Combustion and Flame 159 (2012) 3119–3127

Contents lists available at SciVerse ScienceDirect

Combustion and Flame

journal homepage: www.elsevier.com/locate/combustflame

Computational diagnostics for *n*-heptane flames with chemical explosive mode analysis

Ruiqin Shan [a], Chun Sang Yoo [c], Jacqueline H. Chen [b], Tianfeng Lu [a,*]

[a] *Department of Mechanical Engineering, University of Connecticut, Storrs, CT 06269-3139, USA*
[b] *Combustion Research Facility, Sandia National Laboratories, Livermore, CA 94551, USA*
[c] *School of Mechanical and Advanced Materials Engineering, Ulsan National Institute of Science and Technology, Ulsan 689-798, Republic of Korea*

ARTICLE INFO

Article history:
Received 13 February 2012
Received in revised form 26 April 2012
Accepted 29 May 2012
Available online 6 July 2012

Keywords:
Chemical explosive mode analysis
Computational flame diagnostics
n-Heptane
Homogenous charge compression ignition
Direct numerical simulation

ABSTRACT

Computational flame diagnostics (CFLDs) are systematic tools to extract important information from simulated flames, particularly when detailed chemical kinetic mechanisms are involved. The results of CFLD can be employed for various purposes, e.g. to simplify detailed chemical kinetics for more efficient flame simulations, and to explain flame behaviors associated with complex chemical kinetics. In the present study, the utility of a recently developed method of chemical explosive mode analysis (CEMA) for CFLD will be demonstrated with a variety of flames for *n*-heptane including auto-ignition, ignition and extinction in steady state perfectly stirred reactors (PSRs) and laminar premixed flames. CEMA was further utilized for analyses and visualization of a direct numerical simulation (DNS) dataset for a 2-D *n*-heptane–air flame under homogeneous charge compression ignition (HCCI) conditions. CEMA was found to be a versatile method for systematic detection of many critical flame features including ignition, extinction, premixed flame fronts, and flame stabilization mechanisms. The effects of cool flame chemistry for *n*-heptane on ignition, extinction and flame stability were also investigated with CEMA.

1. Introduction

The coupling of detailed chemical kinetics with turbulence is important for high-fidelity combustion simulations, e.g. large eddy simulations (LESs) and direct numerical simulations (DNSs), because it can provide accurate detailed descriptions of complex turbulence-chemistry interactions. In particular, the virtue of DNS is that it resolves the Navier–Stokes equations fully down to the Kolmogorov length scale, thus can provide accurate and rich information regarding the chemical and transport processes in turbulent flames for solving many energy related problems: e.g. fuel efficiency, pollutant emissions and fire safety. Detailed chemical kinetic mechanisms, however, consist of a large number of species and elementary reactions. As such, it is still prohibitive to directly apply them in multi-dimensional high-fidelity combustion simulations due to the high computational cost. Mechanism reduction is therefore necessary to accommodate the large mechanisms in large scale combustion simulations.

Computational flame diagnostics (CFLDs) is an integral component for mechanism reduction because it can be used for analyzing detailed mechanisms thoroughly prior to the reduction. There have been a variety of methods developed for mechanism reduction through skeletal reduction by eliminating unimportant species and reactions from detailed mechanisms [1–7], and timescale-based reduction such as quasi steady state approximations (QSSAs) [8–15], rate controlled constrained equilibrium (RCCE) [16], low-dimensional manifold (ILDM) [17] and computational singular perturbation (CSP) [18–20]. Mechanism reduction is also achieved through tabulation methods such as *in situ* adaptive tabulation (ISAT) [21], pre-image curves [22], and piecewise reusable implementation of solution mapping (PRISM) [23], and optimization based methods such as that in [24].

