Computational Flame Diagnostics with Bifurcation Analysis and Chemical Explosive Mode Analysis

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Computational Flame Diagnostics with Bifurcation Analysis

and Chemical Explosive Mode Analysis

Ruiqin Shan, PhD

University Of Connecticut, 2014

Limit flame phenomena, such as flame ignition, extinction and onset of instabilities, are important for fire safety, engine efficiency and pollutant emissions. Systematic identification of such limit phenomena and understanding of the underlying physicochemical processes are critical to develop a predictive capability for practical combustion systems. In the present study, systematic approaches for computational flame diagnostics are developed based on eigen-analysis of the governing equations of combustion systems to systematically extract information of the controlling processes for the limit phenomena. Specifically, a bifurcation analysis is developed based on the full Jacobian of the governing equations including both chemical and non-chemical source terms. The bifurcation analysis identifies bifurcation points of steady state combustion systems, across which the stability of the system changes, as demonstrated with perfectly stirred reactors (PSRs) as representative steady state combustion systems featuring the “S”-curve behaviors. It was shown that flame extinction may occur either at the upper turning point on the “S”-curve, which is widely accepted as the extinction state of strongly burning flames, or at a Hopf bifurcation point on the upper branch of the “S”-curve, particularly when the negative temperature coefficient (NTC) behaviors are involved. A bifurcation index is further defined to quantify the contribution of each reaction to the bifurcation points, such that the physicochemical processes controlling the limit phenomena can be identified. The bifurcation analysis is further exploited to obtain highly reduced mechanisms and to understand jet fuel
combustion at high-temperature conditions. Chemical explosive mode analysis (CEMA) as another approach for computational flame diagnostics, defined based on the Jacobian of the chemical source term, is further investigated to extract salient flame features, e.g. local ignition, extinction and flame fronts, from a variety of combustion systems, including 0-D auto-ignition, PSRs, 1-D laminar premixed flames, and a turbulent flame simulated with direct numerical simulation (DNS) under the homogeneous charge compression ignition (HCCI) condition for \( n \)-heptane–air mixtures featuring NTC behaviors.
Computational Flame Diagnostics with Bifurcation Analysis
and Chemical Explosive Mode Analysis

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Doctor of Philosophy Dissertation

Computational Flame Diagnostics with

Bifurcation Analysis and Chemical Explosive Mode Analysis

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thank my great brothers for their love and support. I also would like to thank my husband, Huangwei Zhang, for his support during my Ph.D pursuit.
List of Figures

Figure 1-1: A folded “S”-curve with multiple solutions and distinct ignition and extinction states [49].................................................................12

Figure 1-2: Evolution of fast and slow modes based on CSP [49].................................13

Figure 2-1: a) Temperature as a function of residence time, and b) the first two eigenvalues of the full Jacobian for methane–air in steady state PSRs. “sign()” denotes the signum function. ..................................................................................33

Figure 2-2: a) Temperature as a function of residence time, and b) the first two eigenvalues of the Jacobian, for DME–air in steady state PSRs. Solid lines: \( \lambda_1 \); Dashed lines: \( \lambda_2 \); Dash-dot-dot lines: \( \lambda_1 \) and \( \lambda_2 \) are a complex conjugate pair. “sign()” denotes the signum function; “Re()” denotes the real part of a complex number. .........................................................34

Figure 2-3: Temperature as a function of time in unsteady PSRs for DME–air, starting from steady state solutions with a perturbation in residence time of \( \tau' = 0.05 \) ms at a) the cool flame ignition point I\(_1\), and b) the strong flame ignition point I\(_2\), sampled on the “S”-curve in Fig. 2-2a........................................................................................................35

Figure 2-4: Temperature as a function of time in unsteady PSRs for DME–air with equivalence ratio of \( \phi = 5.0 \), pressure of 30 atm, and inlet temperature of 700 K, starting from steady state solutions with temperature perturbations by \( T' = \pm 0.1 \) K at a) Point P\(_1\) with residence time \( \tau = 4.9 \) ms, \( \lambda_1 = -2.1E2 \) s\(^{-1}\), and b) Point P\(_2\) with residence time \( \tau = 0.1 \) ms, \( \lambda_1 = -9.5E3 + 4.2E4i \) s\(^{-1}\). P\(_1\) and P\(_2\) were sampled on the upper branch of the “S”-curve as shown in the inset in (a). ........................................................................................................36

Figure 2-5: Temperature as a function of time in unsteady PSRs for DME–air with equivalence ratio of \( \phi = 5.0 \), pressure of 30 atm, and inlet temperature of 700 K, starting from steady state solutions with temperature perturbations by \( T' = \pm 0.1 \) K at a) Point P\(_3\) with residence time \( \tau = 0.07 \) ms, \( \lambda_1 = 7.8E3 + 3.5E4i \) s\(^{-1}\), and b) Point P\(_4\) with residence time \( \tau = 0.06 \) ms, \( \lambda_1 = 5.0E4 \) s\(^{-1}\) and \( \lambda_2 = 0 \). P\(_3\) and P\(_4\) were sampled on the “S”-curve as shown in the inset in (b) and P\(_4\) is identical to the turning point E\(_2\).........................................................................................................37

Figure 2-6: Temperature as a function of time in unsteady PSRs for DME–air with equivalence ratio of \( \phi = 5.0 \), pressure of 30 atm, and inlet temperature of 700 K, starting from steady state solutions with temperature perturbation by \( T' = \pm 0.1 \) K at a) Point P\(_5\) with residence time \( \tau = 0.1 \) ms, \( \lambda_1 = -8.5E3 + 3.5E4i \) s\(^{-1}\), b) Point P\(_6\) with residence time \( \tau = 0.04 \) ms, \( \lambda_1 = 1.8E3 + 3.5E4i \) s\(^{-1}\). P\(_5\) and P\(_6\) were sampled on the cool flame branch of the “S”-curve as shown in the inset in (a). ........................................................................................................38

Figure 2-7: Temperature as a function of time in unsteady PSR for DME–air with equivalence ratio of \( \phi = 5.0 \), pressure of 30 atm, and inlet temperature of 700 K, starting from steady state solutions with temperature perturbation of \( T' = \pm 0.1 \) K at Point P\(_7\) with residence time \( \tau = 0.07 \) ms, \( \lambda_1 = 3.0E3 + 5.6E4i \) s\(^{-1}\). P\(_7\) was sampled on the cool flame branch of the “S”-curve as shown in the inset .................................................................39

VIII
Figure 2-8: Extinction temperature and residence time of PSRs as functions of the normalized equivalence ratio for DME–air, calculated based on the definition of Re(\(\lambda_1\)) = 0, in comparison with that based on the turning points. “Re(\(\lambda\))” denotes the real part of a complex number. .................................................................40

Figure 3-1: Temperature as a function of residence time for a rich DME–air mixture in PSRs, at pressure p = 30 atm, equivalence ratio \(\phi = 5.0\) and inlet temperature \(T_{in} = 700\) K. Blue solid line: stable states, red dashed line: unstable states. .............................................................................58

Figure 3-2: Reactions ranked in \(|BI|\) for (a) extinction of the strong flames, \(E_2'\), and (b) extinction of the cool flames, \(E_1'\), at pressure p = 30 atm, equivalence ratio \(\phi = 5.0\) and inlet temperature \(T_{in} = 700\) K in PSRs .............................................................................................................59

Figure 3-3: Reactions ranked in \(|BI|\) for (a) ignition of the strong flames, \(I_2\), and (b) ignition of the cool flames, \(I_1\), at pressure p = 30 atm, equivalence ratio \(\phi = 5.0\) and inlet temperature \(T_{in} = 700\) K in PSRs. .............................................................................................................60

Figure 3-4: “S”-curves for DME–air at pressure p = 30 atm, equivalence ratio \(\phi = 5.0\) and inlet temperature \(T_{in} = 700\) K in PSRs with perturbations in the “A”-factors of (a) R26 and R27, and (b) R157 and R132. .............................................................................................................61

Figure 3-5: Constant-pressure auto-ignition staring from (a) the extinction of the strong flames \(E_2'\) and (b) the ignition of the cool flames \(I_1\) calculated based on the mechanisms with perturbations in the “A”-factors of R26 and R27, respectively .............................................................................................................62

Figure 3-6: Constant-pressure auto-ignition staring from (a) the extinction of the cool flames \(E_1'\) and (b) the ignition of the cool flames \(I_1\) calculated based on the mechanisms with perturbations in the “A”-factors of R26 and R27, respectively. .............................................................................................................63

Figure 3-7: Correlation of the BI values with the normalized sensitivity coefficients at (a) \(E_2'\) and (b) \(E_1'\) for DME–air at pressure p = 30 atm, equivalence ratio \(\phi = 5.0\) and inlet temperature \(T_{in} = 700\) K in PSRs. .............................................................................................................64

Figure 3-8: Correlation of the BI values and the normalized sensitivity coefficients at (a) \(I_2\) and (b) \(I_1\) for DME–air at pressure p = 30 atm, equivalence ratio \(\phi = 5.0\) and inlet temperature \(T_{in} = 700\) K in PSRs. .............................................................................................................65

Figure 3-9: Extinction temperature of (a) the strong flames and (b) the cool flames calculated with the original, reduced and tuned mechanisms, respectively, for DME–air at different equivalence ratios and pressure p = 30 atm and inlet temperature \(T_{in} = 700\) K in PSRs. .............................................................................................................66

Figure 3-10: Temperature as a function of time, calculated with the original, reduced and tuned mechanisms, respectively, for DME–air under different equivalence ratios at pressure p = 30 atm and inlet temperature \(T_{in} = 700\) K in a transient PSRs with fluctuating residence time starting from a cool flame .............................................................................................................67

Figure 3-11: Temperature as a function of time, calculated with the original, reduced and tuned mechanisms, respectively, for DME–air under different equivalence ratios at pressure p = 30 atm and inlet temperature \(T_{in} = 700\) K in a transient PSRs with fluctuating residence time starting from a strong flame .............................................................................................................68

IX
Figure 4-1: (a) Ignition delay as a function of initial temperature in constant-pressure auto-ignition at pressure $p = 1$ and $10$ atm, equivalence ratio $\phi = 0.7$, and (b) the “$S$”-curves of PSRs at pressure $p = 10$ atm, equivalence ratio $\phi = 0.7$ and inlet temperature $T_{in} = 1000$ K, for $n$-dodecane, $n$-decane and $n$-octane, respectively.

Figure 4-2: (a) Extinction temperature and (b) extinction residence time as functions of inlet temperature in PSRs at pressure $p = 10$ atm for $n$-dodecane, $n$-decane and $n$-octane, respectively.

Figure 4-3: (a) Ignition delay as a function of initial temperature in constant-pressure auto-ignition at pressure $p = 10$ atm, equivalence ratio $\phi = 0.7$, and (b) the “$S$”-curves of PSRs at pressure $p = 10$ atm, equivalence ratio $\phi = 0.7$ and inlet temperature $T_{in} = 1000$ K, for $n$-dodecane, $n$-butyl-cyclohexane and toluene, respectively.

Figure 4-4: (a) Extinction temperature and (b) extinction residence time as functions of inlet temperature in PSRs at pressure $p = 10$ atm for $n$-dodecane, $n$-butyl-cyclohexane, toluene, and binary mixtures of $50\%$ $n$-dodecane and $50\%$ $n$-butyl-cyclohexane in mole, respectively.

Figure 4-5: (a) Ignition delay as a function of initial temperature in constant-pressure auto-ignition at pressure $p = 10$ atm, equivalence ratio $\phi = 0.7$, and (b) the “$S$”-curves of PSRs at pressure $p = 10$ atm, equivalence ratio $\phi = 0.7$ and inlet temperature $T_{in} = 1000$ K, for $n$-dodecane, toluene, and binary mixtures of $n$-dodecane and toluene with $20\%$ and $50\%$ toluene in mole, respectively.

Figure 4-6: (a) Extinction temperature and (b) extinction residence time as functions of inlet temperature in PSRs at pressure $p = 10$ atm for $n$-dodecane, toluene, and binary mixtures of $n$-dodecane and toluene with $20\%$ and $50\%$ toluene in mole, respectively.

Figure 4-7: (a) Temporal profile of temperature in constant-pressure auto-ignition, and (b) the “$S$”-curves of PSRs at pressure $p = 10$ atm, equivalence ratio $\phi = 0.7$ and initial and inlet temperatures of $1000$ K, for pure $n$-dodecane and the binary mixture of $80\%$ $n$-dodecane and $20\%$ toluene in mole, respectively, predicted by three different mechanisms.

Figure 4-8: Reactions ranked in bifurcation index for the (a) extinction and (b) ignition states on the “$S$”-curves of PSRs in Fig. 4-5b for binary mixtures of $n$-dodecane and toluene with $0$, $20\%$, and $50\%$ toluene in mole, respectively.

Figure 4-9: (a) Maximum temperature $T_{max}$, as a function of the strain rate calculated with the detailed, lumped and reduced mechanisms, respectively; (b) Normalized total mass fraction of $C_{4+}$ species, and the primary fuel cracking products, including $CH_4$, $C_2H_4$ and $C_3H_6$, calculated with the detailed mechanism for three different strain states in counterflow non-premixed flames at atmospheric pressure. Fuel inlet: $50\%$ $n$-dodecane and $50\%$ $N_2$ in mole with inlet temperature of $300$ K. Oxidizer inlet: air with inlet temperature of $300$ K.

Figure 4-10: (a) Maximum temperature $T_{max}$, as a function of the strain rate calculated with the detailed, lumped and reduced mechanisms, respectively; (b) Normalized total mass fraction of $C_{4+}$ species, and the primary fuel cracking products, including $CH_4$, $C_2H_4$ and $C_3H_6$, calculated with the detailed mechanism for three different strain states, in counterflow premixed
flames of \( n \)-dodecane–air with equivalence ratio of 0.7, inlet temperature of 300 K and atmospheric pressure. .................................................................92

Figure 5-1: Time dependence of temperature and \( \lambda_e \) in auto-ignition under constant pressure at different initial temperatures for \( n \)-heptane. The color at each data point indicates the value of \[ \text{sign}(\text{Re}(\lambda_e))\times\log_{10}(1+|\text{Re}(\lambda_e)|). \] “\( \text{sign()} \)” denotes the signum function; “\( \text{Re()} \)” denotes the real part of a complex number. ........................................................................................................114

Figure 5-2: Temporal evolution of a) \( \lambda_e \) and temperature, and b) EI for different species for auto-ignition of a lean \( n \)-heptane–air mixture under constant pressure and initial temperature of 800K. Lines with symbols in panel (b) indicate EI data. .................................................................115

Figure 5-3: “S”-curves of PSR for a) ethylene–air and b) \( n \)-heptane–air. The colors superposed to the data points on the “S”-curves indicate the values of \[ \text{sign}(\text{Re}(\lambda_e)-1/\tau)\times\log_{10}(1+|\text{Re}(\lambda_e)-1/\tau|). \] The color of the data points in the inset in (b) shows the values of \[ \text{sign}(\text{Re}(\lambda_e)-1/\tau)\times\log_{10}(1+|\text{Re}(\lambda_e)-1/\tau|). \] “\( \text{sign()} \)” denotes the signum function; “\( \text{Re()} \)” denotes the real part of a complex number. ........................................................................................................116

Figure 5-4: Temperature evolution in unsteady PSR of \( n \)-heptane–air after a small initial perturbation (\( \Delta T = -10 \) K) to the steady state solutions, at a) a point between \( E_2 \) and \( E_2' \) in Fig. 5-3b with a residence time larger than that at \( I_1 \), and b) a point between \( E_2 \) and \( E_2' \) with a residence time shorter than that at \( I_1 \). The values of temperature in the titles indicate the steady state solutions without the perturbation. .....................................................................................117

Figure 5-5: Temperature profiles of 1-D planar freely propagating laminar \( n \)-heptane–air premixed flames with different equivalence ratios at atmospheric pressure. The color superposed to each data point indicates the value of \[ \text{sign}(\text{Re}(\lambda_e))\times\log_{10}(1+|\text{Re}(\lambda_e)|). \] “\( \text{sign()} \)” denotes the signum function; “\( \text{Re()} \)” denotes the real part of a complex number. ........................................................................................................118

Figure 5-6: Profiles of temperature and \( Nu_e \) for ethylene–air for a) 1-D steady state freely propagating laminar premixed flame with equivalence ratio of 1.0 and free stream temperature of 300 K, and b) 1-D steady state burner stabilized flame with equivalence ratio of 0.2 and inlet temperature of 1200 K. The color superposed to each data point indicates the value of \[ \text{sign}(\text{Re}(\lambda_e))\times\log_{10}(1+|\text{Re}(\lambda_e)|). \] “\( \text{sign()} \)” denotes the signum function; “\( \text{Re()} \)” denotes the real part of a complex number. ........................................................................................................119

Figure 5-7: Spatial distribution of \( \lambda_e \) (left column), OH concentration (middle column) and temperature (right column) for 2-D \( n \)-heptane–air mixture with an equivalence ratio, \( \phi = 0.3 \), initial pressure, \( p_0 = 40 \) atm, initial mean temperature, \( T_0 = 900 \) K with a RMS fluctuation of \( T'' = 100 \) K. The rows from top to bottom correspond to the time instants: \( t = 0, 0.35 \) ms, 1 ms, 1.7 ms, and 2 ms, respectively. The white isolines denote \( \text{Re}(\lambda_e) = 0 \). .....................................................................................120

Figure 5-8: “S”-curves of PSR for methane–air at a) pressure \( p = 1 \) atm, and b) pressure \( p = 30 \) atm, under equivalence ratio \( \phi = 0.5, 1 \) and 2, and inlet temperature \( T_{in} = 1000 \) K. The symbols denote the extinction states identified from the reduced CEMA description based on Eq. (5-19).........................................................................................................121

XI
Figure 5-9: (a) Extinction temperature and (b) extinction residence time as functions of equivalence ratio calculated with the full and reduced CEMA descriptions, respectively, for methane–air in PSRs at inlet temperature $T_{in} = 1000$ K and pressure $p = 1$ and 30 atm. ..........122

Figure 5-10: “$S$”-curves of PSR for ethylene–air at a) pressure $p = 1$ atm, and b) pressure $p = 30$ atm, under equivalence ratio $\phi = 0.5$, 1 and 2, and inlet temperature $T_{in} = 1000$ K. The symbols denote the extinction states identified from the reduced CEMA description based on Eq. (5-20)..................................................................................................................................................123

