacting species, as shown in Figure 3, leading to Da values close to zero for all three systems. A first attempt is then that of filtering out from the Jacobian analysis all the slow scales, i.e. all values above 1000 seconds (limit for slow chemistry processes according to Fox³⁸). This results in the plots of Figure 4, showing the time-scales (Figure 4a) and Da_B values (Figure 4b) for filtered Jacobian matrix. However, the new time-scale analysis does not provide a clear insight into the investigated combustion system. The Da values obtained for the three cases appear very close and simply shifted along the mixture fraction axis going from case HM1 to case HM3. More importantly, the Da values are in all cases fairly large (≈ 15), thus far from what would be expected in flameless conditions. The results shown in Figure 3 indicate that keeping all the thermo-chemical state variables in the Jacobian matrix does not allow identifying the controlling chemical time-scale of the system. It is therefore very important to identify the relevant variables for the time-scale analysis through a rigorous selection method. According to the method shown by Rehm¹¹ one could now select the major species in the system in order to capture the principal τ_c of the system. Selecting a mean mass fraction criteria ≥ 0.01 leaves the major species: CH_4 , H_2 , O_2 , CO_2 , H_2O , and CO . Figure 5 shows the resultant τ_c and Da_B given the major species as PV's. It is observed that the evaluation of Equations 3, 4, and 5 with the major species alone does not guarantee that the most meaningful or relevant chemical time scale will be expressed, in this case it leaves a large maximum time scale, due to the fact that one or more of the

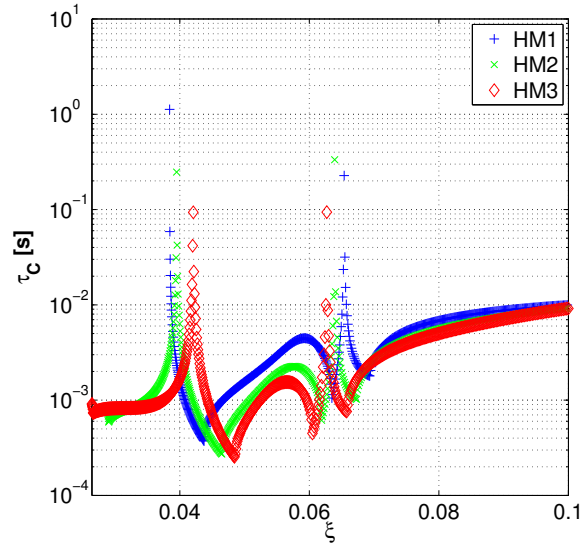


(a)

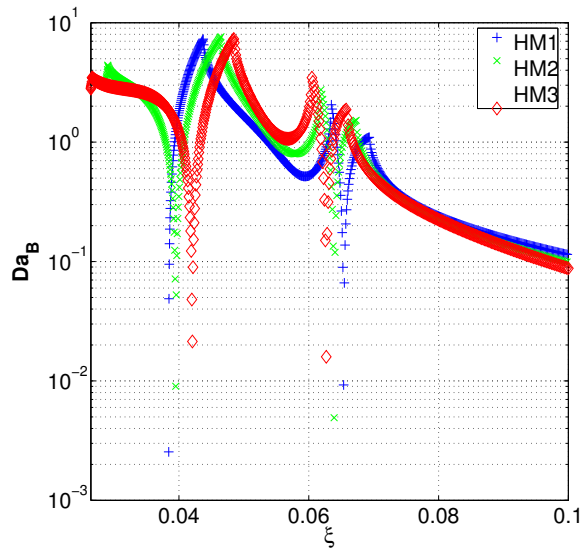


(b)

Figure 3: (a) Chemical time-scale τ_c , and (b) Damköhler values as a function of mixture fraction ξ . Full Jacobian matrix and unfiltered time-scales.