Many of these methods are efficient if the mechanisms are small or moderately large. However, the reduction can become difficult for large hydrocarbons that may consist of hundreds or thousands of species [25–28]. In such cases, extremely high efficiency is required for the reduction. The method of direct relation graph (DRG) [5,29–31] is a linear-time method that is suitable for skeletal reduction of extremely large mechanisms. DRG has been extended to take advantage of error propagation (DRGEP) [3,6,32–34] and was combined with sensitivity analysis in DRG aided sensitivity analysis (DRGASA) [31,35–37] and DRGEP with sensitivity analysis (DRGEPSA) [3]. A path flux analysis (PFA) was recently developed to consider species couplings through the creation and consumption of a species respectively [7], and the diffusion effect was considered in a transport flux based DRG [38]. Due to their low computational cost, the DRG based methods have also been employed for adaptive reduction [32,33,38].

A suite of algorithms with DRG as the first step were recently developed to systematically derive reduced mechanisms suitable

---

[*] Corresponding author.
E-mail address: tlu@engr.uconn.edu (T. Lu).

0010-2180/$ - see front matter © 2012 The Combustion Institute. Published by Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.combustflame.2012.05.012

for DNS [39], which are highly demanding in terms of the efficiency, accuracy and robustness of the reduced mechanisms. Algorithms based on analytic computing, such as graph theory and analytic differentiation, were extensively involved in these methods as outlined in [39]. Procedurally, unimportant species and reactions were first eliminated using DRG and DRGASA from the detailed mechanisms; correlated isomers are then lumped to reduce the number of transported variables [40]; quasi steady state (QSS) species are systematically identified using an algorithm based on CSP [11] and the algebraic equations for QSS approximations (QSSAs) are solved analytically based on graph theory [41]. Diffusive species are then bundled for the mixture-averaged transport model [42] such that the computational cost for diffusion coefficient evaluation can be mostly eliminated. Chemical stiffness is removed ultimately on-the-fly [43] such that the low-cost explicit integration solvers, such as the explicit 4th order Runge–Kutta method in [44], can be adopted in DNS instead of the substantially more expensive implicit solvers. Consequently, the cost of DNS becomes linearly proportional to the number of species in contrast to the quadratic or cubic dependence in flame simulations with implicit solvers [43,45]. Realistic chemistry for practical fuels, e.g. methane, ethylene [35,46–48], *n*-heptane [43,45], and iso-octane, therefore became affordable for DNS.

Although large scale flame simulations can now be routinely performed with reduced mechanisms of practical fuels, new challenges emerge because of the large datasets generated by the simulations. One of the challenges is caused by the complex chemical kinetic couplings in detailed chemistry, particularly those for large hydrocarbons involving cool flame chemistry that is important at low temperatures. Due to the negative temperature coefficient (NTC) behavior associated with cool flame chemistry, the flame behavior can become rather complex at near limit conditions. Another challenge is associated with the large datasets generated in flame simulations with detailed chemistry. For example, a recent 3-D DNS of a laboratory-scale lifted ethylene jet flame simulated with a 22-species reduced mechanism at Sandia National Laboratories generated 240TB of field data and 50TB of particle data [46]. Such massive datasets defy almost any currently available methods for DNS data mining that depend on empirical selection of criteria requiring human interactions, and resulted in a need for CFLD to systematically extract salient information from the datasets.

In response to this need, a method of chemical explosive mode analysis (CEMA) [45,49,50] was recently developed to systematically detect important flame features, e.g. ignition, extinction, premixed flame fronts and diffusion flame kernels, from simulated results at general flame conditions. As a utility for CFLD, the development of CEMA has benefited from many ideas in mechanism reduction, particularly the timescale analyses based on CSP. In contrast to the methods based on timescale analyses for the overall flame behavior that involve both chemistry and transport, CEMA is focused on the diagnostics on the chemical properties of the mixtures, and was primarily based on eigen-analysis of the Jacobian for the chemical source term in the governing equations. As such CEMA is simple and efficient to perform while it was found to be advantageous in limit phenomena detection compared with conventional methods based on temperature or a species concentration.

In the following, the utility of CEMA for CFLD will be reviewed and demonstrated with realistic fuel chemistry for *n*-heptane in a variety of flame configurations.