Figure 5-11: (a) Extinction temperature and (b) extinction residence time as functions of equivalence ratio calculated with the detailed and reduced CEMA descriptions, respectively, for ethylene–air in PSRs at inlet temperature $T_{in} = 1000$ K and pressure $p = 1$ and 30 atm. ..........124

Figure 5-12: “$S$”-curves of PSR for $n$-heptane–air at a) pressure $p = 1$ atm, and b) pressure $p = 30$ atm, under equivalence ratio $\phi = 0.5$, 1 and 2, and inlet temperature $T_{in} = 1000$ K. The symbols denote the extinction states identified from the reduced CEMA description based on Eq. (5-21). .................................................................125

Figure 5-13: (a) Extinction temperature and (b) extinction residence time as functions of equivalence ratio, calculated with the detailed and reduced CEMA descriptions, respectively, for $n$-heptane–air in PSRs at inlet temperature $T_{in} = 1000$ K and pressure of 1 and 30 atm. ...........126
# Table of Contents

ACKNOWLEDGEMENTS ........................................................................................................... VI

List of Figures ........................................................................................................................ VIII

Table of Contents .................................................................................................................. XIII

Chapter 1  Introduction ........................................................................................................... 1

1.1  Background ....................................................................................................................... 1

1.2  Systematic Detection of Ignition and Extinction ............................................................... 4

1.3  Identification of Reactions Controlling Limit Flame Phenomena ..................................... 6

1.4  Organization of the Dissertation ....................................................................................... 10

1.5  List of Peer-Reviewed Papers .......................................................................................... 11

Chapter 2  Identification of Ignition and Extinction in PSRs with Bifurcation Analysis .. 14

2.1  Introduction ....................................................................................................................... 14

2.2  Methodologies ................................................................................................................... 16

2.3  Results and Discussion ...................................................................................................... 19

2.3.1  Flame stability analysis for methane–air in PSRs ......................................................... 19

2.3.2  Flame stability analysis for DME–air in PSRs ........................................................... 20

2.3.3  Ignition and extinction of DME–air with different equivalence ratios ....................... 27

2.4  Concluding Remarks ........................................................................................................ 29

Chapter 3  Identification of the Chemical Kinetics Controlling Ignition and Extinction in PSRs with Bifurcation Analysis ......................................................................................... 41

3.1  Introduction ....................................................................................................................... 41

3.2  Methodologies ................................................................................................................... 42

3.3  Results and Discussion ...................................................................................................... 45

3.3.1  Identification of the controlling reactions for ignition and extinction ....................... 46
Chapter 3
3.3.2 Significance of the reactions with large BI values .............................................47
3.3.3 Comparison with sensitivity analysis .................................................................50
3.4 Model Reduction and Tuning based on the Bifurcation Analysis .........................52
3.5 Concluding Remarks ..........................................................................................54

Chapter 4
Effects of Surrogate Composition and Lumped Fuel Cracking Reactions on High-Temperature Combustion of Jet Fuels .................................................................69
4.1 Introduction ..........................................................................................................69
4.2 Selection of Surrogate Mixtures .........................................................................71
  4.2.1 Ignition and extinction of single-component surrogates .................................71
  4.2.2 Ignition and extinction of surrogate mixtures ................................................72
4.3 Effects of Fuel Cracking Reactions on Ignition and Extinction with Bifurcation
Analysis ..................................................................................................................75
4.4 Validation of a Reduced Mechanism with Lumped Fuel Cracking Steps in Counterflow
Flames ....................................................................................................................77
  4.4.1 A brief review of the reduced mechanism ......................................................77
  4.4.2 Mechanism validation in counterflow flames ................................................77
4.5 Concluding Remarks ..........................................................................................80

Chapter 5
Computational Diagnostics for n-Heptane Flames with Chemical Explosive Mode Analysis .................................................................93
5.1 Introduction ..........................................................................................................93
5.2 Formulation of CEMA .........................................................................................95
5.3 Detection of Auto-ignition ...................................................................................98
5.4 Ignition and Extinction in Steady State PSRs .....................................................99
5.5 Diagnostics of 1-D Steady State Laminar Premixed Flames ...............................103
  5.5.1 Location of premixed flame fronts ..............................................................103
  5.5.2 Propagation of premixed flame vs. auto-ignition reaction front ..................104

XIV
5.6 2-D DNS for n-Heptane at HCCI Conditions.................................................................106
5.7 Reduced Descriptions of CEMA ....................................................................................107
5.8 Concluding Remarks ......................................................................................................111

Chapter 6  Summaries and Future Perspectives.................................................................127

References ..........................................................................................................................131
Chapter 1 Introduction

1.1 Background

Combustion is an important energy-conversion process that affects almost every aspect of our society, as over 80% of the global energy consumption is attributed to the combustion of fossil fuels derived from petroleum, coal and natural gas [1, 2]. While the heat and power generated from combustion processes can benefit our daily life, adverse effects, such as fire hazards, accidental explosions and pollutant emissions, may also result from combustion. In particular, air pollution associated with the emissions of carbon monoxide (CO), unburned hydrocarbons, nitrogen oxides (NOx), sulfur oxides (SOx), and particular matters (PM) etc. leads to many human health issues and the climate change. On the other hand, the increasing energy demand and the depleting fossil fuel sources are pointing to an energy crisis on the horizon. To search for alternative energy sources, one needs to understand and quantify the properties of a large number of new chemical species and to predict their combustion such that efficient and robust combustors can be designed.

Combustion processes are complicated by the vastly different time and length scales and the chemistry–flow interactions that frequently involve limit flame phenomena, such as ignition and extinction. In our daily life, examples of ignition can be striking a match or starting a car engine. In internal combustion (IC) engines, ignition timing of fuel–air mixtures will not only affect the fuel efficiency and pollutant emissions, but also is important for engine safety as knocking attributed to poor ignition control in spark-ignition and homogeneous charge compression ignition (HCCI) processes may severely damage the engines. For extinction, a
prominent example is lean blow-out (LBO) in jet engine and low-temperature combustion (LTC) applications, which may lead to safety issues and reduce the range of the operating conditions.

Experiments play a critical role in understanding combustion problems involving limit phenomena, while Computational Fluid Dynamics (CFD) has become another important approach in combustion research. Numerical simulations are routinely performed with reduced costs and improved models to generate flow information that can be difficult to access in experiments. Common approaches for CFD simulations of turbulent flames include Direct Numerical Simulation (DNS), Large Eddy Simulation (LES) and Reynolds-Averaged Navier–Stokes equations (RANS). However, although CFD combined with realistic chemistry can provide rich information of the chemistry–flow interaction, the high computational cost induced by the large number of species and reactions renders it prohibitive to employ fully detailed chemistry of practical fuels in CFD simulations [3].

An important approach to enable the application of realistic chemistry in large scale flame simulations is mechanism reduction. A variety of methods have been developed for mechanism reduction over the last few decades, through skeletal reduction by eliminating unimportant species and reactions from detailed mechanisms [4-10], and timescale-based reduction such as quasi steady state approximations (QSSA) [11-18], partial equilibrium approximations (PEA) [19, 20], rate controlled constrained equilibrium (RCCE) [21], low-dimensional manifold (ILDM) [22] and computational singular perturbation (CSP) [23-25]. Reduction in computational cost is also achieved through tabulation methods such as in situ adaptive tabulation (ISAT) [26], pre-image curves [27], and piecewise reusable implementation of solution mapping (PRISM) [28], and optimization based methods such as that in [29]. 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 [30-33]. In such cases, extremely high efficiency is required for the reduction. The method of direct relation graph (DRG) [8, 34-36] 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) [6, 9, 37-39] and was combined with sensitivity analysis in DRG aided sensitivity analysis (DRGASA) [36, 40-42] and DRGEP with sensitivity analysis (DRGEPSA) [6]. A path flux analysis (PFA) was recently developed to consider species couplings through the creation and consumption of a species respectively [10], and the diffusion effect was considered in a transport flux based DRG [43]. Due to their low computational cost, the DRG based methods have also been employed for adaptive reduction [37, 38, 43].

As a result, reduced mechanisms have been routinely utilized in large scale flame simulations of practical fuels, such as primary reference fuels (PRF) [44, 45], jet fuels [46] and biodiesels [36, 47]. However, new challenges emerge from the simulations due to the massive datasets generated and the complex flame features involved that are difficult to diagnose. For example, a 3-D DNS of a laboratory-scale lifted ethylene jet flame simulated with a 22-species reduced mechanism performed at Sandia National Laboratories resulted in 240TB of field data and 50TB of particle data [48]. Such large datasets defy almost any empirical or semi-empirical methods involving frequent human interactions for computational diagnostics. Another challenge is that large hydrocarbons involving cool flame chemistry and the negative temperature coefficient (NTC) behaviors typically involve complex reaction pathways and large species sets, and the flame behaviors are typically more complex than that of small fuel molecules near the ignition and extinction limits. Furthermore, for near-limit flame features, e.g. ignition and extinction, induced by the competition between finite rate chemistry and mixing, the flame
diagnostics is further complicated by the transport process especially in turbulent flows. Thus it is necessary and challenging to develop rigorous and efficient methods to systematically extract salient information from the large simulation datasets, and this constitutes a major objective of the present study.

The present study is focused on understanding the fundamental physics behind the critical combustion phenomena, especially for ignition and extinction which also attract practical interest. Through developing and utilizing advanced computational tools for flame diagnostics, this dissertation will investigate systematic methods for effectively and accurately identifying limit flame phenomena and understanding the underlying physicochemical processes controlling the limit phenomena in various combustion applications.

1.2 Systematic Detection of Ignition and Extinction

Ignition and extinction are transitions between burning and non-burning states. The criteria for identification of ignition and extinction may vary in different types of combustion systems, e.g. steady state vs. transient combustion.

For steady state systems, multiple solutions may be present due to the nonlinearity of chemical kinetics, characterized by the “$S$”-curves as shown in Fig. 1-1 [49]. The “$S$”-curve is a profile of a dependent variable, e.g. temperature or burning rate, plotted against the residence time in perfectly stirred reactors (PSRs), or the reciprocal strain rate in 1-D counterflow flames. Alternatively Damköhler number, $Da$, which represents the ratio of a characteristic transport time to a reaction time, can be used as the x-axis. An “$S$”-curve typically consists of three branches, namely the upper, middle and lower branches, connected by two turning points. The upper and the lower branches of the “$S$”-curve are physically stable, while the middle branch is
unstable and difficult to obtain in experiments. The upper branch of the “S”-curve indicates the intensely burning states, and the lower branch indicates weakly reacting states without identifiable flames. The upper turning point is commonly regarded as the extinction state of the strong flames as the solution will jump to the lower branch with further decreased $Da$ or residence time. The lower turning point is known as the ignition state as the solution will jump to the upper branch with further increased $Da$ or residence time. For the fuels with NTC behaviors, the “S”-curves can nevertheless involve additional branches and turning points, and thus the identification of ignition and extinction become more involved.

The limit phenomena associated with the turning points on the “S”-curves are important for many combustion applications, e.g. the development and validation of detailed chemistry, and can be experimentally measured or numerically obtained by marching along the stable branches of the “S”-curves [41, 50-57]. Since the Jacobian matrix becomes singular at the turning points, it is typically difficult to numerically obtain solutions close to the turning points, and methods such as arc-length continuation are frequently employed to compute the turning points [56, 58-63].

In transient combustion systems, such as auto-ignition and unsteady stirred reactors, methods for the identification of ignition and extinction can involve rather arbitrary criteria. The ignition delay time in auto-ignition strongly depends on fuel properties, and is typically measured experimentally, e.g. with shock tube and rapid compression machine (RCM). The inflection points on the temperature or a species concentration profile are frequently defined as the ignition points, while empirically selected threshold values for temperature or species concentrations, e.g. temperature increase by 400 K as used in CHEMKIN [64], are also widely adopted to define ignition. In diesel engine research, ignition delay is frequently defined as the
time from the start of injection (SOI) to the point where the integrated heat release reaching a certain amount, e.g. 5%, of total heat release [65, 66]. In the study of general turbulent flames, OH and CH concentrations are frequently employed to define local ignition, extinction and flame fronts in experiments [67-72] and numeric simulations [48, 73-76]. These empirical or semi-empirical criteria however may only be valid over a limited range of flame conditions and reliable methods that are valid over a wide range of flame conditions are needed. In the present study, approaches based on eigen-analyses will be developed for rigorous detection of critical flame features in complex flow fields.

1.3 Identification of Reactions Controlling Limit Flame Phenomena

Once the limit flame phenomena, e.g. ignition and extinction, are identified, it is important to further identify and understand the underlying processes controlling these flame features. This is complicated by the strong coupling between the flow and chemistry, particularly when detailed chemistry with a large number of species and reactions is involved. In previous studies, systematic methods have been developed to understand the couplings using both analytic and numerical approaches, such as asymptotic analysis [77], sensitivity analysis [78], computational singular perturbation (CSP) [23, 25, 79, 80], and chemical explosive mode analysis (CEMA) [81]. Asymptotic analysis is generally based on highly simplified, typically one-step, chemistry, such that approximate analytic solutions can be obtained to explain ignition and extinction [82-87] and flame instabilities [88-92] etc. Nevertheless, it is difficult to perform asymptotic analysis when detailed or multi-step chemistry is involved. In such cases, numerical methods such as sensitivity analysis, CSP and CEMA can be used instead.

Sensitivity analysis is an extensively used method in studying chemical kinetics problems [93-96]. It can be performed through numerically perturbing the input parameters around the
nominal values and then measuring the responses of the model outputs, known as the global sensitivity analysis. In contrast, local sensitivity analysis can be performed for systems that can be described by ordinary differential equations (ODEs) in the form of

$$\frac{dY}{dt} = g(Y; a)$$  \hspace{1cm} (1-1)$$

where $Y$ is the vector consisting of dependent variables, such as temperature and species concentrations. The vector of $a$ consists of model parameters, such as the pre-exponential “$A$”-factors and other rate constants.

The local sensitivities of the dependent variables on the model parameters are defined as

$$S = \frac{\partial Y}{\partial a},$$  \hspace{1cm} (1-2)$$

and can be computed by solving the following ODE system together with Eq. (1-1)

$$\frac{\partial S}{\partial t} = \frac{\partial}{\partial t} \left( \frac{\partial Y}{\partial a} \right) = \frac{\partial}{\partial a} \left( \frac{\partial Y}{\partial t} \right) = \frac{\partial g}{\partial a} + J \frac{\partial Y}{\partial a}, \hspace{1cm} (1-3a)$$

$$J = \frac{\partial g}{\partial Y}. \hspace{1cm} (1-3b)$$

This method for local sensitivity analysis has been implemented in the CHEMKIN applications [64] and many other numerical codes for combustion simulations. It is noted that, in addition to chemical kinetic parameters, the sensitivity can also be defined with respect to the transport [97-101] and thermodynamic parameters [102-105].
When combustion systems with disparate timescales are of interest, the CSP method is frequently used as a timescale analysis to decouple fast and slow processes and understand their couplings. CSP is originally formulated for chemically reacting systems described by ODEs:

\[
dY/dt = g(Y),
\]

where the vector of \( Y \) includes the concentrations of chemical species and other state variables, e.g. temperature and pressure. In CSP, \( g \) can be expressed in terms of a set of linearly independent column vectors:

\[
g = A \cdot f,
\]

where \( A \) is composed of column basis vectors and \( f \) is the vector of modes. By introducing a matrix \( B \) as the inverse of \( A \), i.e. \( B = A^{-1} \), the modes can be defined as \( f = B \cdot g \) and the rate of \( f \) can be further formulated by using the chain rule:

\[
df/dt = \Lambda \cdot f, \quad \Lambda = (B \cdot J + dB/dt) \cdot A.
\]

A refinement procedure [25] can then be employed to iteratively obtain \( A \) and \( B \) to decouple the fast and slow subspaces:

\[
\frac{df_{fast}}{dt} = \Lambda_{fast} \cdot f_{fast}, \quad \frac{df_{slow}}{dt} = \Lambda_{slow} \cdot f_{slow},
\]

\[
\Lambda = \begin{pmatrix} \Lambda_{fast} \\ \Lambda_{slow} \end{pmatrix}, \quad A = \begin{pmatrix} A_{fast} \\ A_{slow} \end{pmatrix}, \quad B = \begin{pmatrix} B_{fast} \\ B_{slow} \end{pmatrix},
\]
\[ \Lambda_{\text{fast}} = \left( B_{\text{fast}} \cdot J + \frac{dB_{\text{fast}}}{dt} \right) \cdot A_{\text{fast}}, \quad \Lambda_{\text{slow}} = \left( B_{\text{slow}} \cdot J + \frac{dB_{\text{slow}}}{dt} \right) \cdot A_{\text{slow}}. \] (1-7c)

\( \Lambda_{\text{fast}} \) is comprised of negative eigenvalues with larger magnitude than \( \Lambda_{\text{slow}} \). The fast modes associated with \( \Lambda_{\text{fast}} \) become exhausted after a transient period as shown in Fig. 1-2, which can be used to reduce the stiffness of the system. The contribution of a reaction or species to a mode can be subsequently quantified using the CSP data.

While sensitivity analysis, CSP and other systematic methods have been frequently used in combustion problems and much information can be obtained, sensitivity analysis and the refinement procedure in CSP can be rather time consuming when large mechanisms and complex simulations are involved. Other methods for the identification of limit flame phenomena depending on empirical and semi-empirical criteria frequently involve human interactions, resulting in reduced efficiency and accuracy when large datasets and complex flames are involved. CEMA is a recently developed method based on Jacobian analysis that is efficient and robust in identification of ignition, extinction and flame fronts [81]. CEMA has been applied to heated coflows of hydrogen [81] and ethylene [106], and 2-D simulation of PRF under homogeneous charge compression ignition (HCCI) conditions [44]. In the present study, CEMA will be extended to study the engine fuel flames involving the negative temperature coefficient (NTC) behaviors.