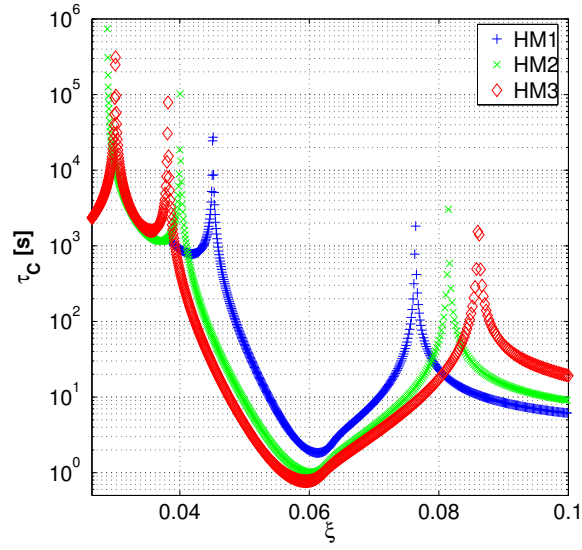


(a)

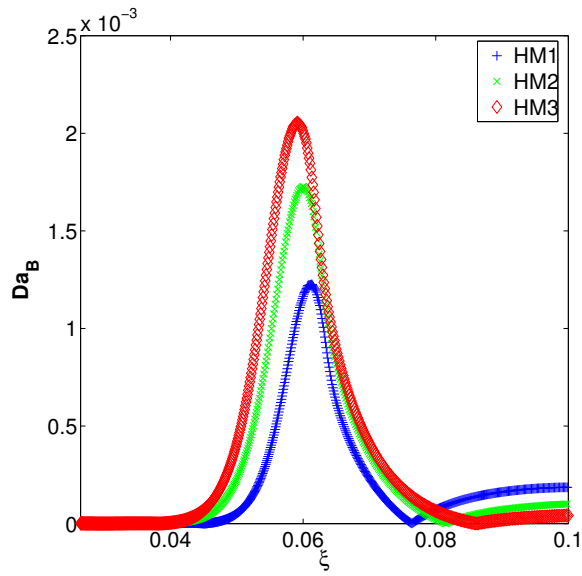


(b)

Figure 4: Chemical time-scale τ_c (a), and Damköhler values Da_B (b) as a function of mixture fraction ξ for the full Jacobian matrix. Time-scales above 1000 seconds have been removed.



(a)



(b)

Figure 5: Chemical time-scale, τ_c , and Damköhler values as a function of mixture fraction, ξ using only the Major Species in the reduced Jacobian matrix.

species may contain dormant reaction rates (in this case the addition of CO is highly sensitive to the large time scale), thus yielding an unrealistic Damköhler number. The Principal Variables of the system which lead to the calculation of a realistic τ_c can be identified using the methodology shown above. Equation 10 provides the normalized trace of the lost covariance given a guess for q , the number of discarded variables. The criterion of Equation 10 is met when $q \geq 10$ for all three cases. Figure 6 shows the normalized trace of the variance which is lost based on a given value of q . It can be inferred that retaining 10 PV's will yield a 1% loss of variance explained

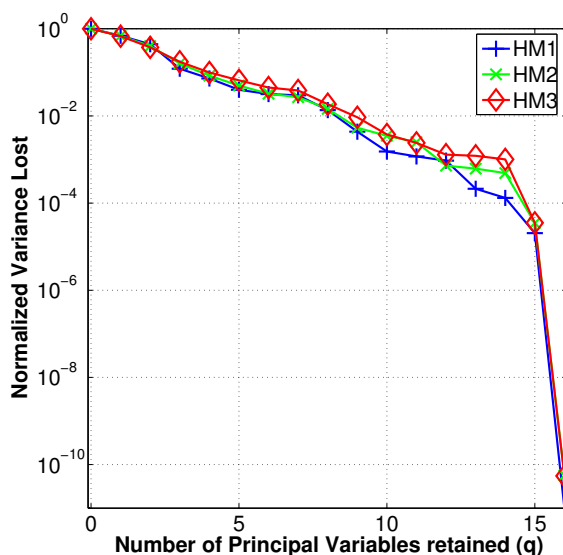


Figure 6: Trace plot for cases HM1, HM2 and HM3. Y axis gives a normalized variance which is lost based on the selection of q , the x-axis.

by keeping all of the variables. Figure 7 shows in black and red, respectively, the chemical time-scales associated to the Jacobian matrix of system HM1 with all the state variables and with a 10 PV's, determined with method B2 (See Methodology Section). It can be observed that the slowest chemical time scale, which is mostly pertaining to the species CO_2 in the present case, allows for a description of the slow governing dynamics of the reacting system without showing the peaks displayed by the largest (meaningful) time-scale of the full system, which come from the complex interactions between the different chemical species. Figure 8 shows the chemical time-scale, τ_c , and Damköhler, Da , values as a function of mixture fraction, ξ , for the Jacobian