2. Formulation of CEMA

For a general chemically reacting system, the discretized conservation equations can be expressed in the following form

$$\frac{D\mathbf{y}}{Dt} = \mathbf{g}(\mathbf{y}) \equiv \boldsymbol{\omega}(\mathbf{y}) + \mathbf{s}(\mathbf{y}), \tag{1}$$

where $\mathbf{y}$ is the vector of the dependent variables including species concentrations and other state variables. In CEMA, temperature and species mole concentrations are included in $\mathbf{y}$. Note that the same quantity at different grid points is corresponding to different entries in $\mathbf{y}$. D/Dt is the material derivative. $\boldsymbol{\omega}$ is the chemical source term, and $\mathbf{s}$ is the mixing term. For spatially homogeneous systems such as perfectly stirred reactors (PSRs), the material derivative becomes the total derivative and $\mathbf{s}$ is the homogeneous mixing term. The Jacobian of the RHS of Eq. (1) is therefore comprised of the contributions from the chemical source term and the mixing term, respectively:

$$\mathbf{J_g} = \frac{\partial \mathbf{g}(\mathbf{y})}{\partial \mathbf{y}} = \mathbf{J}_\omega + \mathbf{J_s}, \ \mathbf{J}_\omega = \frac{\partial \boldsymbol{\omega}(\mathbf{y})}{\partial \mathbf{y}}, \quad \mathbf{J_s} = \frac{\partial \mathbf{s}(\mathbf{y})}{\partial \mathbf{y}}. \tag{2}$$

Embedded with rich information of the system, the full Jacobian $\mathbf{J_g}$ is important for the analyses of the system dynamics, e.g. flame stability [51–55]. Similarly, chemical information of the local mixture is embedded in the chemical Jacobian, $\mathbf{J}_\omega$, which is useful to determine the chemical properties of the mixtures, e.g. for mechanism reduction with intrinsic low dimensional manifold (ILDM) [17,56], computational singular perturbation (CSP) [4,18–20], and quasi steady state (QSS) species identification [11,14,15,57]. In CEMA, the chemical Jacobian is utilized to systematically detect critical flame features that are associated with drastic spatial and/or temporal changes in chemical properties [45,49,50]. It is noted that the chemical Jacobian is a block diagonal matrix because the chemical source term only directly depends on the local species concentrations and thermodynamic variables. Therefore the analyses of the chemical Jacobian can be performed independently on different grid points, i.e., the size of the chemical Jacobian at each grid point is $(K + 1)$ by $(K + 1)$, where K is the number of species, while the large Jacobian involving all the variables at all grid points is not needed in CEMA.

For simplicity, we shall refer the chemical Jacobian in the present work to the specific block in $\mathbf{J}_\omega$ that is corresponding to a local grid point of interest. Furthermore, Eq. (1) is assumed to be formulated in species concentrations, and the constant volume heat capacity of the mixture is treated as a constant for simplicity. In terms of accuracy, this assumption has little effect on the eigenvalue and eigenvector of the CEM. However, if the heat capacity is assumed a constant, there is a conservative mode with zero eigenvalue associated with energy conservation in addition to the M conservative modes associated with element conservations, where M is the number of participating elements. Without this assumption, the eigenvalue for the energy conservation mode is small but nontrivial, thus can induce numerical difficulty in distinguishing the CEM from the energy conservation mode near the zero-crossings of CEM. Therefore, the chemical Jacobian in the present work always involves $M + 1$ conservative modes that can be readily identified and excluded in CEMA, and the real parts of the remaining eigenvalues are assumed to be sorted in descending order without loss of generality. It is then defined that λ_e is the first and λ_i the ith remaining eigenvalue. The eigenmode associated with λ_e is defined as a chemical explosive mode (CEM) if

$$\mathrm{Re}(\lambda_e) > 0, \quad \lambda_e = \mathbf{b}_e \mathbf{J}_\omega \mathbf{a}_e \tag{3}$$

where $\mathbf{b}_e$ and $\mathbf{a}_e$ are the left and the right eigenvectors, respectively, associated with λ_e. The existence of a CEM indicates the propensity of a local mixture to auto-ignite if it is put in an isolated environment (adiabatic, constant volume). It was further found that the transition of a CEM from explosive, i.e. $\mathrm{Re}(\lambda_e) > 0$, to non-explosive, i.e. $\mathrm{Re}(\lambda_e) < 0$, is strongly correlated to critical flame features such as ignition, extinction, and premixed flame front locations [49,50].