A bifurcation analysis based on eigen-analysis of the full Jacobian is further developed the present study as a computational flame diagnostic. The bifurcation analysis and CEMA will be validated in 0-D reactors and further applied to multi-dimensional flames, including the large-scale DNS data from Sandia National Laboratories.
1.4 Organization of the Dissertation

Chapter 2 introduces a bifurcation analysis to analyze the limit flame phenomena in steady state systems. It is observed that extinction may not occur at the turning points, and in such cases the bifurcation analysis can be employed to identify the physical extinction and ignition states. Chapter 3 is focused on understanding the important chemical kinetics and transport processes at extinction and ignition states based on the bifurcation analysis. The results from the bifurcation analysis are compared with that from sensitivity analysis. The bifurcation analysis is then extended to obtain highly reduced chemistry with tuned rate parameters. Chapter 4 extends the methods in Chs. 2 and 3 to study the fuel cracking reactions of practical fuels and to further obtain reduced mechanisms based on lumped fuel cracking steps at high-temperature conditions. A viable surrogate for high-temperature combustion of jet fuels is identified and the bifurcation analysis is applied to quantify the importance of the fuel cracking processes for ignition and extinction and to justify the lumping of the fuel cracking reactions into a few semi-global steps. Chapter 5 extends CEMA to analyze 0-D and 1-D elementary flames and 2-D DNS of HCCI combustion of \textit{n}-heptane featuring the NTC behaviors. Chapter 6 summarizes the findings and makes recommendations for future work.
1.5 List of Peer-Reviewed Papers


Figure 1-1: A folded “S”-curve with multiple solutions and distinct ignition and extinction states [49].
Figure 1-2: Evolution of fast and slow modes based on CSP [49].
Chapter 2  Identification of Ignition and Extinction in PSRs with Bifurcation Analysis

2.1  Introduction

As mentioned in Ch. 1, for steady state systems, the ignition and extinction states were conventionally defined as the turning points, which are frequently thought of as the only types of bifurcation points on the “S”-curve as shown by the schematics in Fig. 1-1 [49]. However, while the “S”-curve in Fig. 1-1 correctly describes the responses of many combustion systems to the variation in flow straining or mixing, it was found that multiple bifurcations may exist for practical fuels such as dimethyl ether (DME) and n-heptane [53, 107, 108]. As such, the conventional definition of ignition and extinction states based on the turning points may not be applicable for such practical fuels. Thus a bifurcation analysis is proposed in the present study to identity physical ignition and extinction states through analyzing the flame stability.

Linear flame stability in the bifurcation analysis is determined by the eigenvalues of the Jacobian matrix based on the steady state solutions. The Jacobian is important for combustion analyses involving detailed chemistry, e.g. in CSP [23, 25], ILDM [22], and CEMA [81, 106]. On the “S”-curves of a steady state system, a turning point is known to be associated with a singular Jacobian matrix [109]. As such, a turning point can separate a stable branch without positive eigenvalues, e.g. the upper and the lower branches in Fig. 1-1, from an unstable branch with a positive eigenvalue, e.g. the middle branch in Fig. 1-1. Nevertheless, in cases where the eigenvalues are complex numbers, flame stability is determined only by the sign of the real parts of the eigenvalues, while the imaginary parts of the eigenvalues determine the oscillation frequencies [110, 111]. In such cases, transition between a stable and an unstable flame may no longer occur at a turning point. Furthermore, oscillations, or flame instabilities, may occur near
the transition. For example, flame instabilities were observed in PSRs with near-limit flames for hydrogen and small hydrocarbons with heat losses either promoting or suppressing the oscillations [112, 113]. Flame oscillations were also observed in PSRs for diluted methane–air at low temperatures [114]. However, flame instabilities involving detailed chemistry of practical fuels, particular those involving NTC behaviors, are relatively less understood.

Nonlinear flame stability analyses involve high order expansion of the governing equations, thus can typically only be performed with simplified chemistry with one or a few steps and transport characterized by a Lewis number. Flame extinctions due to nonlinear instabilities prior to the turning points have been observed in previous works [115-117]. Numerical studies with detailed chemistry and transport on pulsating instability induced by thermal–diffusive couplings have been conducted for premixed flames with large Lewis numbers [118-120]. It was found that flame instability may promote extinction and the experimentally determined extinction states may not necessarily agree with the numerically obtained turning points on “S”-curves [120]. The numerical prediction of flame instabilities in Refs. [118-120] however involved time integration of unsteady flames that is rather time consuming, thus is difficult to apply for parametric studies. In the present study, linear flame stability analyses will be employed to study the extinction and ignition of steady state combustion involving detailed chemistry of practical fuels with NTC behaviors, and PSR is selected as a representative steady state combustion system that can be described by an “S”-curve similar to that in Fig. 1-1. Note that a PSR features a unity Lewis number since it only involves a single mixing timescale, that is, the residence time. Nevertheless, the results of flame stability for PSRs may be extended in the future to the study of diffusive systems, such as the counterflow flames.
2.2 Methodologies

The equations of time evolving PSRs can be written as

\[
\frac{dy}{dt} = g(y) = \omega(y) + s(y) , \quad y = [Y_1, Y_2, \ldots, Y_K, T]^T ,
\]  

(2-1a)

\[
\omega_i(y) = \frac{\dot{m}_i}{\rho}, \quad i = 1, 2, \ldots, K , \quad \omega_{K+1}(y) = -\frac{\sum_{i=1,K} \dot{m}_i h_i}{\rho c_p} ,
\]  

(2-1b)

\[
s_i(y) = \frac{Y^0_i - Y_i}{\tau}, \quad i = 1, 2, \ldots, K , \quad s_{K+1}(y) = -\frac{\sum_{i=1,K} Y^0_i (h^0_i - h_i)}{c_p \tau}, \quad \tau = \frac{\rho V}{M_{in}} ,
\]  

(2-1c)

where \( \omega \) is the chemical source term and \( s \) is the mixing term. \( y \) is the vector of dependent variables including species mass fractions, \( Y \), and temperature \( T \). \( \rho \) is density, \( \dot{m}_i \) is the volumetric mass production rate of the \( i \)th species, \( h \) is the specific enthalpy, \( V \) is the volume of the reactor, \( \dot{M}_{in} \) is the inlet mass flow rate, \( K \) is the total number of species, subscript \( i \) indicates the \( i \)th species, and the superscript \( \text{“}0\text{”} \) indicates the inlet condition. The solution of a steady state PSR is characterized by an \textquotedblleft S\textquotedblright\,-curve similar to that in Fig. 1-1. To show the stability of a specific state on the \textquotedblleft S\textquotedblright\,-curve of a steady state PSR, the unsteady equations can be integrated to show the response of the system to small perturbations made to the steady state solution.

Based on linear stability analysis of ODE, the growth of a small perturbation, \( \delta y \), initially superposed to the steady state solution of Eq. (2-1) can be approximated with

\[
\frac{d \delta y}{dt} \approx \mathbf{J}_g(y_0) \cdot \delta y , \quad \delta y = \delta y_0 \text{ at } t = t_0 ,
\]  

(2-2)

where \( y_0 \) is the steady state solution, and \( \mathbf{J}_g \) is the Jacobian matrix defined as
\[ J_g = J_\omega + J_s = \frac{\hat{c}_g(y)}{\partial y}, \quad J_\omega = \frac{\hat{c}_\omega(y)}{\partial y}, \quad J_s = \frac{\hat{c}_s(y)}{\partial y}. \]  

(2-3)

It is seen that \( J_g \) is comprised of two components, namely \( J_\omega \) for the chemical source term and \( J_s \) for the mixing term, respectively. It is noted that the chemical Jacobian describes the chemical properties of a mixture and can be employed to distinguish between the pre- and post-ignition mixtures in CEMA \cite{81, 106}. In the present work, the full Jacobian matrix, \( J_g \), will be employed for the bifurcation analysis through investigating flame stability of PSRs using two representative fuels, methane and DME, respectively. Methane is a hydrocarbon fuel without NTC behaviors and DME, as a diesel fuel surrogate, features NTC behaviors that involve low temperature chemistry.

Using similarity transformation \( J_g(y_0) = A \Lambda B \), Eq. (2-2) can be written as

\[ \frac{d\delta f}{dt} = \Lambda \cdot \delta f, \quad \delta f = B \cdot \delta y, \]  

(2-4)

where \( A \) and \( B \) are matrices that consist of the right and left eigenvectors, respectively. \( \Lambda \) is a diagonal matrix with the diagonal elements being the eigenvalues of \( J_g(y_0) \). Based on Eq. (2-4), the growth of a small perturbation in the direction of the \( i \)th eigenvector can be approximated as

\[ \delta f_i \approx \delta f_{i,0} e^{\lambda_i t}, \quad \delta f_i = b_i \cdot \delta y, \]  

(2-5)

where \( b_i \) is the \( i \)th row in \( B \), that is, the \( i \)th left eigenvector of \( J_g(y_0) \). The perturbation tends to exponentially grow if the real part of an eigenvalue is positive, or to decay if the real parts of all the eigenvalues are negative. A bifurcation point, where \( \text{Re}(\lambda_i) = 0 \), may separate a stable and an unstable segment on the “S”-curve. Note that “\( \text{Re}() \)” indicates the real part of a complex number in the present study. As such, the flame stability may change not only at a turning point, where \( \lambda_i \)
\( \lambda = 0 \), but also at other types of bifurcation, e.g. the Hopf bifurcation where the imaginary part of the eigenvalue is non-trivial \([110]\). While the turning points can be readily located on the “S”-curves, the identification of a Hopf bifurcation requires eigen-analysis which is the basis of the bifurcation analysis and will be demonstrated with PSRs for DME–air in the next section.

To further identify the controlling chemical species and reaction pathways at a bifurcation point, the contribution of a species to the mode involving zero-crossing eigenvalues can be quantified by the species pointer (SP), defined similarly to the explosion index in CEMA \([81, 106]\) and the radical pointer in CSP \([81, 106]\). The contribution of a reaction to a mode can be quantified by the participation index (PI) defined in CSP \([23, 25]\). If oscillatory modes associated with complex conjugate eigenvalues are of interest, the values of SP and PI can be expressed similarly to the radical pointer and PI in Ref. \([121]\) for complex CSP. Specifically, if \( \mathbf{a}_i \) and \( \mathbf{b}_i \) are complex eigenvectors, i.e.

\[
\mathbf{a}_i = a_{i,\text{re}} + a_{i,\text{im}}, \quad \mathbf{b}_i = b_{i,\text{re}} + b_{i,\text{im}},
\]

where the subscripts \( \text{re} \) and \( \text{im} \) indicate the real and imaginary parts of the complex eigenvectors, respectively, the SP can be defined as

\[
\text{SP}_{re} = \frac{\text{diag}(\mathbf{a}_i^\dagger \mathbf{b}_i)}{\text{sum}(\text{diag}(\mathbf{a}_i^\dagger \mathbf{b}_i))}, \quad \text{SP}_{im} = \frac{\text{diag}(\mathbf{a}_i^\dagger \mathbf{b}_i)}{\text{sum}(\text{diag}(\mathbf{a}_i^\dagger \mathbf{b}_i))},
\]

and the PI can be defined as

\[
\text{PI}_{\text{re}} = \frac{\mathbf{b}_{i,\text{re}} \cdot \mathbf{g}_r}{\sum_{r = 1} |\mathbf{b}_{i,\text{re}} \cdot \mathbf{g}_r|}, \quad \text{PI}_{\text{im}} = \frac{\mathbf{b}_{i,\text{im}} \cdot \mathbf{g}_r}{\sum_{r = 1} |\mathbf{b}_{i,\text{im}} \cdot \mathbf{g}_r|},
\]
where the superscript $i$ indicates the $i$th mode and $I$ is the number of reactions in the mechanism. The vector $\mathbf{g}_r$, where $1 \leq r \leq I$, indicates the contribution of the $r$th reaction to the RHS of Eq. (2-1a), and $\mathbf{g}_{I+1} = \mathbf{s}(\mathbf{y})$ is the mixing term. As such, each of the first $K$ entries in the vector $\mathbf{SP}^i_{re}$ indicates the normalized contribution of a species to the eigenvalue zero-crossing for the $i$th mode, and the last entry in $\mathbf{SP}^i_{re}$ indicates the contribution of heat release to the eigenvalue zero-crossing. Furthermore, an entry in $\mathbf{SP}^i_{im}$ indicates the contribution of a species or heat release to the conjugate of the $i$th mode. $\mathbf{Pt}^{i,r}_{re}$ and $\mathbf{Pt}^{i,r}_{im}$, indicate the contribution of the $r$th reaction, or the mixing term if $r = I + 1$, to the eigenvalue zero-crossing of the two conjugate modes that are oscillatory coupled.

To ensure sufficient numerical accuracy in the flame stability analysis, the full Jacobian $\mathbf{J}_g$ of the system in Eq. (2-3) is computed through analytic evaluations of both the chemical Jacobian, $\mathbf{J}_\omega$, and the Jacobian of the mixing term, $\mathbf{J}_s$. Note that the chemical Jacobian consists of the contribution from each individual reaction, which can be efficiently evaluated in analytic forms [3]. In the present work, a computer code was developed to automatically generate mechanism-specific subroutines for analytic Jacobian evaluation for arbitrary detailed mechanisms in CHEMKIN format [64].

2.3 Results and Discussion

2.3.1 Flame stability analysis for methane–air in PSRs

The flame stability of methane–air in PSRs is first studied with GRI-Mech 3.0 [122]. Figure 2-1a shows the “$S$”-curve of the stoichiometric methane–air mixture under atmospheric pressure with inlet temperature $T_0 = 1200$ K. Note that the high inlet temperature is needed to obtain a complete “$S$”-curve including the lower turning point for PSRs. It is seen that the “$S$”-
curve consists of three branches, namely the upper, middle, and lower branches, respectively, being similar to the canonical “S”-curve in Fig. 1-1. The steady state solutions on the “S”-curve are then employed for evaluation and eigen-decomposition of the Jacobian. Without loss of generality, the eigenvalues are sorted in descending order of the real parts. The variation of real parts of the first two eigenvalues, i.e. $\lambda_1$ and $\lambda_2$, with the change in temperature is shown in Fig. 2-1b, and the zero-crossing points of the real part of $\lambda_1$, i.e. $\lambda_1 = 0$, are shown in circles in Fig. 2-1a. It is seen that the zero-crossing points of $\lambda_1$ coincide with the turning points. Further investigation shows that $\lambda_1$ remains a real value on the entire “S”-curve, as such the turning points are the only type of bifurcation for methane–air at the condition shown in Fig. 2-1. Therefore, the turning points separate the stable and unstable branches on the “S”-curve in Fig. 2-1a. The flames on the upper branch are physically stable since $\lambda_1$, and consequently every other eigenvalue, are negative. The flame is unstable on the middle branch because $\lambda_1$ is positive there. This observation for methane–air combustion in PSRs is consistent with the canonical description of the “S”-curve in Fig. 1-1. It is further seen in Fig. 2-1b that while $\lambda_1$ is positive on the middle branch, $\lambda_2$ remains negative along the entire “S”-curve. Therefore the change in flame stability in Fig. 2-1 is determined solely by the zero-crossing of the largest eigenvalue, while the real parts of all the other eigenvalues remain negative along the “S”-curve.

2.3.2 Flame stability analysis for DME–air in PSRs

DME is then studied with a detailed mechanism with NTC chemistry [123], using a PSR with equivalence ratio of 5.0, pressure of 30 atm, and inlet temperature of 700 K. Note that one of the reasons that the rich mixture was chosen is to obtain pronounced NTC behaviors, which were nevertheless also observed under many other conditions. Figure 2-2a shows the “S”-curve for DME–air and Fig. 2-2b shows the real parts of the first two eigenvalues, namely $\lambda_1$ and $\lambda_2$. 
which change with temperature along the “$S$”-curve. Note again that the eigenvalues of the Jacobian are sorted in descending order of the real parts. The segments of the “$S$”-curve where these two eigenvalues are a complex conjugate pair are shown in dash-dot-dot lines in Fig. 2-2b, while the segments with both eigenvalues being real are indicated by the solid and dashed lines for $\lambda_1$ and $\lambda_2$, respectively.

It is seen in Fig. 2-2a that there are four turning points on the “$S$”-curve for DME–air due to the NTC behaviors in comparison to the simple “$S$”-curve for methane–air in Fig. 2-1a. Specifically, there are two extinction turning points, namely $E_1$ and $E_2$, and two ignition turning points, namely $I_1$ and $I_2$, each of which corresponds to the zero-crossing of an eigenvalue. It is further seen in Fig. 2-2b that $I_1$ and $I_2$ are associated with the zero-crossing of $\lambda_1$, i.e. $\lambda_1 = 0$, while $E_1$ and $E_2$ are associated with the zero-crossing of $\lambda_2$, i.e. $\lambda_2 = 0$. Note that at a turning point on the “$S$”-curve, the entire eigenvalue, not just the real part, crosses zero. In addition to the four turning points, there are two more bifurcation points, namely $E_1'$ and $E_2'$, which are associated with the zero-crossing of the real parts of the first two eigenvalues that form a complex conjugate pair, i.e. either $\text{Re}(\lambda_1) = 0$ or $\text{Re}(\lambda_2) = 0$, while their imaginary parts are not trivial. Therefore, $E_1'$ and $E_2'$ are Hopf bifurcation points [110], which may also indicate changes in system stability.

The six bifurcation points are then scrutinized to analyze the flame stability along the “$S$”-curve in Fig. 2-2a. It was shown in Eqs. (2-2)-(2-5) that the flame is stable if the real parts of all the eigenvalues of the full Jacobian are negative, or unstable if any eigenvalue has a positive real part. Therefore, for the present sorted eigenvalues, the flame is stable if $\text{Re}(\lambda_1) < 0$ and unstable if $\text{Re}(\lambda_1) > 0$. Based on this criterion, the stable segments on the “$S$”-curve for DME–air in Fig. 2-2a are shown in solid lines, and the unstable segments are shown in dashed lines. It is
seen that the flame is stable above \( E_2' \) and becomes unstable below it. Therefore, when marching downward along the “S”-curve, \( E_2' \) is the critical point beyond which a stable strongly burning flame cannot be sustained. Similarly, \( E_1' \) is a critical point above which the cool flame is stable, while below which the flame is unstable. Therefore \( E_2' \) can be defined as the physical extinction point of the strong flames, and \( E_1' \) is the physical extinction point of the cool flames. When marching upward along the “S”-curve, it is seen that the segment below \( I_1 \) is associated with the stable weakly reacting states, where a flame cannot be identified, while the segment above \( I_1 \) is unstable. It is expected that beyond \( I_1 \) the flame will jump to the cool flame branch between \( E_1' \) and \( I_2 \), as will be further discussed in Fig. 2-3. Therefore \( I_1 \) is the ignition point for the cool flames. Similarly, \( I_2 \) indicates the maximum residence time a cool flame can be sustained, thus it can be defined as the ignition state of the strong flames, since beyond \( I_2 \) the solution will jump to the upper branch above \( E_2' \).

It is interesting to see that while the turning points on “S”-curves are conventionally regarded as the ignition or extinction states for steady state combustion, the two turning points, \( E_1 \) and \( E_2 \) in Fig. 2-2a, are not the physical extinction points since on either side of them the flames are unstable. This can be explained by scrutinizing Fig. 2-2b, which shows that the real part of \( \lambda_1 \) is positive on both sides of \( E_1 \) and \( E_2 \). Therefore the zero-crossing of \( \lambda_2 \) does not change the flame stability there.