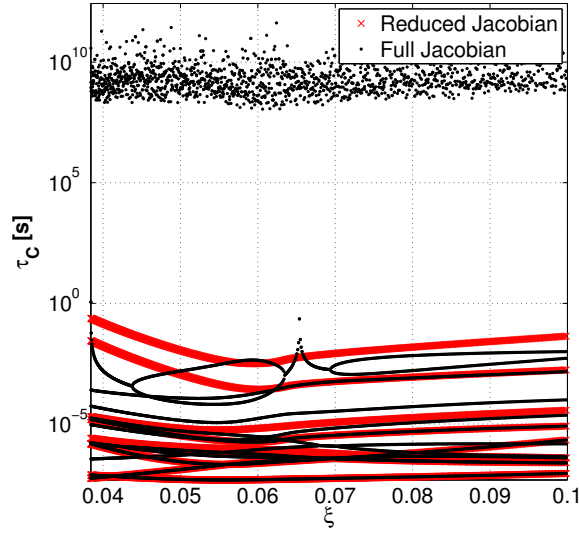
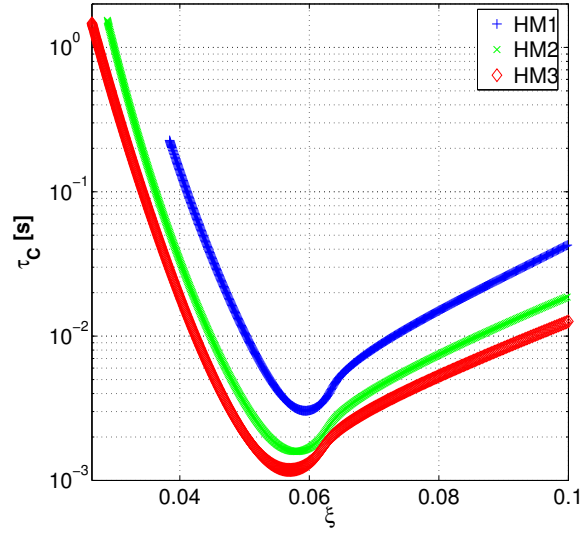
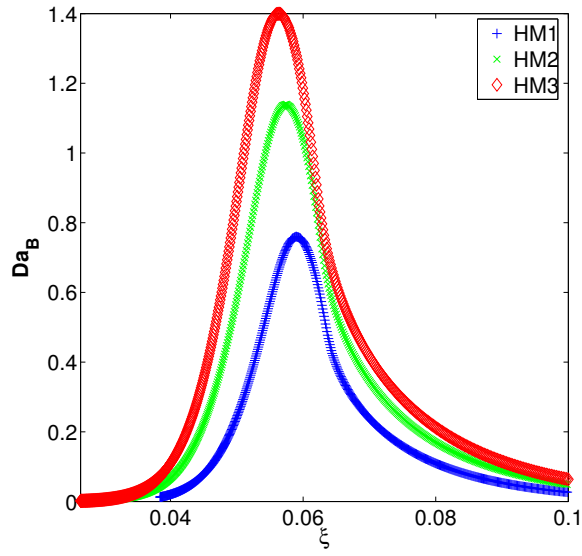


Figure 7: Chemical time-scales associated to the full (black) and reduced (red) Jacobian matrix (red line). Reduced Jacobian obtained using 10 PVs, determined using method B2. HM1 case.

matrix calculated using 10 Principal Variables for all three flames. Differently from Figure 3, the results indicate for the present case a meaningful trend, showing Da numbers around unity for the HM1 case, which is the case intended to be representative of a flameless combustion regime. The Damköhler values increase and almost double when going from HM1 to HM3, i.e. increasing the oxygen in the co-flow from 3% to 9% and moving, therefore, to conventional flame conditions. It is interesting to note that the evaluation of τ_c remains constant while using 1 to 11 PV's, as the 1st PV identified by the system is in fact CO_2 . Upon addition of the 12th PV (CO) the analysis of the time-scales shows again the appearance of large chemical times, which are related to inactive thermo-chemical variables and which should be not considered in the analysis. This is confirmed by the analysis of Figure 9, which shows the Da values as a function of ξ along the burner axis. When the number of PV's is greater than 12, the Da values drop to zero (red dots) due to the appearance of large chemical time-scales. The proposed methodology provides a very robust way for the determination of the limiting time-scale associated to a chemically reacting system. In particular, it can provide the variables that should not be included in a time-scale analysis as they do not add useful information being inactive species. Examination of the Damköhler number using



(a)



(b)

Figure 8: (a) Chemical time-scale, τ_C , and (b) Damköhler values as a function of mixture fraction, ξ . Jacobian matrix restricted to 10 principal variable.