To verify the flame stabilities obtained from the above analyses, unsteady PSRs described by Eq. (2-1) will be used in the following to study the time evolvement of small perturbations to the steady state solutions on the “S”-curve. Procedurally, a small perturbation in residence time or temperature is first made to the steady state solution to obtain the initial
conditions, Eq. (2-1) is then time-integrated using the ODE solver DASAC [124] until the system reaches a steady state or oscillates with a steady amplitude.

The flame stability near the two ignition turning points, $I_1$ and $I_2$, were first investigated with unsteady PSRs. The steady state solutions were used as the initial condition for species and temperature with the residence times increased by $\tau' = 0.05$ ms. Figure 2-3 shows the temperature variation with time at the two ignition turning points. It is seen that the solution started at $I_1$ jumped to a point on the stable cool flame branch between $E_1'$ and $I_2$ in Fig. 2-2a with a final temperature of 941 K. Therefore it is verified that $I_1$ is indeed the ignition point for the cool flames. The solution started from $I_2$ jumped to the strongly burning branch above $E_2'$ on the “$S$”-curve in Fig. 2-2a, with the final temperature being 1421 K. Therefore $I_2$ is shown to be the ignition point for strong flames.

To verify that the strongly burning flames above $E_2'$ are stable, two points were sampled from the “$S$”-curve as shown in the inset of Fig. 2-4a. The first point, $P_1$, has a large residence time such that the mixture is almost in chemical equilibrium, and the other point, $P_2$, is close to $E_2'$. Temperature perturbations by $T' = \pm 0.1$ K were made to the steady state solutions, and the time evolvement of temperature for $P_1$ and $P_2$ is shown in Figs. 2-4a and 4b, respectively. It is seen that the temperature perturbations decay with time for both cases and the solutions eventually converge to the original steady states. Therefore, the flames on the upper branch above $E_2'$ were verified to be stable. It is further seen that, while the small perturbations for $P_1$ in Fig. 2-4a exponentially decay to zero without oscillations, those for $P_2$ in Fig. 2-4b decay with oscillations. This is because $\lambda_1$ is a negative real value at $P_1$, while it is a complex value with a negative real part at $P_2$. For the temperature profiles in Fig. 2-4b, the real part of $\lambda_1$ determines
the timescale for the small perturbations to decay, while the imaginary part determines the frequency of the oscillation.

To further show the unstable nature of the flames between $E_2$ and $E_2'$ in Fig. 2-2a, temperature perturbations by $T' = \pm 0.1$ K were made to two points, namely $P_3$ and $P_4$, shown in the inset of Fig. 2-5b. $P_3$ was below but close to $E_2'$ and $P_4$ is identical to $E_2$. The time evolutions of temperature for these two points are shown in Figs. 2-5a and 5b, respectively. It is seen that for both cases the solutions eventually converge to the lower branch below $I_1$ in Fig. 2-2a, as indicated by the final temperature of 700 K, which is also the inlet temperature. Oscillations were again observed in Fig. 2-5a for the solutions that started from $P_3$ since $\lambda_1$ is complex. The temperature profiles in Fig. 2-5b that started from $P_4$ show no oscillations, at least when the amplitudes are small. Therefore, the turning point $E_2$ is not the physical extinction state for the strong flames since extinction has occurred at $P_3$ before reaching $E_2$.

To further investigate the stability of cool flames near the NTC range, $P_5$ and $P_6$ were sampled between $E_1$ and $I_2$ as shown in the inset of Fig. 2-6a. $P_5$ is located slightly above $E_1'$, while $P_6$ is below $E_1'$ and slightly above $E_1$. Temperature perturbations by $T' = \pm 0.1$ K were again applied to the steady state solutions and the temperature evolutions for $P_5$ and $P_6$ were shown in Figs. 2-6a and 6b, respectively. It is seen that in Fig. 2-6a the perturbations in temperature decay to zero with oscillations and the solutions converge to the initial steady state solutions, indicating that the flame at $P_5$ is physically stable. Oscillations were observed since the eigenvalue $\lambda_1$ at point $P_5$ is complex. In contrast, the perturbation at $P_6$ grows with time and temperature eventually dropped to the inlet value 700 K as shown in Fig. 2-6b, thus flame extinction occurred. Oscillation is also observed in Fig. 2-6b since the eigenvalue $\lambda_1$ at $P_6$ is a complex number. Therefore, $E_1$ is not the physical extinction state for the cool flame because
extinction has occurred at P₆ prior to reaching the turning point E₁. Instead, since flame stability changes at E₁’, which is a Hopf bifurcation point, E₁’ can be defined as the extinction state of the cool flames.

While it is clear that the flames between E₁ and E₁’ are unstable, there can be different types of unstable flames as to be demonstrated with that at P₇, which is located slightly below E₁’ on the “S”-curve. Figure 2-7 shows that the perturbations in temperature, initially by T’ = ±0.1 K, grow at the beginning while eventually evolved to oscillations with a constant amplitude. This result indicates that an unsteady flame may extinguish, i.e. jump to a lower stable branch, ignite, i.e. jump to a higher stable branch, or oscillate with a finite constant amplitude when crossing a Hopf bifurcation point. Nevertheless, E₁’ can still be defined as the extinction state of cool flames considering that the cool flames cannot be stabilized beyond this point.

Based on the above analyses at different segments on the “S”-curve for DME–air in Fig. 2-2, the turning points I₁ and I₂ were shown to be the physical ignition points for the cool flames and the strong flames, respectively, while the turning points E₁ and E₂ were shown not to be the physical extinction points. Instead, the Hopf bifurcation points E₁’ and E₂’ actually separate the stable and unstable flames and can be defined as the physical extinction states of the cool flames and the strong flames, respectively. This observation has significant implications in predicting experimentally measured extinction and ignition states for steady state systems, such as the counterflow flames [41, 50, 55, 108]. A common practice in the previous studies to experimentally measure the extinction state of a steady flame is to first establish a strongly burning flame on the upper branch of the “S”-curve, then by slowly increasing the strain rate, or reducing the residence time, the flame marches along the upper branch of the “S”-curve toward
the extinction state, which is achieved when the strain rate cannot be further reduced without extinguishing the flame. Similarly, ignition states can be measured by marching in the opposite direction along the “S”-curve starting from a stable state on the lower branch. In numerical studies, the ignition and extinction states were typically assumed to occur at the turning points on the “S”-curve, which can be obtained by the arc-length continuation method [63]. It is shown in the present study that it can be problematic to directly compare the numerically obtained turning points with experimentally measured flame ignition and extinction states, e.g. for validation of detailed chemical kinetic mechanisms, particularly when fuels with NTC behaviors are involved. Instead, a bifurcation analysis should be performed to investigate the flame stability for identifying the physical extinction and ignition states.

Once a physical extinction or ignition state is determined through the above bifurcation analysis, the controlling species and reactions can be further identified at these critical states using the SP and PI defined in Eqs. (2-7) and (2-8). To identify the important species and reactions, the values of SP and PI were computed at the two extinction states, E₁’ and E₂’, in Fig. 2-2a, for the cool and strong flames, respectively. The independent variables, including temperature and species concentrations, with SP values larger than 0.1, are listed in Table 2-1. The important processes, including mixing and the elementary reactions, with PI values larger than 0.05, are listed in Table 2-2. Note that the modes of interest form a complex conjugate pair at each of the extinction points. As such both SP and PI involve a real and an imaginary component as shown in Tables 2-(1-2). Table 2-1 shows that temperature and species CH₃OCH₂O₂, CH₃OCH₂O₂H, and CH₂O are important for the cool flame extinction at E₁’. Heat release and CH₂O form one group as indicated by their SP<sub>re</sub> values, and CH₃OCH₂O₂, CH₃OCH₂O₂H form another group as indicated by their SP<sub>im</sub> values. The interaction of the two
groups determines the zero-crossing of the real part of the eigenvalue and the oscillatory behavior near E_1’. Table 2-2 further shows that the competition between the mixing process and two groups of reactions is important for the cool flame extinction. The first group of reactions includes CH_3OCH_2O_2 = CH_2OCH_2O_2H and CH_3OCH_2O_2H = OH + CH_3OCH_2O, which lead to radical formation through the oxygenated species, which are important for NTC chemistry. The other group involves the formation of H_2O and CH_2O that are associated with heat release. At the strong flame extinction, E_2’, CH_2O, DME, O_2, and H_2O_2 were found to be important as shown in Table 2-1, with CH_2O and H_2O_2 form one group while DME and O_2 form another. It is interesting to note that temperature is not a controlling variable at E_2’ due to the very rich mixture. As such the competition between the chain branching and termination reactions plays a predominant role in affecting flame stability at E_2’, as evident by the chain reactions listed in Table 2-2.

2.3.3 Ignition and extinction of DME–air with different equivalence ratios

In the discussions above, the importance of the bifurcation analysis for determining ignition and extinction states of steady state combustion was demonstrated with a rich mixture of DME–air with ϕ = 5.0. By further applying the bifurcation analysis on DME–air mixtures with different equivalence ratios, Figure 2-8 shows the extinction temperature and extinction residence time as functions of the normalized equivalence ratio, obtained by the newly proposed criterion, Re(λ_1) = 0, in solid lines, and the corresponding turning points on the “S”-curves were shown in dashed lines for comparison. It was found that the “S”-curves in PSRs with DME–air feature at least four turning points, because of the NTC chemistry, for mixtures with equivalence ratios between 0.3 and 5.0 at pressure of 30 atm and inlet temperature of 700 K. Two extinction states on each “S”-curve were selected, one for the extinction of strong flames as shown in Fig.
2-8a, and the other for the extinction of cool flames as shown in Fig. 2-8b. Other turning points, if present, are ignored in the present study.

Figure 2-8a shows that the extinction states for strongly burning flames are identical to the upper turning points on the “S”-curves for lean to rich mixtures with a normalized equivalence ratio smaller than approximately 0.75, or \( \phi = 3.0 \). The extinction states are different from the turning points for richer mixtures, with differences by approximately 100 K in extinction temperatures and 10-20% in extinction residence times. Therefore discrepancies between the turning points and the physical extinction states for strong flames of DME–air only occur for very rich mixtures. This is another reason that a rich mixture was selected for the studies in Figs. 2-(2-7).

Substantial differences in the extinction states of cool flames from the corresponding turning points can be observed in Fig. 2-8b for both lean and rich mixtures with normalized equivalence ratios larger than approximately 0.3, or \( \phi = 0.43 \). Specifically, the extinction temperatures can differ by almost 50 K and the extinction residence times can differ by a factor of 2. Therefore, the physical extinction states can be substantially different from the turning points for cool flames involving a variety of mixtures. In such cases flame stability analysis is required to correctly predict flame extinction.

It is further noted that the ignition states for both the cool flames and the strong flames were found to be identical to the corresponding turning points on the “S”-curves within the entire parameter range studied in Fig. 2-8. It is not clear nevertheless whether they can be different at other conditions or when different fuels are involved. Nevertheless, it is clear that flame stability analysis is important in identifying flame at least for extinction states in PSR, particularly for the cool flames.
It is noted that while near-extinction flame instabilities have also been observed in previous studies for diffusion flames with non-unity Lewis number [115-120, 125] and PSRs when heat loss is present [112, 113], the flame extinction prior to the turning points observed in the present study was induced solely by the complex chemical kinetics, since the present PSRs are adiabatic and feature only a unique mixing time scale, i.e. the residence time. This suggests that the prediction of ignition and extinction of steady state flames with practical fuels, e.g. the transportation fuels featuring long carbon chains, can be rather complicated, and flame stability analysis should be performed in addition to obtaining the “$S$”-curves even when heat loss is negligible and the Lewis number is near-unity.

2.4 Concluding Remarks

The ignition and extinction of steady state flames in adiabatic PSRs for methane and DME were investigated using flame stability analysis with emphasis on the changes in flame behaviors at different types of bifurcation points, including the Hopf bifurcation and the turning points, which constitutes a subset of the bifurcation analysis. The results showed that the methane–air combustion in PSRs feature the canonical “$S$”-curves that consist of three branches and the turning points are the only type of bifurcations that define the physical ignition or extinction states. For DME–air, the “$S$”-curves involve additional branches due to the NTC behaviors such that multiple ignition or extinction states are present. Furthermore, it was found that the physical extinction states do not necessarily coincide with turning points on the “$S$”-curves, even when the system is adiabatic and involves only a unique mixing timescale. This result suggests that it can be erroneous to match flame extinction observed in experiments with the turning points on the “$S$”-curves obtained by arc-length continuation method, and flame stability analysis is needed to rigorously predict ignition and extinction of steady state flames,
e.g. in PSRs or counterflow flames, particularly when large hydrocarbons and other fuels with NTC chemistry are involved.

Due to the existence of highly reactive species in detailed chemistry, the Jacobian matrices in the present study involve entries with vastly different orders of magnitude, e.g. ranging from larger than $10^{12}$ s$^{-1}$ to smaller than $10^3$ s$^{-1}$. Such a dramatic difference in timescale renders it difficult to accurately capture the zero-crossing of eigenvalues using Jacobian matrices evaluated through numerical perturbations, which typically consist of only a few significant digits in each entry. Analytically evaluated Jacobian was therefore employed in the present study to ensure the accuracy of the results.

An immediate extension of the present work is the bifurcation analysis for 1-D diffusive systems, e.g. the counterflow flame, which are however more involved in Jacobian formulation and evaluation. The underlying chemical kinetic processes affecting flame extinction and instabilities also merit further study.
Table 2-1: Variables with SP values larger than 0.1 at E₁’ and E₂’

<table>
<thead>
<tr>
<th>Variables</th>
<th>E₁’ (cool flame)</th>
<th>E₂’ (strong flame)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SP_re</td>
<td>SP_im</td>
</tr>
<tr>
<td>Temperature</td>
<td>0.645</td>
<td></td>
</tr>
<tr>
<td>CH₃OCH₂O₂</td>
<td>0.632</td>
<td></td>
</tr>
<tr>
<td>CH₃OCH₂O₂H</td>
<td>0.157</td>
<td></td>
</tr>
<tr>
<td>CH₂O</td>
<td>0.128</td>
<td></td>
</tr>
</tbody>
</table>
Table 2-2: Processes with PI values larger than 0.05 at E₁’ and E₂’

<table>
<thead>
<tr>
<th>Processes</th>
<th>PL₁ₑ</th>
<th>PL₁ᵣᵣ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixing</td>
<td>-0.385</td>
<td>0.090</td>
</tr>
<tr>
<td>CH₃OCH₂O₂ = CH₂OCH₂O₂H</td>
<td>0.193</td>
<td></td>
</tr>
<tr>
<td>OH + CH₃OCH₁ = H₂O + CH₃OCH₂</td>
<td>-0.093</td>
<td></td>
</tr>
<tr>
<td>OH + CH₄O = H₂O + HCO</td>
<td>0.078</td>
<td></td>
</tr>
<tr>
<td>E₁’</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH₃OCH₂ = CH₃ + CH₂O</td>
<td>0.075</td>
<td></td>
</tr>
<tr>
<td>HO₂ + CH₃OCH₁ = H₂O₂ + CH₃OCH₂</td>
<td>-0.061</td>
<td></td>
</tr>
<tr>
<td>CH₃OCH₂O₂H = OH + 2CH₂O</td>
<td>0.060</td>
<td></td>
</tr>
<tr>
<td>CH₃OCH₁ + CH₃OCH₂O₂ = CH₃OCH₂ + CH₃OCH₂O₂H</td>
<td>-0.058</td>
<td></td>
</tr>
<tr>
<td>CH₃OCH₂O₂H = OH + CH₃OCH₂O₂</td>
<td>0.052</td>
<td></td>
</tr>
<tr>
<td>Mixing</td>
<td>-0.214</td>
<td>0.151</td>
</tr>
<tr>
<td>HCO + O₂ = CO + HO₂</td>
<td>0.064</td>
<td>-0.145</td>
</tr>
<tr>
<td>HCO + M = H + CO + M</td>
<td>0.122</td>
<td></td>
</tr>
<tr>
<td>E₂’</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH₃ + CH₃OCH₁ = CH₄ + CH₂OCH₂</td>
<td>0.061</td>
<td>-0.085</td>
</tr>
<tr>
<td>CH₂O + HO₂ = HCO + H₂O₂</td>
<td>0.073</td>
<td>-0.060</td>
</tr>
<tr>
<td>CH₃ + CH₂O = CH₄ + HCO</td>
<td>0.073</td>
<td></td>
</tr>
<tr>
<td>CH₃ + CH₃ (+M) = C₂H₆ (+M)</td>
<td>-0.056</td>
<td>0.054</td>
</tr>
</tbody>
</table>
Figure 2-1: a) Temperature as a function of residence time, and b) the first two eigenvalues of the full Jacobian for methane–air in steady state PSRs. “sign()” denotes the signum function.
Figure 2-2: a) Temperature as a function of residence time, and b) the first two eigenvalues of the Jacobian, for DME–air in steady state PSRs. Solid lines: $\lambda_1$; Dashed lines: $\lambda_2$; Dash-dot-dot lines: $\lambda_1$ and $\lambda_2$ are a complex conjugate pair. “sign()” denotes the signum function; “Re()” denotes the real part of a complex number.
Figure 2-3: Temperature as a function of time in unsteady PSRs for DME–air, starting from steady state solutions with a perturbation in residence time of $\tau' = 0.05$ ms at a) the cool flame ignition point $I_1$, and b) the strong flame ignition point $I_2$, sampled on the “$S$”-curve in Fig. 2-2a.
Figure 2-4: Temperature as a function of time in unsteady PSRs for DME–air with equivalence ratio of \( \phi = 5.0 \), pressure of 30 atm, and inlet temperature of 700 K, starting from steady state solutions with temperature perturbations by \( T' = \pm 0.1 \) K at a) Point P\(_1\) with residence time \( \tau = 4.9 \) ms, \( \lambda_1 = -2.1E2 \) s\(^{-1}\), and b) Point P\(_2\) with residence time \( \tau = 0.1 \) ms, \( \lambda_1 = -9.5E3 + 4.2E4i \) s\(^{-1}\). P\(_1\) and P\(_2\) were sampled on the upper branch of the “S”-curve as shown in the inset in (a).
Figure 2-5: Temperature as a function of time in unsteady PSRs for DME–air with equivalence ratio of $\phi = 5.0$, pressure of 30 atm, and inlet temperature of 700 K, starting from steady state solutions with temperature perturbations by $T' = \pm 0.1$ K at a) Point P$_3$ with residence time $\tau = 0.07$ ms, $\lambda_1 = 7.8E3 + 3.5E4i$ s$^{-1}$, and b) Point P$_4$ with residence time $\tau = 0.06$ ms, $\lambda_1 = 5.0E4$ s$^{-1}$ and $\lambda_2 = 0$. P$_3$ and P$_4$ were sampled on the “S”-curve as shown in the inset in (b) and P$_4$ is identical to the turning point E$_2$. 
Figure 2-6: Temperature as a function of time in unsteady PSRs for DME–air with equivalence ratio of $\phi = 5.0$, pressure of 30 atm, and inlet temperature of 700 K, starting from steady state solutions with temperature perturbation by $T' = \pm 0.1$ K at a) Point P$_5$ with residence time $\tau = 0.1$ ms, $\lambda_1 = -8.5E3 + 3.5E4i$ s$^{-1}$, b) Point P$_6$ with residence time $\tau = 0.04$ ms, $\lambda_1 = 1.8E3 + 3.5E4i$ s$^{-1}$. P$_5$ and P$_6$ were sampled on the cool flame branch of the “S”-curve as shown in the inset in (a).
Figure 2-7: Temperature as a function of time in unsteady PSR for DME–air with equivalence ratio of $\phi = 5.0$, pressure of 30 atm, and inlet temperature of 700 K, starting from steady state solutions with temperature perturbation of $T' = \pm 0.1$ K at Point $P_7$ with residence time $\tau = 0.07$ ms, $\lambda_1 = 3.0E3 + 5.6E4$ s$^{-1}$. $P_7$ was sampled on the cool flame branch of the “S”-curve as shown in the inset.
Figure 2-8: Extinction temperature and residence time of PSRs as functions of the normalized equivalence ratio for DME–air, calculated based on the definition of $\text{Re}(\lambda_1) = 0$, in comparison with that based on the turning points. “$\text{Re()}$” denotes the real part of a complex number.
3.1 Introduction