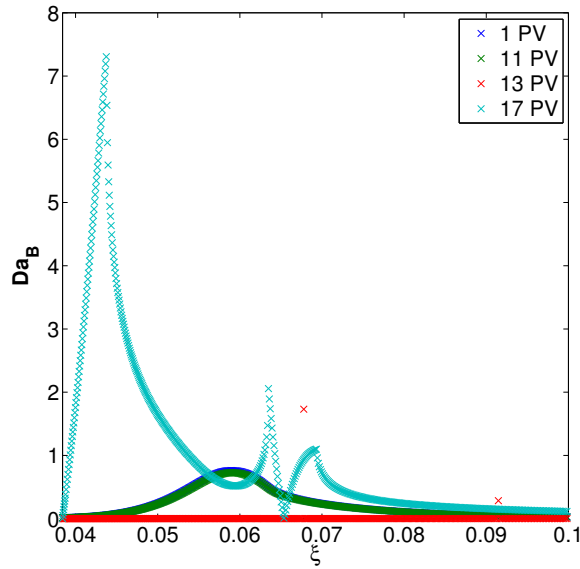


Figure 9: Damköhler values as a function of the mixture fraction along the burner axis for flame HM1, varying the number of principal variables. Full Jacobian matrix filtered to remove scales greater than 1000 s.

different mixing scales is shown in Figures 10, 11, and 12. Here the area between the Damköhler number calculated using the integral time scale Da_I and kolmogorov time scale Da_B is shown. This Damköhler number space is significant as it shows the possible reaction/mixing space. Figure 10 shows that Kolmogorov scales for the case HM1 are small enough to penetrate the thin reaction layer as $Da_B < 1$, however, $Da_I > 1$ leaving an observable flame shape. As would be expected if $Da_I < 1$ a simple Perfectly Stirred Reactor model could accurately represent the system. Because the integral time scales are much larger than the reaction scales the system requires mixing physics. Figures 11 and 12 show the smallest mixing scales are larger than the reaction scales thus the flame preserves a flamelet shape were a thin distinct reaction zone is present. When $Da_B < 1$ the reaction scales are slower than the mixing scales (HM1 case) thus a mixed flame front is expected. Figure 13 shows the contour plots of the Damköhler number for the three cases including stream lines of constant Temperature. As one would expect a higher O_2 content in the co-flow stream leads to faster combustion, and higher Damköhler numbers (see Figure 8), the effect of this is seen in Figure 13 as the reaction zone is stretched along the burner for the diluted O_2 case, leaving lower

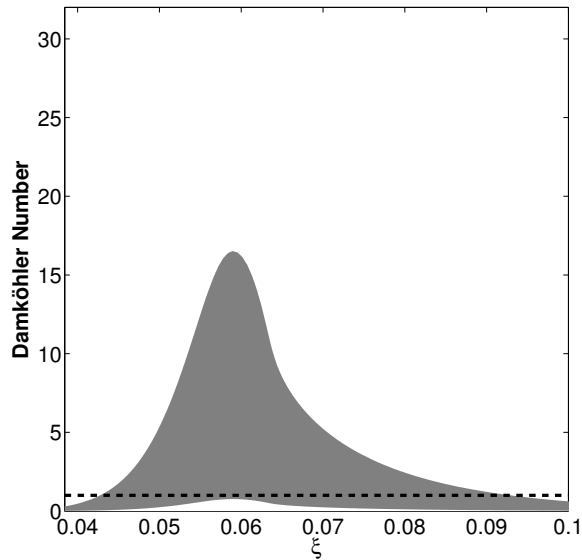


Figure 10: Damköhler numbers calculated using the integral time scale and the Batchelor time scale. Here the area bounded between the curves represents the possible reaction/mixing space bounded by the largest mixing scales (Da_I) and the smallest mixing scales (Da_B). The dashed line represents a Damköhler number of 1 along the entire mixture fraction space. Here the Damköhler region for the case HM1 is shown.

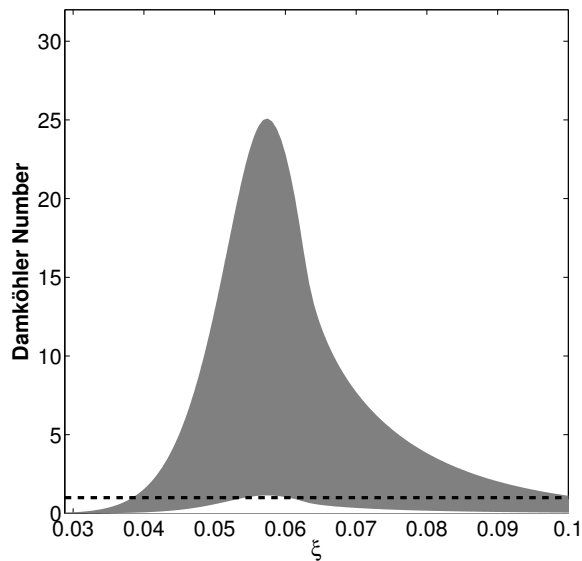


Figure 11: Damköhler region for the case HM2.

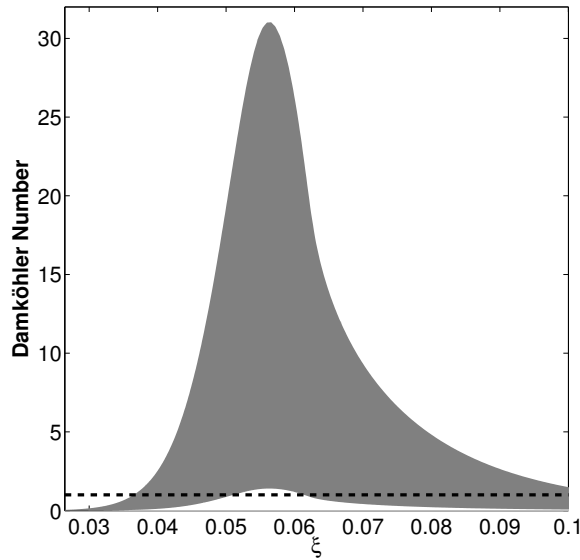
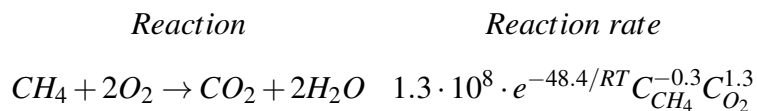


Figure 12: Damköhler region for the case HM3.

Temperatures, Damköhler numbers, and chemical time scales. The chemical time scale approach by Fox¹ allows additional insight into the reaction times by observing weights in the eigenvector matrix from the decomposition of the Jacobian of the source terms. Figure 14 shows the weights for the eigenvectors corresponding to the calculated time scales. The stacked bar chart shows the sensitivity of the chemical time mode to the principal variables. As would be expected the slow time scales correspond to species such as CO_2 , O_2 , N_2 and rapid time scales correspond to radical species where characteristic reaction times are expected to be very small (H , HCO , H_2O_2 , O , HO_2 , CH). A simple comparison between the newly outlined approach for calculating τ_c and the global chemistry approach¹⁰ can be made using the one-step Westbrook and Dryer mechanism,³⁹ assuming the oxidation of CH_4 is the slower predominant chemical process in the system. The one-step Westbrook and Dryer reaction is given with units of $kcal$, mol , K , m^3 , and s as:



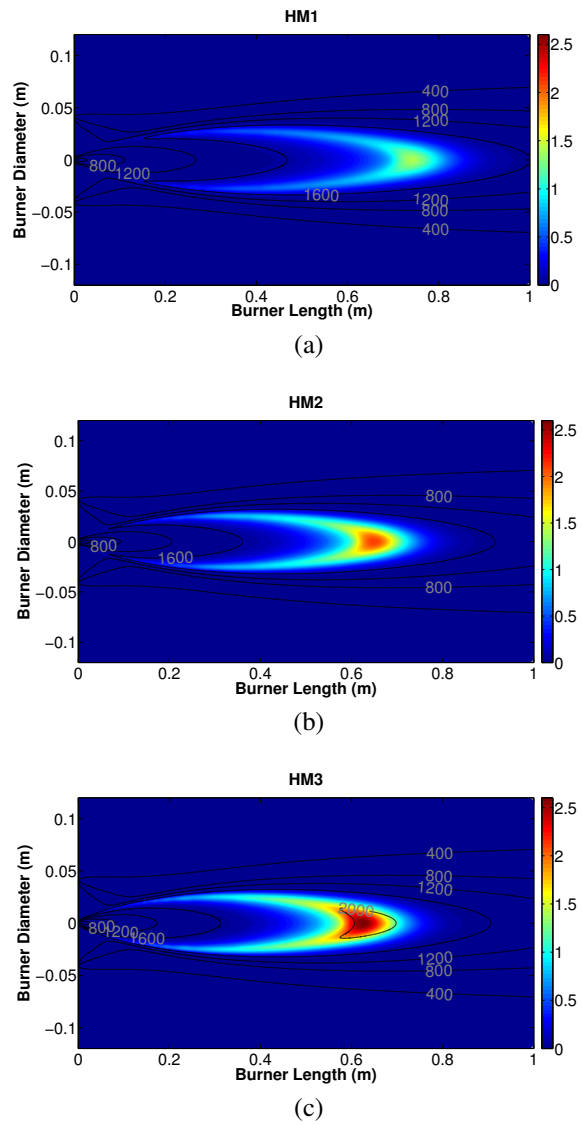


Figure 13: Contour showing Damköhler values along the burner cross section and burner length. Colors in the graphs indicate Damköhler number and isolines show the the temperature. Plots (a), (b), and (c) show the contours for the cases HM1, HM2, and HM3 respectively.

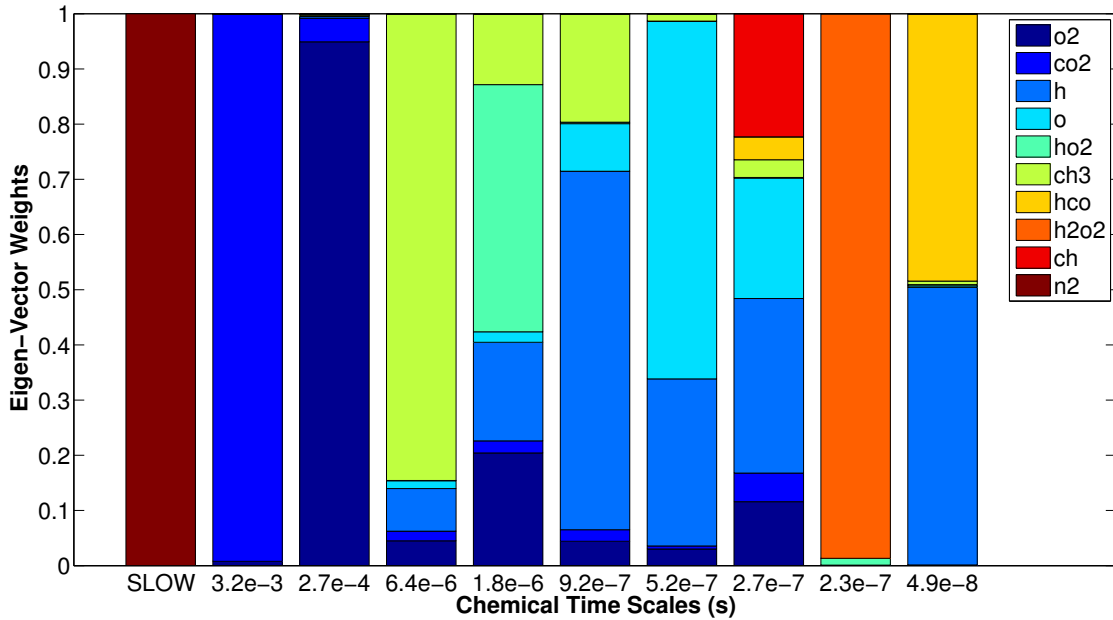


Figure 14: Stacked bar chart showing normalized chemical species weights from the eigenvector matrix, corresponding to chemical time scales from the inverse of the eigenvalues.

The units for the reaction rate constant are $1/s$ leaving a simple expression which gives τ_c under the assumption that the one-step global reaction correctly models the system. Figure 15 shows the results for the one-step global reaction time scale in comparison to the Principal Variable approach for the HM1 data set. A similar value for the smallest scale time scale near the stoichiometric mixture fraction is observed, with large differences moving in either direction of Z_{st} .