Based on the previous chapter, steady state combustion systems typically feature “S”-curves shown in Fig. 1-1 [49] and it was found that limit flame phenomena, e.g. extinction and onset of flame instabilities, can possibly occur prior to reaching the turning points, particularly when the “S”-curve consists of multiple branches resulting from the negative temperature coefficient (NTC) and cool flame behaviors [126]. The bifurcation analysis is therefore needed to rigorously identify the ignition and extinction states involving different types bifurcation points on the “S”-curves, where flame stability changes. To identify the underlying physicochemical processes controlling the limit phenomena, systematic methods have been developed to understand the couplings involved in limit phenomena using analytical and numerical approaches such as asymptotic analysis [77], sensitivity analysis [78], CSP [23, 25, 79, 80], and CEMA [81], the last three method of which have been found more suitable for detailed chemistry. Nevertheless, sensitivity analysis can be time consuming for large mechanisms and complex systems due to the large number of perturbations and the subsequent reevaluations. CSP and CEMA are based on timescale analysis based on the Jacobian matrix of either the full governing equations or the chemical source term. Specifically, CSP has been extensively studied in the mechanism reduction literature to identify exhausted fast processes and understand the controlling reactions in stiff chemistry [15, 127, 128]. In particular, a concept of timescale importance index, or eigenvalue participation index, was used to quantify the contribution of each reaction to the corresponding CSP mode in studying NOx chemistry in premixed flames [129], two-stage ignition in a homogenous combustor [130], and biochemical applications [131-
Compared to CSP, CEMA was formulated on the chemical Jacobian and was found effective in identifying ignition, extinction, flame fronts and other critical flame features based on the interactions of the chemical explosive mode and the local mixing, where the timescale of the flow is frequently characterized by the reciprocal scalar dissipation rate in turbulent flames \[81, 106, 134\].

In the present study, a bifurcation analysis based on the Jacobian of the full governing equations is employed to rigorously identify the ignition and extinction and are demonstrated with PSRs. A bifurcation index (BI) is then defined to identify important chemical and flow processes controlling the limit flame phenomena in a similar manner as the timescale importance index in CSP.

### 3.2 Methodologies

The spatially discretized governing equations of a combustion system and the corresponding Jacobian matrices can be expressed as shown in below:

\[
\frac{d\mathbf{y}}{dt} = \mathbf{g}(\mathbf{y}) = \mathbf{\omega}(\mathbf{y}) + \mathbf{s}(\mathbf{y}), \tag{3-1}
\]

\[
\mathbf{J}_g = \frac{\partial \mathbf{g}(\mathbf{y})}{\partial \mathbf{y}} = \mathbf{J}_\omega + \mathbf{J}_s, \quad \mathbf{J}_\omega = \frac{\partial \mathbf{\omega}(\mathbf{y})}{\partial \mathbf{y}}, \quad \mathbf{J}_s = \frac{\partial \mathbf{s}(\mathbf{y})}{\partial \mathbf{y}}, \tag{3-2}
\]

where \(\mathbf{y}\) is the vector of dependent variables. Note that for spatially inhomogeneous systems, variables at different grid points are corresponding to different entries in the \(\mathbf{y}\) vector. \(\mathbf{\omega}\) is the chemical source term. \(\mathbf{s}\) is the non-chemical term, e.g. mixing. In spatially homogeneous systems such as PSRs that are employed in the present study, the dependent variables \(\mathbf{y}\) typically include species concentrations, temperature and other relevant variables. The detailed governing equations of PSRs can be found at Ch. 2. In Eq. (3-2), \(\mathbf{J}_g\) consists of two components, namely the
Jacobian of the chemical source term, $J_\omega$, and the Jacobian of the non-chemical term, $J_s$. It was shown in Ch. 2 that a specific eigenvalue of $J_g$, $\lambda^*$, which has the largest real part among all the eigenvalues, determines the absolute stability of the system, and thus a bifurcation point with $\text{Re}(\lambda^*) = 0$ separates a stable branch from an unstable branch on the “$S$”-curve. The flame is stable if $\text{Re}(\lambda^*) < 0$ and unstable if $\text{Re}(\lambda^*) > 0$. Note that the “Re()” operator returns the real part of a complex number in the present study. The physical ignition and extinction states can therefore be identified as the bifurcation points where $\text{Re}(\lambda^*) = 0$.

To identify the important reactions controlling the ignition and extinction states, the eigenvalue $\lambda^*$ can be decomposed into:

$$\lambda^* = \lambda_{\omega}^* + \lambda_s^*, \quad \lambda_{\omega}^* = b^* J_\omega a^*, \quad \lambda_s^* = b^* J_s a^*, \quad (3-3)$$

such that

$$\text{Re}(\lambda^*) = \text{Re}(\lambda_{\omega}^*) + \text{Re}(\lambda_s^*) = 0, \quad (3-4)$$

where $b^*$ and $a^*$ are the left and right eigenvectors associated with $\lambda^*$, respectively. It is seen in Eq. (3-4) that the zero-crossing of the eigenvalue $\lambda^*$ is attributed to the competition between chemistry and the mixing process. Note that the eigenvalue $\lambda_s^*$ is approximately the negative reciprocal residence time, $-1/\tau$, in a steady state PSR. The Jacobian can be further decomposed based on the contribution of each elementary reaction:

$$J_g = J_\omega + J_s = \sum_{r=1}^{f+1} J_r, \quad J_\omega = \sum_{r=1}^{f} J_r, \quad J_s = J_{f+1}, \quad (3-5)$$
where $I$ is the total number of reactions. $J_r$ is the contribution of the $r$th reaction to the Jacobian if $r \leq I$, and $J_{I+1}$ is the Jacobian of the mixing term. Consequently, the zero-crossing eigenvalue at the bifurcation point can be further decomposed to:

$$\text{Re}(\lambda^*) = \sum_{r=1}^{I} \text{Re}(b^r J_r a^r) = \sum_{r=1}^{I} \text{Re}(\lambda_r) = 0,$$  \hspace{1cm} (3-6)$$

where $\lambda_r$ is attributed to the $r$th reaction ($r \leq I$) or the mixing process ($r = I + 1$). It is seen in Eq. (2-6) that the bifurcation point with $\text{Re}(\lambda^*) = 0$ is resulting from the competition of the reactions and the mixing process, and a bifurcation index (BI) can be defined to measure the importance of each reaction and the mixing process to the bifurcation point:

$$\text{BI}_r = \frac{\text{Re}(\lambda_r)}{\max_{1 \leq r \leq I+1} |\text{Re}(\lambda_r)|}. \hspace{1cm} (3-7)$$

It is seen in Eq. (3-7) that the BIs are normalized to $[-1, 1]$, and $|\text{BI}_r|$ indicates the contribution of the $r$th reaction ($r \leq I$) or the mixing process ($r = I + 1$) to the bifurcation. If $|\text{BI}_r|$ is close to unity, the $r$th reaction is important to the bifurcation. If $|\text{BI}_r|$ is close to zero, the $r$th reaction has a negligible contribution to the bifurcation. In addition, different signs of the BI values indicate the opposite effects of the corresponding reactions on the bifurcation.

It is noted that while the definition of BI is similar to that of the timescale importance index in CSP [129, 130], the two concepts carry distinct physical meanings and differ in two major aspects. First, the timescale importance index was defined based on the timescales of CSP modes, while BI is defined for the specific mode leading to the limit phenomenon at a bifurcation point, where $\text{Re}(\lambda^*) = 0$ and the concept of timescale doesn’t apply. Second, BI is defined on eigenmodes that may involve complex eigenvalues and eigenvectors, while the timescale importance index in CSP was defined in the real space.
It is further noted that the Jacobian $J_g$ in the bifurcation analysis was obtained in the present study through analytical evaluation of $J_{io}$ and $J_s$ to ensure sufficient numerical accuracy in the calculations of the eigenvalues and eigenvectors. The analytical Jacobian is nevertheless only used for the eigenanalysis in the present study, while it can be readily extended to expedite the integration of ODEs. Analytic Jacobian is required for BI evaluation because the small number (typically less than 6) of significant digits in numerical Jacobian, which is evaluated through numerical perturbations, is typically inadequate to correctly compute the eigenvectors associated with the zero-crossing eigenvalue, which can be smaller than the largest eigenvalues by many, say nine or ten, orders of magnitude. In addition to the accuracy requirement, analytic evaluation of the Jacobian is substantially faster than that through numerical perturbations [3], and can significantly expedite the BI-based analysis.

3.3 Results and Discussion

The bifurcation analysis in the present study is first performed in PSRs for a rich dimethyl ether (DME)–air mixture with a 39-species skeletal mechanism [135], which was derived from a detailed mechanism with 55 species [123, 126]. Figure 3-1 shows the “$S$”-curve for DME–air in a steady PSR under pressure of 30 atm, equivalence ratio of 5, and inlet temperature of 700 K. It is noted that the fuel-rich and high-pressure condition is selected such that the “$S$”-curve shows a pronounced cool flame branch and complex ignition and extinction behaviors to be discussed in the following.

It is seen in Fig. 3-1 that the “$S$”-curve of DME–air is the same with Fig. 2-2 using the detailed DME–air mechanism, while it is rather different from the canonical “$S$”-curve shown in Fig. 1-1, as multiple criticalities and a cool flame branch induced by the NTC chemistry can be observed. The flame stabilities on the “$S$”-curve are determined using the flame stability analysis
introduced in Ref. [126] and shown in Fig. 3-1 with the blue solid line representing the stable states and the red dashed line for unstable states. While the turning points I_2 and I_1 are the actual ignition states for the strong flames and cool flames, respectively, determinations of the extinction states are complicated by the two additional Hopf bifurcation points [110], E_2' and E_1', where \( \lambda^* \) are purely imaginary values, in addition to the two turning points E_2 and E_1. As discussed in Ref. [126], the two Hopf bifurcation points, E_2' and E_1', are the actual separatrices of stable and unstable states, and thus are the physical extinction states of the strong flames and cool flames, respectively. Once the extinction and ignition states are identified, the BIs can be calculated to quantify the importance of each reaction and the mixing process for the limit phenomena.

3.3.1 Identification of the controlling reactions for ignition and extinction

The physical extinction points of the strong flames, E_2', and the cool flames, E_1', are first studied using the BI values to identify the controlling physicochemical processes. The BI values are computed and then sorted in descending order based on their magnitudes. The reactions and mixing process with large BI values are shown in Fig. 3-2 for E_2' and E_1', respectively. It is seen in Fig. 3-2a that the extinction point E_2' is primarily controlled by the competition between the mixing process and the reactions involving small molecules, such as HCO, CO, CH_2O, and CH_3. In particular, the controlling reactions at E_2' are related to CO formation through HCO + M = H + CO + M and HCO + O_2 = CO + HO_2, which are important reactions for heat release. In addition, it is seen in Fig. 3-2a that the BI values of the two reactions differ in signs, indicating the opposite effects of the two reactions on the extinction of the strong flames. Figure 3-2b shows the reactions with large BI values at the extinction state of the cool flames, E_1'. It is seen that the controlling reactions competing with the mixing process are primarily related to the large
molecules in the NTC chemistry, such as the peroxides. Specifically, reactions \( \text{CH}_2\text{OCH}_2\text{O}_2\text{H} = \text{OH} + \text{CH}_2\text{O} + \text{CH}_2\text{O} \) and \( \text{CH}_3\text{OCH}_3 + \text{OH} = \text{CH}_3\text{OCH}_2 + \text{H}_2\text{O} \), are found to be the most important reactions with opposite effects on the cool flame extinction, as suggested by their large absolute BI values and different signs.

Figure 3-3 shows the important reactions for the ignition states, I\(_2\) and I\(_1\), of the strong flames and the cool flames, respectively. It is seen in Fig. 3-3a that \( \text{H}_2\text{O}_2 (+\text{M}) = \text{OH} + \text{OH} (+\text{M}) \) is the most important reaction for the ignition of the strong flames, I\(_2\). This is expected because temperature at I\(_2\) is around 943 K, where \( \text{H}_2\text{O}_2 \) becomes increasingly unstable, resulting in effective chain branching, and the OH radical produced through the degenerate chain branching is important for the strong flame ignition. For the cool flame ignition, I\(_1\), Fig. 3-3b shows that the isomerization reaction \( \text{CH}_3\text{OCH}_2\text{O}_2 = \text{CH}_2\text{OCH}_2\text{O}_2\text{H} \), which is relevant to the NTC chemistry, is the primary reaction in the competition with the mixing process. In addition, it is seen that I\(_1\) is primarily controlled by the reactions involving large molecules due to the low reactor temperature (712 K), which is only slightly above the inlet temperature of 700 K.

3.3.2 Significance of the reactions with large BI values

To assess the importance of the reactions with large BI values, the pre-exponential “A”-factors in the Arrhenius rate expression, \( k = AT^n \exp(-\frac{E_a}{RT}) \), which will be referred to as “A”-factors henceforth, of the important reactions identified in Fig. 3-2 are perturbed to examine the response of the “S”-curve, where \( E_a \) denotes the activation energy and \( R \) is the ideal gas constant. Four reactions are first selected based on their BI values at different bifurcation points, as listed in Table 3-1. Specifically, the first two reactions, R26: \( \text{HCO} + \text{M} = \text{H} + \text{CO} + \text{M} \) and R27: \( \text{HCO} + \text{O}_2 = \text{CO} + \text{HO}_2 \), are important for the physical extinction state of the strong flames E\(_2\)’ where their absolute BI values are close to unity. Reaction R26 is also the most important reaction (BI \( \approx \))
1) for the turning point $E_2$, where R27 has a smaller BI of -0.14. In addition, the BI values for R26 and R27 have opposite signs at $E_2'$ and $E_2$, indicating their opposite heat release effects that are crucial to flame extinction. It is also seen in Table 3-1 that the absolute BI values for R26 and R27 are relatively small at the other four bifurcation points, $I_2$, $E_1'$, $E_1$ and $I_1$. In contrast, the next two reactions, R157: $\text{CH}_2\text{OCH}_2\text{O}_2\text{H} = \text{OH} + \text{CH}_2\text{O} + \text{CH}_2\text{O}$, and R132: $\text{CH}_3\text{OCH}_3 + \text{OH} = \text{CH}_3\text{OCH}_2 + \text{H}_2\text{O}$, are important for the physical extinction state of the cool flames, $E_1'$ and the turning point $E_1$, while their absolute BI values are small at the other four bifurcation points, $E_2'$, $E_2$, $I_2$ and $I_1$.

Each of the “$A$”-factors of R26, R27, R157 and R132 is then perturbed, and the “$S$”-curve for the steady PSR is recalculated at the same reactor condition after each perturbation. Figure 3-4 compares the “$S$”-curves obtained from the original and the perturbed mechanisms, where “fac” indicates the multiplier to the “$A$”-factors of the reactions, with “fac = 1” indicating the unperturbed rates. It is seen that the perturbations in R26 and R27 have significant effects on both $E_2'$ and $E_2$ and minor effects on the other four bifurcation points, $E_1'$, $E_1$, $I_2$ and $I_1$. The relative changes in the residence time induced by the perturbations in R26 and R27 are around 50% and 140% at $E_2'$, and around 30% and 75% at $E_2$, respectively, indicating the importance of the two reactions to the strong flame extinction and their insignificance to the cool flame extinction and flame ignitions. The results with perturbed R26 and R27 are consistent with their BI values at $E_2'$ and $E_2$ shown in Table 3-1. It is also seen in Fig. 3-4a that the perturbations of R26 and R27 have opposite effects on $E_2'$ and $E_2$, which is again consistent with their BI values. A faster R26 tends to promote the extinction of the strong flames due to its endothermic nature, while a faster exothermic reaction R27 tends to prevent the extinction.
In Fig. 3-4b the perturbations in R132 (blue dotted line) and R157 (red dashed line) have distinct effects on the bifurcation points near the cool flame branch and negligible effects on the bifurcation points above the strong flame ignition point $I_2$, which is consistent with the BI values in Table 3-1. Furthermore, the opposite effects are observed for the perturbations in R132 and R157, which is expected because of the opposite signs in their BI values as listed in Table 3-1.