In order to verify the proposed methodology, the DNS data set (described in the Test Cases Section) is also analyzed using the new chemical time scale approach. First τ_c is calculated using the full Jacobian matrix containing the information from all of the variables, including that which may produce slow dormant reaction times. Figure 16 shows the results using the full Jacobian matrix. Similar to the analysis shown in Figure 3 the dormant reaction times hide the actual governing time scales of the system. In order to perform the proposed approach, Equation 10 was used again to determine the number of Principal Variables required for sufficient description of the data set. Figure 17 shows the normalized trace of the variance which is lost based on a given value of q , where $q \geq 3$ will yield a 1% or less loss of variance. Figure 18 shows τ_c and Da_B calculated for

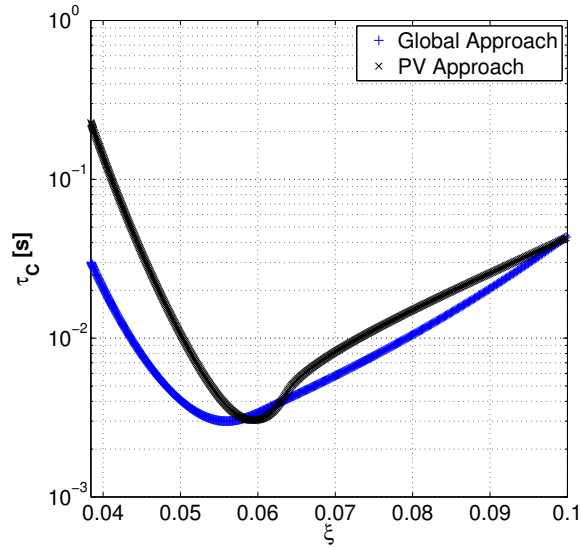
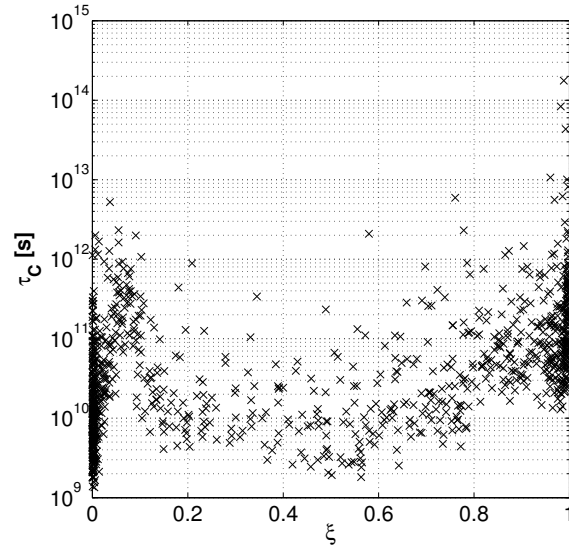


Figure 15: Comparison between the presented Principal Variable approach to calculating τ_c and the global approach which is shown using the one step Westbrook and Dryer reaction.

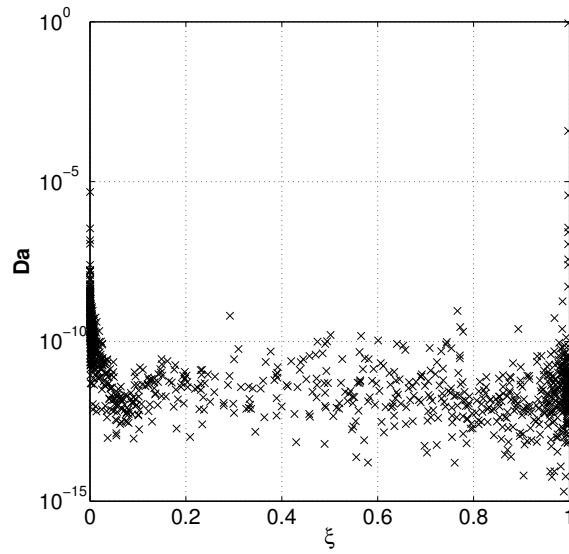
the given DNS data set. The analysis showed a clear definition of the dominant reaction time scale while using 3 to 8 principal variables. Upon addition of the 9th principal variable, which was H_2O in this case, dormant reaction times are observed. The results from the chemical time scale analysis on the DNS data indicate that the methodology is able to select the dominant chemical time scales of the investigated process.

Conclusion

A proposed methodology is suggested for the calculation of Da in case of complex kinetic schemes. In particular, Principal Component Analysis and Principal Variables based approaches appear well suited to the purpose, as they are able to identify the directions and variables carrying most of the information in a multivariate system. The methodology was successfully tested on flameless combustion data sets, for which validated numerical data obtained using a complex kinetic scheme are available, as well as a DNS data set of non-premixed, CO/H_2 combustion. In particular, the proposed methodology was able to identify the limiting time-scale for different configurations,



(a)



(b)

Figure 16: Chemical time-scale (τ_C) and Damköhler values as a function of mixture fraction (ξ) using the full Jacobian matrix.