To further show the importance of the selected four reactions, the mixtures at different bifurcation points are put into constant-pressure auto-ignition systems and calculated with perturbations of each selected reaction as shown in Figs. 3-(5-6). With respect to the perturbations of R26 and R27, Fig. 3-5 shows the temperature as a function of time obtained from the original and the perturbed mechanisms for the strong flame extinction $E_2'$ and cool flame ignition $I_1$, respectively. As seen in Fig. 3-5a, the ignition delay times with respect to the perturbations are significantly different from the original one shown in black solid line. Specifically, the perturbation of R26 induces the opposite effects from that of R27 on the ignition delay which can be indicated the opposite signs of their BI values on $E_2'$ as mentioned before. It is also noted that the ignition delays have distinct differences, while the equilibrium temperatures are not sensitive to the perturbations. This is because the former is determined by the intrinsic chemical kinetics while the latter is only affected by the conditions of the initial mixtures which are the same in this case. For $I_1$, it is seen in Fig. 3-5b that R26 and R27 have negligible effects on the ignition delays indicating these two reactions are not important to the point $I_1$ which are consistent with their BI values shown in Table 3-1.

With respect to the perturbations of R157 and R132, Fig. 3-6 shows the temperature profiles in auto-ignition with initial mixture compositions being the solutions at $E_1'$ and $I_1$, respectively. As seen in Fig. 3-6a for $E_1'$, the perturbations of R157 and R132 induce obvious
differences to the ignition delay based on the original mechanism and the relative differences are about 16% and 7%, respectively. For the point I₁ shown in Fig. 3-6b, the perturbation of R157 results in about 18% difference from the original ignition delay shown in the black solid line, while that of R132 have negligible effects which is also indicated by its small BI value of 6E-3.

Based on the above results with perturbed “A”-factors, the BI-based method was shown to be effective in identifying important reactions for ignition and extinction. It is further noted that the above results show that controlling reactions can be dramatically different at different ignition or extinction states, for strong or cool flames. Therefore it is important to select specifically validated detailed or reduced mechanisms in flame simulations involving different flame features. For instance, a reduced mechanism that is validated only for ignition problems should not be employed to predict flame holding, e.g. lean blow-out, problems.

3.3.3 Comparison with sensitivity analysis

The present BI-based method is next compared with the sensitivity analysis, which has been extensively employed in chemical kinetics study. To identify the controlling reactions for ignition and extinction using the sensitivity analysis, the normalized sensitivity coefficient is defined as the sensitivity of the residence time for given temperature at the bifurcation point with respect to the “A”-factor of each reaction:

\[
SA' = \frac{|d \log \tau / d \log A'|}{\max_r |d \log \tau / d \log A'|},
\]

where \( \tau \) is the residence time for the fixed reactor temperature and \( A' \) represents the “A”-factor of the \( r \)th reaction. \( SA' \) is normalized to [0, 1] and can quantify the sensitivity of the residence time
to the $r$th reaction rate at the bifurcation point with brute force. The $r$th reaction is important for the bifurcation point if $SA^r$ is close to unity, and unimportant if $SA^r$ is close to zero.

Figures 3-(7-8) compare the absolute BI values and the normalized sensitivity coefficients for the different extinction and ignition states, respectively, of the strong flames and the cool flames. It is seen that in Fig. 3-7 for the extinction states, $E_2'$ and $E_1'$, the absolute BI values are overall linearly correlated with the normalized sensitivity coefficients in logarithmic scale. Similar correlation can also be observed in Fig. 3-8 for the strong flame ignition, $I_2$, and the cool flame ignition, $I_1$. It is therefore evident that the BI values are consistent with the sensitivity information in identifying important reactions for ignition and extinction. In terms of computational efficiency, the sensitivity analysis is nevertheless known to be computationally expensive due to a large number of rate parameter perturbations and subsequent simulations. In contrast, the BI values can be directly evaluated from the local solution and thus induce a low computational overhead. The BI-based method is therefore particularly suitable for analyzing large mechanisms. Furthermore, the concept of BI is based on bifurcation analysis, which provides information required to distinguish between physical extinction and ignition states from the turning points on “$S$”-curves, while no such information on flame ignition or extinction is directly available in the sensitivity analysis.

Compared with other eigen-based tools, such as CSP and CEMA, the rigorous identification of flame ignition and extinction states remains a unique feature of the BI-based method. Specifically, while the concept of timescale importance index has been defined in the CSP literature to quantify the contribution of each reaction to the timescale of a CSP mode [129, 130], the BI-based method further provides information required to isolate the process that controls ignition and extinction. In the CEMA method, the chemical eigenmode is computed
exactly whereas the interactions between the chemical explosive mode and mixing are measured based on estimated flow time, such as the residence time in PSRs and the reciprocal scalar dissipation time in turbulent flows \([81, 106, 134]\). In contrast, the BI-based method employs the full Jacobian and provides exact information on the chemistry-flow interaction. The BI values are therefore more accurate to identify the controlling processes for ignition and extinction, while the computational cost of BI is higher than that of CEMA.

### 3.4 Model Reduction and Tuning based on the Bifurcation Analysis

Once the important reactions for ignition and extinction are identified using the BI values, such reactions can form a skeletal mechanism that can be subsequently tuned to capture the ignition and extinction states of the full reaction set. The accumulative error induced by the elimination of the reactions with small BI values can be compensated by slightly adjusting the rate parameters of the important reactions because of the high sensitivities of ignition and extinction to these reactions. Furthermore, the BI-based method can also identify critical reactions in detailed mechanisms as candidates for rate parameters improvements to better predict the ignition and extinction behaviors. In the following, the mechanism tuning method will be demonstrated with PSR starting from the skeletal mechanism for DME–air with 39 species and 175 reactions.

To obtain a reduced reaction set, the BI values for each reaction are first evaluated at the bifurcation points on the “S”-curves for DME–air mixtures with equivalence ratios from 0.4 to 5.0. A reaction is considered unimportant and removed if its absolute BI value is smaller than a threshold value, say 0.01 in the present study, at all the bifurcation points. A species is removed if it is not involved in any retained reaction. A skeletal mechanism consisting of 38 species and 107 reactions was consequently obtained. Note that the reaction set is substantially reduced while
most species are retained. The extinction states predicted by the 38-species skeletal mechanism for the strong flames and cool flames are shown in Figs. 3-9a and b, respectively, for various equivalence ratios. It is seen in Fig. 3-9 that the reduction induces minor differences in the strong flame extinction, and significant differences in the cool flame extinction. To shift the bifurcation points on the “S”-curves of the reduced mechanism back to the original locations, 15 reactions with large absolute BI values at different bifurcation points are selected as shown in Table 3-2. The “A”-factors of these reactions are then tuned to suppress the reduction error. It is noted that at least one reaction should have a large BI value at each of the bifurcation points and the vector of the BI values of the selected reactions should be linearly independent to allow for an effective optimization. The optimized multipliers to the “A”-factors are listed in Table 3-2. It is seen that the “A”-factors only need to be slightly changed to minimize the reduction error due to the high sensitivity.

The tuned mechanism is validated and shown as the blue dashed line with circles in Fig. 3-9. It is seen that in addition to the extinction of the strong flames as shown in Fig. 3-9a, the tuned model can accurately reproduce the original extinction states of the cool flames as shown in Fig. 3-9b. To further validate the tuned model, a transient PSR is employed with fluctuating resident time under various equivalence ratios as shown in Figs. 3-(10-11), where the residence time (the blue dash-dotted line) fluctuates sinusoidally in logarithmic scale with a frequency of 10 Hz and both the ignition and the extinction states are involved. Specifically, the residence time in Figs. 3-(10-11) fluctuates starting from a steady state cool flame and a strong flame solution, respectively. The temperatures as a function of time shown in Figs. 3-(10-11) are calculated with the original (red solid line), reduced (black dotted line) and tuned mechanisms (blue circles), respectively. It is seen that in Figs. 3-10a and b, for \( \phi = 0.4 \) and 1.0, respectively,
the untuned reduced model predicts significantly earlier extinction and later re-ignition of the cool flame. For the rich case with $\phi = 5.0$ shown in Fig. 3-10c, the untuned model tends to extinguish earlier (near 0.019 s) and fails to capture the re-ignition (near 0.09 s). In contrast, the tuned model closely follows the original mechanism with both the extinction and the re-ignition accurately captured for the transient PSR, including even the temperature overshooting and oscillations after the re-ignition. Figure 3-11 shows the validation of the reduced and tuned models for extinction and re-ignition of a strong flame induced by fluctuating residence time. It is seen that the tuned model can capture the extinction accurately, which is consistent with the results shown in Fig. 3-9a. For re-ignition, moderate errors can be observed for both the tuned and the reduced models, while the tuned model captures the re-ignition more accurately compared with the untuned model. The extendibility of reduced modes obtained by the BI-based method with rate constant tuning is hereby demonstrated.

3.5 Concluding Remarks

A bifurcation analysis was employed to identify ignition and extinction in steady state combustion systems, and the physicochemical processes controlling the limit phenomena are identified based on the concept of bifurcation index (BI). The method was demonstrated using DME–air mixtures involving the NTC chemistry in PSRs, in which extinctions may not occur at the turning points. Once the physical extinction and ignition states are identified with the bifurcation analysis, a BI is defined as the normalized contribution of each reaction or the mixing process to the zero-crossing of the real part of the eigenvalues at the bifurcation point. For a rich DME–air mixture in PSRs, it was found that the extinction of the strong flames is primarily controlled by the reactions involving small molecules, such as CO and HCO, while the extinction of the cool flames is controlled by the reactions relevant to the NTC chemistry involving large
molecules. The effectiveness to identify important reactions using BI is validated against the sensitivity analysis through perturbations in the “A”-factors of selected reactions. It was shown that the changes in the “S”-curves resulting from the perturbed reactions are consistent with the BI values, and the BI values are overall linearly correlated with the normalized sensitivity coefficients in the logarithmic scale, indicating that the bifurcation analysis is an effective and computationally efficient approach to identify controlling processes for limit phenomena.

The BI information is further exploited in model reduction through removing reactions with small BI values and subsequently tuning the rate parameters of selected reactions with large BI values. A tuned model with a substantially reduced reaction set is obtained and validated in steady state and transient PSRs. The model accurately captures the extinction of both the strong flames and the cool flames in steady PSRs and closely follows the original model in transient PSRs, with both the extinction and the re-ignition states correctly captured. The BI-based method can possibly be extended to improve detailed mechanisms and to construct severely reduced models that can accurately predict limit phenomena in complex flows.
Table 3-1: BI of important reactions for the bifurcation points on the “S”-curve in Fig. 3-1

<table>
<thead>
<tr>
<th>Reactions</th>
<th>E$_2'$</th>
<th>E$_2$</th>
<th>I$_2$</th>
<th>E$_1'$</th>
<th>E$_1$</th>
<th>I$_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>R26: HCO + M = H + CO + M</td>
<td>-1</td>
<td>1</td>
<td>2e-3</td>
<td>1.2e-2</td>
<td>-4e-3</td>
<td>-4.6e-7</td>
</tr>
<tr>
<td>R27: HCO + O$_2$ = CO + HO$_2$</td>
<td>0.89</td>
<td>-0.14</td>
<td>-6e-3</td>
<td>-0.03</td>
<td>0.02</td>
<td>-1.8e-5</td>
</tr>
<tr>
<td>R157: CH$_2$OCH$_2$O$_2$H = OH + CH$_2$O + CH$_2$O</td>
<td>-8.8e-6</td>
<td>7e-4</td>
<td>0.03</td>
<td>-1</td>
<td>1</td>
<td>-0.1</td>
</tr>
<tr>
<td>R132: CH$_3$OCH$_3$ + OH = CH$_3$OCH$_2$ + H$_2$O</td>
<td>0.08</td>
<td>7e-3</td>
<td>0.01</td>
<td>0.86</td>
<td>-0.13</td>
<td>6e-3</td>
</tr>
</tbody>
</table>
Table 3-2: List of reactions with optimized “A”-factors

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Chemical Equation</th>
<th>( A_{\text{optimized}}/A )</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>( H + O_2 = O + OH )</td>
<td>1.15</td>
</tr>
<tr>
<td>R8</td>
<td>( H + OH + (M) = H_2O + (M) )</td>
<td>1.78</td>
</tr>
<tr>
<td>R13</td>
<td>( HO_2 + OH = H_2O + O_2 + (M) )</td>
<td>1.0</td>
</tr>
<tr>
<td>R16</td>
<td>( H_2O_2 + (M) = OH + OH + (M) )</td>
<td>0.81</td>
</tr>
<tr>
<td>R25</td>
<td>( CO + OH = CO_2 + H )</td>
<td>1.0</td>
</tr>
<tr>
<td>R26</td>
<td>( HCO + M = H + CO + M )</td>
<td>1.46</td>
</tr>
<tr>
<td>R27</td>
<td>( HCO + O_2 = CO + HO_2 )</td>
<td>1.44</td>
</tr>
<tr>
<td>R40</td>
<td>( CH_2O + OH = HCO + H_2O )</td>
<td>1.0</td>
</tr>
<tr>
<td>R42</td>
<td>( CH_2O + HO_2 = HCO + H_2O_2 )</td>
<td>1.0</td>
</tr>
<tr>
<td>R43</td>
<td>( CH_2O + CH_3 = HCO + CH_4 )</td>
<td>1.0</td>
</tr>
<tr>
<td>R132</td>
<td>( CH_3OCH_3 + OH = CH_3OCH_2 + H_2O )</td>
<td>3.0</td>
</tr>
<tr>
<td>R138</td>
<td>( CH_3OCH_2 = CH_2O + CH_3 )</td>
<td>1.0</td>
</tr>
<tr>
<td>R156</td>
<td>( CH_3OCH_2O_2 = CH_2OCH_2O_2H )</td>
<td>1.95</td>
</tr>
<tr>
<td>R157</td>
<td>( CH_2OCH_2O_2H = OH + CH_2O + CH_2O )</td>
<td>1.49</td>
</tr>
<tr>
<td>R158</td>
<td>( CH_2OCH_2O_2H + O_2 = O_2CH_2OCH_2O_2H )</td>
<td>1.0</td>
</tr>
</tbody>
</table>
Figure 3-1: Temperature as a function of residence time for a rich DME–air mixture in PSRs, at pressure $p = 30$ atm, equivalence ratio $\phi = 5.0$ and inlet temperature $T_{in} = 700$ K. Blue solid line: stable states, red dashed line: unstable states.
Figure 3-2: Reactions ranked in |\(B_1|\) for (a) extinction of the strong flames, \(E_2'\), and (b) extinction of the cool flames, \(E_1'\), at pressure \(p = 30\) atm, equivalence ratio \(\phi = 5.0\) and inlet temperature \(T_{in} = 700\) K in PSRs.
Figure 3-3: Reactions ranked in $|BI|$ for (a) ignition of the strong flames, $I_2$, and (b) ignition of the cool flames, $I_1$, at pressure $p = 30$ atm, equivalence ratio $\phi = 5.0$ and inlet temperature $T_{in} = 700$ K in PSRs.
Figure 3-4: “S”-curves for DME–air at pressure $p = 30$ atm, equivalence ratio $\phi = 5.0$ and inlet temperature $T_{in} = 700$ K in PSRs with perturbations in the “$A$”-factors of (a) R26 and R27, and (b) R157 and R132.
Figure 3-5: Constant-pressure auto-ignition staring from (a) the extinction of the strong flames $E_2'$ and (b) the ignition of the cool flames $I_1$ calculated based on the mechanisms with perturbations in the “A”-factors of R26 and R27, respectively.
Figure 3-6: Constant-pressure auto-ignition starting from (a) the extinction of the cool flames $E_1'$ and (b) the ignition of the cool flames $I_1$ calculated based on the mechanisms with perturbations in the “A”-factors of R26 and R27, respectively.
Figure 3-7: Correlation of the BI values with the normalized sensitivity coefficients at (a) $E_2'$ and (b) $E_1'$ for DME–air at pressure $p = 30$ atm, equivalence ratio $\phi = 5.0$ and inlet temperature $T_{in} = 700$ K in PSRs.
Figure 3-8: Correlation of the BI values and the normalized sensitivity coefficients at (a) $I_2$ and (b) $I_1$ for DME–air at pressure $p = 30$ atm, equivalence ratio $\phi = 5.0$ and inlet temperature $T_{in} = 700$ K in PSRs.
Figure 3-9: Extinction temperature of (a) the strong flames and (b) the cool flames calculated with the original, reduced and tuned mechanisms, respectively, for DME–air at different equivalence ratios and pressure $p = 30$ atm and inlet temperature $T_{in} = 700$ K in PSRs.
Figure 3-10: Temperature as a function of time, calculated with the original, reduced and tuned mechanisms, respectively, for DME–air under different equivalence ratios at pressure $p = 30$ atm and inlet temperature $T_{in} = 700$ K in a transient PSRs with fluctuating residence time starting from a cool flame.
Figure 3-11: Temperature as a function of time, calculated with the original, reduced and tuned mechanisms, respectively, for DME–air under different equivalence ratios at pressure $p = 30$ atm and inlet temperature $T_{in} = 700$ K in a transient PSRs with fluctuating residence time starting from a strong flame.
Chapter 4  Effects of Surrogate Composition and Lumped Fuel Cracking
Reactions on High-Temperature Combustion of Jet Fuels

4.1  Introduction

Practical jet fuels contain a large number of components with different molecular structures of hydrocarbons primarily ranging from C_7 to C_{16} [136]. Conventional jet fuels derived from petroleum, e.g. Jet A and JP-8, are typically comprised of normal- and branched-alkanes (55-70% by volume), cyclo-alkanes (20-35%), alkyl-benzenes (up to 20%) and small amounts of polycyclic aromatic hydrocarbons (PAH), etc [137]. Alternative jet fuels derived from Fischer-Tropsch (F-T) synthesis may contain more than 99% alkanes and a trace amount of other hydrocarbons [138]. The compositional complexity of jet fuels induces high computational cost in flame simulations, and thus surrogate mixtures with one or a few surrogate components have been frequently employed for jet fuel combustion simulations. Jet fuel surrogates are typically comprised of large \( n \)-alkanes, cyclo-alkanes, iso-alkanes, aromatics, and alkenes etc [33, 136, 139-141]. A variety of detailed mechanisms for jet fuel surrogates have been developed [33, 142-145] to capture such physical properties as the distillation curve, viscosity, thermal conductivity and heat capacity [146-150], and such chemical properties as ignition delay, extinction behaviors and flame speed [140, 142, 151-154]. In particular, ignition and extinction are important combustion features for engine safety, fuel efficiency and pollutant emissions etc, and surrogate fuel composition can have significant effects on predicting flame behaviors. For instance, the addition of cyclo-alkanes, iso-alkanes and aromatics to \( n \)-alkanes was found to have significant effects on low-temperature ignition [154, 155]. In the present study, the effects of the jet fuel compositions will be further investigated to identify a viable jet fuel surrogate for high-temperature combustion problems.
The selection of jet fuel surrogate in the present study is primarily based on reaction states relevant to auto-ignition and ignition and extinction of steady state flames, which are typically described by the “S”-curves. The turning points on the “S”-curves are widely accepted as the ignition or extinction states [49]. The bifurcation analysis introduced in the previous chapters has been used to systematically identify the controlling reactions and species for the limit flame phenomena, and will be employed in the present study to explain the effects of different surrogate compositions on the ignition and extinction behaviors.