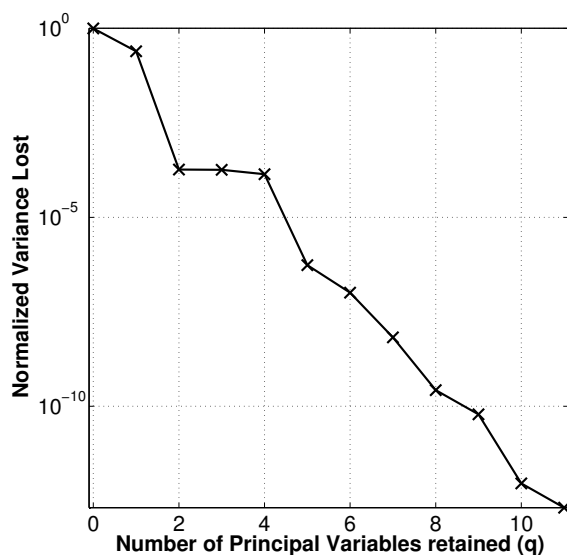
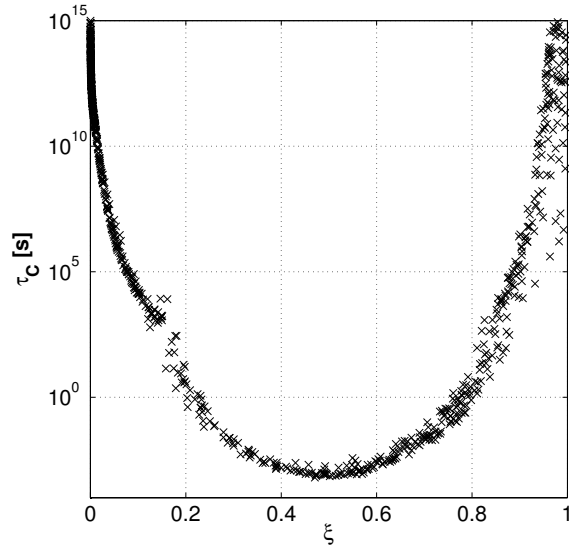


Figure 17: Trace plot for DNS case. Y-axis gives a normalized variance which is lost based on the selection of q , the x-axis.

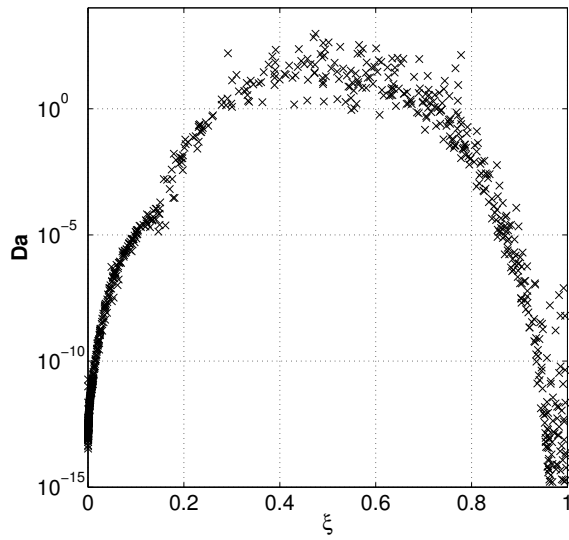
yielding to a subset of variables (called principal variables) for which the Damköhler resulted invariant. Identification of relevant chemical time scales leads to an informative evaluation of the Damköhler number. The Damköhler number analysis can then be used to help determine the correct turbulent combustion models as well as aid in the development of combustion models for a specific combustion regime.

Acknowledgments

We thank Dr. Alberto Cuoci for the assistance in the development of the JACOBEN software. In addition we thank our sponsor for which part of the present research was funded: The National Nuclear Security Administration under the Accelerating Development of Retrofittable CO₂ Capture Technologies through Predictivity program through DOE Cooperative Agreement DE NA 00 00 740.



(a)



(b)

Figure 18: Chemical time-scale (τ_C), and Damköhler values as a function of mixture fraction (ξ), using 3 Principal Variables.

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