Another factor resulting in large jet fuel mechanisms is the myriad intermediate species created during the fuel cracking process. At high-temperature conditions, fuel cracking can occur rather fast compared to the subsequent reactions of small molecules primarily including the C₁–C₄ species [156, 157]. In previous works, the fuel cracking processes were lumped into a few semi-global reaction steps and grafted to the detailed USC-Mech II for C₁–C₄ species oxidation [158], to obtain a compact scheme to for high-temperature jet fuel combustion [156, 157]. A reduced mechanism consisting of 24 species was further developed based on the JetSurF mechanism with lumped fuel cracking reactions, and has been employed in a DNS of counterflow spray flames [46]. The reduced mechanism was developed using DRG [8, 34, 35], DRGASA [40, 42], and linearized quasi-steady-state approximations (LQSSA) [159] and based on reaction states sampled from auto-ignition and PSRs. Nevertheless, while the reduced mechanism has been validated for 0-D ignition and extinction and 1-D laminar premixed flames, its validity for stretched flames at near-extinction conditions is not clear.

In the following, the validity of the reduced mechanism based on lumped fuel cracking reactions will be further investigated at extreme flame conditions, including the extinction of 1-D
premixed and non-premixed counterflow flames. The validity of the lumping of fuel cracking reactions will be further investigated at the near-limit conditions.

4.2 Selection of Surrogate Mixtures

To identify a viable surrogate mixture for high-temperature jet fuel combustion, the effects of jet fuel components on ignition and extinction are first studied with the JetSurF v.2.0 mechanism [145], which is a detailed chemical kinetic model of the jet fuel surrogates for high-temperature combustion and has been extensively validated against experimental data over a wide range of conditions. The JetSurF mechanism consists of reaction pathways for a variety of surrogate components, among which $n$-octane, $n$-decane, $n$-dodecane, $n$-butyl-cyclohexane and toluene will be used as representative species in the following study and their molecular structures are shown in Table 4-1.

4.2.1 Ignition and extinction of single-component surrogates

The pure surrogate components listed above are first investigated in auto-ignition and PSRs using the detailed JetSurF v.2.0 mechanism. Figure 4-1a shows the ignition delay of the three $n$-alkanes in constant-pressure auto-ignition with initial temperatures between 1000 K and 1600 K, pressure $p = 10$ atm, and equivalence ratio $\phi = 0.7$. It is seen that the ignition delays for the three different $n$-alkanes are mostly identical at each condition, indicating that the reactivities of the large $n$-alkanes are not sensitive to the chain length for high-temperature ignition. This result is consistent with the previous experimental measurements [160]. Figure 4-1b shows the “$S$”-curves of the three $n$-alkanes in PSRs calculated at pressure $p = 10$ atm, equivalence ratio $\phi = 0.7$ and inlet temperature $T_{in} = 1000$ K. It is seen that the “$S$”-curves of the three fuels, including the ignition and extinction states, are mostly identical. For a more comprehensive comparison on the extinction state, Fig. 4-2 shows the extinction temperature and extinction
residence time as functions of the inlet temperature at different equivalence ratios from 0.5 to 1.0 in PSRs at pressure \( p = 10 \text{ atm} \). It is seen that the extinction states of the three different \( n \)-alkanes are collapsed with the largest difference being approximately 0.7% in the extinction temperature of the stoichiometric mixtures. Therefore, the large \( n \)-alkanes feature similar ignition and extinction properties at high temperatures and can be represented by a single species, e.g. \( n \)-dodecane to be used in the following, in terms of limit phenomena prediction.

Due to the different molecular structures and the associated bond energies, the ignition and extinction properties for alkanes and aromatics are rather different as shown in Fig. 4-3 for \( n \)-dodecane, \( n \)-butyl-cyclohexane and toluene. It is seen in Fig. 4-3a that the ignition delays for \( n \)-dodecane and \( n \)-butyl-cyclohexane are similar, while that of toluene is significantly longer. Figure 4-3b shows the “S”-curves for the three fuels in PSRs at pressure \( p = 10 \text{ atm} \), equivalence ratio \( \phi = 0.7 \) and inlet temperature \( T_{\text{in}} = 1000 \text{ K} \). It is seen that \( n \)-dodecane and \( n \)-butyl-cyclohexane feature almost identical ignition states and similar extinction states, with a less than 25% relative difference in the extinction residence time, while the “S”-curve for toluene is significantly different from those of \( n \)-dodecane and \( n \)-butyl-cyclohexane, indicating that toluene is more difficult to ignite and more prone to extinguish.

4.2.2 Ignition and extinction of surrogate mixtures

Jet fuels of different types may consist of a significant amount of cyclo-alkanes and moderately high concentrations of aromatics. To investigate the effects of such components in jet fuel combustion, the binary mixture of 50% (in mole) \( n \)-dodecane and 50% \( n \)-butyl-cyclohexane is first used as a surrogate mixture. Figure 4-4 shows the differences in the extinction temperature and extinction residence time of pure \( n \)-dodecane, pure \( n \)-butyl-cyclohexane, pure toluene, and the binary mixture of 50% \( n \)-dodecane and 50% \( n \)-butyl-cyclohexane over a wide
range of inlet temperatures and equivalence ratios in PSRs. It is seen in Fig. 4-4 that both the extinction temperature and extinction residence time of toluene are significantly different from that of the alkanes, while the extinction results for the binary mixture of n-butyl-cyclohexane and n-dodecane are close to those of pure n-dodecane with the relative difference being smaller than 30% in the worst case. Therefore blending a moderate amount of n-butyl-cyclohexane to n-dodecane has only some minor effects on the extinction behaviors.

Binary mixtures of n-dodecane and toluene, with 0, 20%, and 50% toluene in mole, respectively, are then studied in auto-ignition and PSRs. Note that typically less than 20% toluene has been used in jet fuel surrogates in previous studies [161, 162]. Figure 4-5a shows that toluene addition by 20% induces only a relative difference of about 10% in ignition delay compared with pure n-dodecane, and with 50% toluene addition the ignition delay is increased by approximately 30%. The ignition delays of the two n-dodecane and toluene mixtures are therefore similar to that of pure n-dodecane, and are significantly lower than that of pure toluene. This result indicates that the n-alkane chemistry dominates the ignition delay for mixtures of n-alkanes and a small to moderate amount of aromatics at high-temperature and fuel-lean conditions. The underlying reason of this effect will be further investigated in the next section.

Figure 4-5b shows the “S”-curves in PSRs for different n-dodecane and toluene mixtures at inlet temperatures of 1000 K. Similar to the observation made in ignition delays, 50% toluene addition results in only about 30% relative differences from pure n-dodecane for the ignition and extinction states in PSRs, while 20% toluene addition has mostly negligible effects on the “S”-curve. In contrast, the solution of pure toluene differs significantly from those of the fuel blends. To further show the effects of toluene addition in extinction of PSRs at different conditions, Fig. 4-6 presents the extinction temperature and extinction residence time as functions of inlet
temperature for lean to stoichiometric mixtures. It is again observed that the 50% toluene addition induces only approximately 30% differences in the extinction residence time and less than about 30 K differences in the extinction temperature, while the 20% toluene addition has mostly negligible effects on the extinction states.

The above results in Figs. 4-6 therefore indicate that the ignition and extinction of mixtures of n-dodecane with a moderate amount of n-butyl-cyclohexane or a small concentration of toluene in PSRs at high temperatures are primarily determined by n-dodecane that is in high concentration, and thus pure n-dodecane is a viable jet fuel surrogate to capture ignition and extinction behaviors in lean premixed jet fuel combustion at high-temperature conditions. For comparison, it was found in Ref. [163] that aromatic addition has important effects on counterflow non-premixed flames, while the reason of the difference merits further study.

To further compare the effects of toluene addition with the uncertainties in different chemical kinetic mechanisms, two additional detailed mechanisms developed at Lawrence Livermore National Laboratory (LLNL) for n-alkanes are compared with the JetSurF v.2.0 mechanism. In Fig. 4-7, “LLNL1” denotes the detailed mechanism for n-alkanes ranging from n-octane to n-hexadecane [33], and “LLNL2” denotes the mechanism for 2-methyl-alkanes and n-alkanes up to C_{12} [164, 165]. It is seen that the effects of 20% toluene addition in auto-ignition delay and steady state ignition and extinction in PSRs are overall much smaller than the uncertainties induced by using different kinetic mechanisms. As such, pure n-dodecane will be selected as a jet fuel surrogate for the reduced mechanism development in the present study.
4.3 Effects of Fuel Cracking Reactions on Ignition and Extinction with Bifurcation Analysis

The effects of fuel cracking reactions are investigated with the bifurcation analysis introduced in Chs. 2-3 to systematically identify the controlling species and reactions for ignition of extinction in steady state PSRs, where the ignition and extinction are resulting from the competition between chemistry and the homogeneous mixing process.

The bifurcation analysis introduced in the previous chapters proposed a concept of bifurcation index (BI), which has been validated for quantifying the importance of the reactions and other non-chemical processes through decomposing the contribution of each reaction and the mixing process on the eigenmode of the Jacobian of the governing equations at the bifurcation points. To further analyze the results on surrogate mixture selection in the last section, the BI values are calculated to identify the controlling reactions for the ignition and extinction states in PSRs in Fig. 4-5b, for the binary mixtures of \( n \)-dodecane and toluene with 0, 20\%, and 50\% toluene in mole, respectively.

The reactions with large BI values are listed in Figs. 4-8a and b for the extinction and ignition states, respectively. It is seen in Fig. 4-8a that the extinction states of the different binary mixtures with different amounts of toluene addition are controlled by, in addition to the mixing process, a similar set of reactions involving small molecules. Specifically, the reaction for product formation, \( \text{CO} + \text{OH} = \text{CO}_2 + \text{H} \), and the chain branching reaction \( \text{H} + \text{O}_2 = \text{O} + \text{OH} \) play the most important roles at extinction. Reactions for CO formation also show moderate importance at extinction. Note that the reactions for fuel cracking do not play a significant role at the extinction states for either \( n \)-dodecane or toluene because the temperature is higher than 1800 K as shown in Fig. 4-5b. Since \( \beta \)-scission becomes exceedingly fast at high temperatures,
e.g. above 1500 K, the fuel cracking reactions are typically not rate-limiting at the extinction state, and thus none of the reactions in Fig. 4-8a involve large molecules.

For the ignition state, it is seen in Fig. 4-8b that the controlling reactions for the different mixtures primarily involve ethylene, vinyl radical, alkyl radical and other small species that are important intermediate products of fuel cracking. It is interesting to observe that for the case with 50% toluene addition, the H-abstraction of toluene, i.e. \( \text{C}_6\text{H}_5\text{CH}_3 + \text{O}_2 = \text{C}_6\text{H}_5\text{CH}_2 + \text{HO}_2 \), also plays an important role, indicating the increasing importance of the endothermic effect as the toluene concentration increases. As a result, the H-abstraction of toluene tends to retard the ignition process. However, this effect is largely suppressed by the subsequent chain branching reaction involving the benzyl radical, \( \text{C}_6\text{H}_5\text{CH}_2 + \text{HO}_2 = \text{C}_6\text{H}_5\text{CHO} + \text{H} + \text{OH} \), such that the ignition states are overall not significantly altered even with the 50% toluene addition. The fuel cracking of \( n \)-dodecane is sufficiently fast at a temperature of 1000 K, such that it is not rate-limiting the ignition process. Consequently \( n \)-dodecane and its radicals are not involved in the important reactions shown in Fig. 4-8b.

The above results based on the bifurcation analysis show that the fuel cracking reactions are fast and not rate-limiting at ignition and extinction conditions for high-temperature jet fuel oxidation. Instead, the limit phenomena are controlled by the reactions of small molecules ranging from \( \text{C}_0 \) to \( \text{C}_4 \), which are products of the fuel cracking process. In such cases, the fast fuel-cracking reactions can be lumped by assuming that the intermediate species formed during the fuel cracking process are in quasi-steady-state. This strategy can lead to significant reduction in the chemical complexity of large hydrocarbons at high-temperature conditions, since the majority of species in detailed chemistry of large hydrocarbons are intermediate fuel cracking products. Furthermore, such a reduction strategy can be universally applied to different fuels and
is simple to implement. The effectiveness of this approach is demonstrated in the following using a JetSurF mechanism with lumped fuel cracking reactions.

4.4 Validation of a Reduced Mechanism with Lumped Fuel Cracking Steps in Counterflow Flames

4.4.1 A brief review of the reduced mechanism

The strategy to lump the fuel cracking reactions has been demonstrated in Refs. [156, 157] that the fuel cracking processes for \(n\)-alkanes are lumped to a simplified model containing a minimal set of semi-global reactions with 9 species, i.e. from \(n\)-pentane to \(n\)-dodecane less undecane plus 1-pentene and 1-hexene, starting from the JetSurF v.1.0 mechanism involving 194 species and 1450 reactions [166]. The lumped fuel cracking model is subsequently combined with the base model of \(\text{H}_2/\text{CO}/\text{C}_1-\text{C}_4\), i.e. the USC-Mech II mechanism [158] to obtain a complete mechanism with 123 species and 977 reactions. The lumped model has been validated against experiments over a wide range of conditions. A reduced mechanism with 24 species based on the lumped mechanism was developed and employed in a simulation of \(n\)-dodecane spray combustion in a counterflow configuration [46]. This 24-species reduced mechanism is developed at the University of Connecticut and will be used in the following for the mechanism validation in counterflow flames.

4.4.2 Mechanism validation in counterflow flames

The 24-species reduced mechanism has been validated in auto-ignition, PSRs, and 1D laminar premixed flame at the University of Connecticut [167]. Therefore the reduced mechanism with \(n\)-dodecane as jet fuel surrogate can be considered an accurate and comprehensive model for high-temperature jet-fuel combustion. In this section, the detailed
JetSurF v.1.0 mechanism, the JetSurF Mechanism with lumped fuel cracking reactions and the reduced mechanism are compared in non-premixed and premixed counterflow flames, respectively, to further investigate the validity of the lumping of fuel cracking reactions in the extinction of stretched flames.

These results were computed in collaboration with Yang Gao and Cong Li at the University of Connecticut [167, 168]. For the non-premixed flames, the mixture at the fuel inlet is comprised of 50% n-dodecane and 50% N₂ in mole, and the mixture at the oxidizer inlet is air. Both inlet streams are at temperature of 300 K and pressure is atmospheric. Figure 4-9a shows the maximum temperature, $T_{\text{max}}$, in the counterflow non-premixed flames as a function of the strain rate $a_2$, which is defined in Ref. [169] as

$$a_2 = \frac{2|v_2|}{L} \left(1 + \frac{|v_1|\sqrt{\rho_1}}{|v_2|\sqrt{\rho_2}}\right).$$

The subscripts 1 and 2 indicate the fuel and oxidizer boundaries, respectively. $V, \rho, L$ are the axial component of the inlet velocity, density and the burner separation distance, respectively. It is seen in Fig. 4-9a that the lumped mechanism agrees tightly with the detailed mechanism for the entire curve, including the turning point that is widely accepted as the extinction state of the flame. The reduced mechanism gives a worst case error of about 10% near the extinction state. Figure 4-9b further shows the normalized total mass fraction of the species with four or more C atoms, denoted as $C_{4+}$, and the important intermediate products of fuel cracking, including CH₄, C₂H₄ and C₃H₆, as a function of temperature for the detailed mechanism. Note that the species mass fractions are normalized by the fuel mass fraction at the fuel boundary. The three profiles in Fig. 4-9b involve significantly different strain rates spanning both strongly burning and near-extinction flame conditions. Specifically, the $C_{4+}$ species mostly vanish at about 1500 K, indicating that the fuel cracking process is mostly completed before entering the flame zone with
temperature higher than 1600 K. It is noted that the trace amount of remaining C$_4$+ species at temperatures higher than 1500 K are primarily soot precursors, e.g. C$_6$H$_{10}$-13 (1, 3-hexadiene), C$_5$H$_8$-13 (1, 3-pentadiene) and C$_4$H$_2$ (diacetylene).

In the counterflow premixed flames, the streams at both burner inlets consist of fresh $n$-dodecane–air mixture with equivalence ratio of 0.7 at temperature of 300 K and atmospheric pressure. Figure 4-10 shows the maximum temperature as a function of the strain rate for the flames under different strain rates. It is seen that the lumped and reduced mechanisms feature good agreements with the detailed mechanism near the extinction state, while relatively larger errors are observed at lower strain rates due to the high sensitivity of the flame temperature to the location of the flames and consequently the heat loss to the burner inlets. The normalized mass fraction of species C$_4$+ and the primary fuel cracking products including CH$_4$, C$_2$H$_4$ and C$_3$H$_6$ as a function of temperature is shown in Fig. 4-10b for the three states with different strain rates and maximum temperatures. Similar trend of fuel cracking is observed in Fig. 4-10b compared to that of the non-premixed flames shown in Fig. 4-9b. Again, the fuel cracking processes are mostly completed at 1500 K with only a trace amount of C$_4$+ species, such as C$_6$H$_{10}$-13 and C$_5$H$_8$-13, remaining at higher temperatures. The results in Figs. 4-(9-10) therefore show that the lumping of fuel cracking reactions is not only valid for 0-D ignition and extinction processes but also applicable for strained flames at near-extinction conditions.

Furthermore, by comparing the 24-species reduced mechanism with the 22-species reduced mechanism for ethylene [106] developed from USC-Mech II, it is interesting to note that the two reduced mechanisms share the majority of the species, while only three species specific to ethylene chemistry, namely HCCO, CH$_2$CO and CH$_3$CHO, are not included in the reduced mechanism for $n$-dodecane. This result implies the paramount importance of C$_2$ chemistry for
high-temperature oxidation of large hydrocarbons, as ethylene is known to be an important intermediate product of beta-scission. It is reasonable to expect that the present reduction approach can be universally applied to most large hydrocarbons, and the resulting reduced mechanisms will feature comparable in sizes to that of ethylene mechanism, involving only 20–30 species, and be amenable to large-scale flame simulations.

4.5 Concluding Remarks

The validity of the concept of the lumped fuel cracking reactions is extensively investigated using three different mechanisms for jet fuel combustion at high-temperature conditions: a detailed JetSurF mechanism developed at the University of Southern California, a JetSurF based mechanism with lumped fuel cracking reactions, and a recently developed 24-species reduced mechanism based on the lumped mechanism generated at the University of Connecticut.

To identify a viable surrogate for high-temperature jet fuel combustion, the effects of frequently used jet fuel surrogate components and their mixtures on auto-ignition and ignition/extinction in PSRs are first investigated, including n-octane, n-decane and n-dodecane, n-butyl-cyclohexane and toluene. It was found that the ignition and extinction behaviors of pure large n-alkanes are mostly identical at high-temperature and fuel-lean conditions, being consistent with the previous observations in the literature. Furthermore, blending a moderate amount of n-butyl-cyclohexane or a small amount of toluene to n-dodecane only induces minor changes in the ignition and extinction behaviors, and the differences are comparable to, or smaller than, the uncertainties induced by using different detailed chemical kinetic mechanisms. As such, pure n-dodecane was selected as a jet fuel surrogate for high-temperature combustion.
To further understand the chemical kinetic processes behind the observations on the surrogate selection, the bifurcation analysis is employed to identify the reactions controlling the ignition and extinction states in PSRs. It was found that both the ignition and extinction in PSRs with high inlet temperatures for pure $n$-dodecane and the binary mixtures of $n$-dodecane and toluene (up to 20% in mole) are primarily controlled by the reactions involving such small molecules as hydrogen and $C_1$-$C_3$ species, and the fuel cracking reactions are not rate-limiting at high-temperature conditions. Therefore the fuel cracking reactions can be lumped to a few semi-global steps by assuming that a large number of intermediate species created by fuel cracking are in quasi-steady-state. The lumped steps can be grafted to a detailed reaction kernel for small molecules such as USC-Mech II as in Refs. [156, 157].

The lumped and reduced mechanisms are then validated in premixed and non-premixed counterflow flames. The validation shows that the lumped and reduced mechanism agree closely with the detailed mechanism for the extinction of non-premixed and premixed counterflow flames, showing the applicability of the lumping of fuel cracking reactions in strained conditions at high-temperature conditions. It is worth emphasizing that the size of the reduced mechanism is comparable to those for small molecules such as methane and ethylene, showing that the reduction strategy based on lumped fuel cracking steps is highly effective in obtaining smallest mechanisms for high-temperature combustion of large hydrocarbons, while remarkable fidelity and comprehensiveness are retained.
Table 4-1: The components and molecular structures of jet fuel surrogates

<table>
<thead>
<tr>
<th>Species name</th>
<th>Molecular structure</th>
<th>Molecular formula</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>n</em>-octane</td>
<td></td>
<td>C_{8}H_{18}</td>
</tr>
<tr>
<td><em>n</em>-decane</td>
<td></td>
<td>C_{10}H_{22}</td>
</tr>
<tr>
<td><em>n</em>-dodecane</td>
<td></td>
<td>C_{12}H_{26}</td>
</tr>
<tr>
<td><em>n</em>-butyl-cyclohexane</td>
<td>(\text{Cyclic structure} \text{-(CH}_2\text{)}_n\text{-CH}_3)</td>
<td>C_{4}H_{9}C_{6}H_{11}</td>
</tr>
<tr>
<td>Toluene</td>
<td>(\text{Cyclic structure} \text{-CH}_3)</td>
<td>C_{6}H_{5}CH_{3}</td>
</tr>
</tbody>
</table>
Figure 4-1: (a) Ignition delay as a function of initial temperature in constant-pressure auto-ignition at pressure $p = 1$ and 10 atm, equivalence ratio $\phi = 0.7$, and (b) the “$S$”-curves of PSRs at pressure $p = 10$ atm, equivalence ratio $\phi = 0.7$ and inlet temperature $T_{in} = 1000$ K, for $n$-dodecane, $n$-decane and $n$-octane, respectively.
Figure 4-2: (a) Extinction temperature and (b) extinction residence time as functions of inlet temperature in PSRs at pressure $p = 10$ atm for $n$-dodecane, $n$-decane and $n$-octane, respectively.
Figure 4-3: (a) Ignition delay as a function of initial temperature in constant-pressure auto-ignition at pressure $p = 10$ atm, equivalence ratio $\phi = 0.7$, and (b) the “S”-curves of PSRs at pressure $p = 10$ atm, equivalence ratio $\phi = 0.7$ and inlet temperature $T_{\text{in}} = 1000$ K, for $n$-dodecane, $n$-butyl-cyclohexane and toluene, respectively.
Figure 4-4: (a) Extinction temperature and (b) extinction residence time as functions of inlet temperature in PSRs at pressure $p = 10$ atm for $n$-dodecane, $n$-butyl-cyclohexane, toluene, and binary mixtures of 50% $n$-dodecane and 50% $n$-butyl-cyclohexane in mole, respectively.
Figure 4-5: (a) Ignition delay as a function of initial temperature in constant-pressure auto-ignition at pressure $p = 10$ atm, equivalence ratio $\phi = 0.7$, and (b) the “$S$”-curves of PSRs at pressure $p = 10$ atm, equivalence ratio $\phi = 0.7$ and inlet temperature $T_{in} = 1000$ K, for $n$-dodecane, toluene, and binary mixtures of $n$-dodecane and toluene with 20% and 50% toluene in mole, respectively.
Figure 4-6: (a) Extinction temperature and (b) extinction residence time as functions of inlet temperature in PSRs at pressure $p = 10$ atm for $n$-dodecane, toluene, and binary mixtures of $n$-dodecane and toluene with 20% and 50% toluene in mole, respectively.
Figure 4-7: (a) Temporal profile of temperature in constant-pressure auto-ignition, and (b) the “S”-curves of PSRs at pressure $p = 10$ atm, equivalence ratio $\phi = 0.7$ and initial and inlet temperatures of 1000 K, for pure $n$-dodecane and the binary mixture of 80% $n$-dodecane and 20% toluene in mole, respectively, predicted by three different mechanisms.
Figure 4-8: Reactions ranked in bifurcation index for the (a) extinction and (b) ignition states on the “S”-curves of PSRs in Fig. 4-5b for binary mixtures of n-dodecane and toluene with 0, 20%, and 50% toluene in mole, respectively.
Figure 4-9: (a) Maximum temperature $T_{\text{max}}$, as a function of the strain rate calculated with the detailed, lumped and reduced mechanisms, respectively; (b) Normalized total mass fraction of C₄⁺ species, and the primary fuel cracking products, including CH₄, C₂H₄ and C₃H₆, calculated with the detailed mechanism for three different strain states in counterflow non-premixed flames at atmospheric pressure. Fuel inlet: 50% n-dodecane and 50% N₂ in mole with inlet temperature of 300 K. Oxidizer inlet: air with inlet temperature of 300 K.
Figure 4-10: (a) Maximum temperature $T_{\text{max}}$, as a function of the strain rate calculated with the detailed, lumped and reduced mechanisms, respectively; (b) Normalized total mass fraction of C$_4$+ species, and the primary fuel cracking products, including CH$_4$, C$_2$H$_4$ and C$_3$H$_6$, calculated with the detailed mechanism for three different strain states, in counterflow premixed flames of n-dodecane–air with equivalence ratio of 0.7, inlet temperature of 300 K and atmospheric pressure.
Chapter 5  Computational Diagnostics for \(n\)-Heptane Flames with Chemical Explosive Mode Analysis

5.1  Introduction

The couplings of detailed chemical kinetics with turbulence are important for high-fidelity combustion simulations, e.g. LES and DNS, 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.

There are many methods developed for mechanism reduction as reviewed in Ch. 1. In particular, a suite of algorithms with DRG were developed to systematically derive reduced mechanisms suitable for DNS [3], 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 [3]. 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 [170]; QSS species are systematically identified using an algorithm based on CSP [14] and the algebraic equations for QSS approximations are solved.
analytically based on graph theory [159]. Diffusive species are then bundled for the mixture-averaged transport model [171] such that the computational cost for diffusion coefficient evaluation can be mostly eliminated. Chemical stiffness is removed ultimately on-the-fly [45] such that the low-cost explicit integration solvers, such as the explicit 4th order Runge–Kutta method in [172], 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 [45, 173]. Realistic chemistry for practical fuels, e.g. methane, ethylene [40, 48, 174, 175], $n$-heptane [45, 173], and iso-octane, therefore became affordable for DNS.

Although highly reduced mechanisms can be derived and applied to the large scale flame simulations, the massive datasets generated from simulations cause another challenge to 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) [81, 106, 173] 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. The efforts are also
made in further improving the computational efficiency of CEMA which will be introduced in
the end.

5.2 Formulation of CEMA

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

\[
\frac{Dy}{Dt} = g(y) \equiv \omega(y) + s(y),
\]

where \( y \) is the vector of the dependent variables including species concentrations and other state
variables. In CEMA, temperature and species mole concentrations are included in \( y \). Note that
the same quantity at different grid points is corresponding to different entries in \( y \). \( D/Dt \) is the
material derivative. \( \omega \) is the chemical source term, and \( s \) is the mixing term. For spatially
homogeneous systems such as PSRs, the material derivative becomes the total derivative and \( s \) is
the homogeneous mixing term. The Jacobian of the RHS of Eq. (5-1) is therefore comprised of
the contributions from the chemical source term and the mixing term, respectively:

\[
J_g = \frac{\partial g(y)}{\partial y} = J_\omega + J_s, \quad J_\omega = \frac{\partial \omega(y)}{\partial y}, \quad J_s = \frac{\partial s(y)}{\partial y}.
\]

Embedded with rich information of the system, the full Jacobian \( J_g \) is important for the analyses
of the system dynamics, e.g. flame stability [111, 115-117, 176]. Similarly, chemical information
of the local mixture is embedded in the chemical Jacobian, \( J_\omega \), which is useful to determine the
chemical properties of the mixtures, e.g. for mechanism reduction with ILDM [22, 177], CSP [7, 23-25], and QSS species identification [14, 17, 18, 178]. 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 [81, 106, 173]. 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 \(J_\omega\) that is corresponding to a local grid point of interest. Furthermore, Eq. \((5-1)\) 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 \(\lambda_e\) is
the first and $\lambda_i$ the $i$th remaining eigenvalue. The eigenmode associated with $\lambda_e$ is defined as a chemical explosive mode (CEM) if

$$\text{Re}(\lambda_e) > 0, \quad \lambda_e = b_e^T \mathbf{J} a_e \tag{5-3}$$

where $b_e$ and $a_e$ are the left and the right eigenvectors, respectively, associated with $\lambda_e$. 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. $\text{Re}(\lambda_e) > 0$, to non-explosive, i.e. $\text{Re}(\lambda_e) < 0$, is strongly correlated to critical flame features such as ignition, extinction, and premixed flame front locations [81, 106]. This observation can be utilized for CFLD of complex combustion problems, e.g. turbulent flames simulated with DNS [48, 81, 106, 173].

Furthermore, the detailed chemical kinetic processes that control the critical flame features can be identified through the quantification of their contributions to the CEM:

$$\mathbf{EI} = \frac{|a_e \otimes b_e^T|}{\text{sum}(|a_e \otimes b_e^T|)}, \tag{5-4}$$

$$\mathbf{PI} = \frac{|(b_e \cdot \mathbf{S}) \otimes \mathbf{R}|}{\text{sum}((b_e \cdot \mathbf{S}) \otimes \mathbf{R})}, \tag{5-5}$$

where $\mathbf{S}$ is the stoichiometric coefficient matrix, $\mathbf{R}$ is the vector of the net rates for the reactions, and “$\otimes$” denotes element-wise multiplication of two vectors. $\mathbf{EI}$ is the vector of explosion indices that indicate the normalized contribution of each species to the CEM, and $\mathbf{PI}$ is the vector of participation indices that indicate the normalized contribution of each reaction to the CEM. The definitions of $\mathbf{EI}$ and $\mathbf{PI}$ are similar to the radical pointer and the participation index, respectively, in the CSP theory [23, 25].
In the following, the utility of CEMA in detection of ignition, extinction, and premixed flames will be demonstrated with a 88-species skeletal mechanism for \( n \)-heptane [173]. A 32-species skeletal mechanism for ethylene [106] will be also employed to analyze the premixed flames controlled by auto-ignition and diffusion. The chemical Jacobian matrices are analytically evaluated using mechanism-specific subroutines generated with an in-house computer code to ensure adequate numerical accuracy.

### 5.3 Detection of Auto-ignition

Auto-ignition of spatially homogeneous and adiabatic systems can be described by a simplified form of Eq. (5-1):

\[
\frac{dy}{dt} = \omega(y),
\]

where the mixing term is absent. In such cases, a CEM indicates an explosive process characterized by local exponential growth.

Figure 5-1 shows the temporal evolution of \( \lambda_e \) and temperature for auto-ignition of lean \( n \)-heptane–air mixtures. The red colors in Fig. 5-1 indicate positive and blue indicates negative values of \( \text{Re}(\lambda_e) \), respectively. Note that “\( \text{Re()} \)” denotes the real part of a complex number in the present study. It is seen that the zero-crossing of \( \text{Re}(\lambda_e) \) is mostly identical to the inflection points on the temperature profiles at all the different conditions. Therefore the zero-crossing of CEM can be used as an alternative definition of ignition point for auto-ignition. A similar conclusion was also made in the auto-ignition study of ethylene using CEMA [106]. It is noted that, while the ignition of \( n \)-heptane at high initial temperatures is single-staged, it features two-stage ignition at low initial temperatures due to the cool flame chemistry. As such, the zero-
crossing of Re(λ_e) occurs near the ignition points in both stages for n-heptane as shown for the case with initial temperature of 800 K in Fig. 5-1.

To further distinguish between the first and second ignition stages and the corresponding post-ignition mixtures for n-heptane, Fig. 5-2 shows the evolution of Re(λ_e) and the EI of species larger than 0.2. The zero-crossing of the CEM can be clearly seen in Fig. 5-2a near both ignition points on the temperature profile. Furthermore, it is seen from Fig. 5-2b that the EI of temperature remains small prior to the first ignition point while it is large between the first and the second ignition points. As such, the first stage ignition is primarily controlled by radical proliferation and the second ignition stage is primarily thermal runaway. It is further seen that while EI of CO is large after both ignition points, the EI of C_2H_2 is large only for the cool flame after the first stage ignition, and the EI of OH is moderately large only after the second ignition point. As such, the direction of the EI vector, when combined with the value of λ_e, can be used to distinguish the two ignition stages in auto-ignition of large hydrocarbons, while the zero-crossing of λ_e alone does not provide adequate information to distinguish between the two stages.

5.4 Ignition and Extinction in Steady State PSRs

Steady state combustion is characterized by the canonical “S”-curve [49], and the turning points on the “S”-curve are frequently used in the literature for validation of near-limit responses of chemical kinetics, e.g. using counterflow flames [41, 50, 51, 55, 56]. In the present study, PSRs will be employed to investigate the ignition and extinction of steady state flames with CEMA.

The governing equations of an unsteady PSR can be written in a simplified form of Eq. (5-1):
\[
\frac{dy}{dt} = \omega(y) + s(y),
\]

(5-7)

where \( s \) is the homogeneous mixing term. Since a steady state PSR features only a single mixing timescale, i.e. the residence time, and the mixing of different scalars are mostly independent, the Jacobian of the homogeneous mixing term in PSRs can be approximated as a diagonal matrix, i.e.

\[
J_s \approx -\frac{1}{\tau} I.
\]

(5-8)

where \( I \) is the identity matrix. In such cases, the eigenvectors of the chemical Jacobian are also eigenvectors of the full Jacobian, and the first eigenvalue of the full Jacobian, \( J \), is

\[
\lambda_1(J) \approx \lambda_e - \frac{1}{\tau}.
\]

(5-9)

Since the full Jacobian is singular at the turning points on the “S”-curves [109], at least one of the eigenvalues of \( J \) is zero there. If \( \lambda_1(J) = 0 \), the timescale of the CEM will balance that of the mixing term at the turnings points:

\[
\lambda_e \approx \frac{1}{\tau}.
\]

(5-10)

It is further noted that the zero-crossing of \( \lambda_1(J) \) requires a positive \( \lambda_e \) based on Eq. (5-9). As such, the presence of a CEM is the necessary condition to result in a turning point for the PSR if the turning is associated with the zero-crossing of \( \lambda_1(J) \). For mixtures with large activation energies, i.e. when \( \lambda_e \) is highly sensitive to temperature change, the zero-crossing points of \( \lambda_1(J) \) and \( \lambda_e \) are very close to each other.
To demonstrate the correlation of the CEM zero-crossing with extinction and ignition in PSRs, Fig. 5-3a shows the “S”-curve for the stoichiometric ethylene–air in PSRs and Fig. 5-3b for a lean \( n \)-heptane–air. The value of \((\lambda_e - 1/\tau)\) is indicated as the color superposed to each data point. Red colors in Fig. 5-3 indicate CEM faster than mixing, and blue colors indicate the lack of CEM or CEM slower than mixing. It is observed from Fig. 5-3a that the “S”-curve for ethylene is canonical with three branches. In the previous study of ethylene–air in PSRs [106], \( \text{Re}(\lambda_e) \) was used solely to identify the upper and middle branches of the “S”-curve and it was found that the zero-crossing point of \( \text{Re}(\lambda_e) \) did not agree with the turning point. However, in Fig. 5-3a, the zero-crossing points of \( \text{Re}(\lambda_e - 1/\tau) \) mostly conform to the turning points, and as such, the CEM balances mixing at the turning points for ethylene.

The “S”-curve for \( n \)-heptane–air shown in Fig. 5-3b is, however, more complex compared with that of ethylene. Due to the cool flame chemistry, the “S”-curve for \( n \)-heptane consists of two additional branches in the low temperature range near 800 K. It is observed that zero-crossings of \( \text{Re}(\lambda_e - 1/\tau) \) occur at points \( E_1, E_2, I_1, \) and \( I_2 \), respectively, as indicated by the transitions between red and blue dots. Note that while \( E_1, I_1 \) and \( I_2 \) conform to the turning points, \( E_2 \) is substantially different from the turning point \( E_2' \). As shown in the inset in Fig. 5-3b, the turning point \( E_2' \) is nearly identical to the zero-crossing of \( \text{Re}(\lambda_2 - 1/\tau) \) instead, where \( \lambda_2 \) is the second eigenvalue of the chemical Jacobian, which also has a positive real part near the cool flame branch. Since the first eigenvalue \( \lambda_1(J) \) of the full Jacobian determines the stability of the flame and \( E_2 \) approximates the zero-crossing of \( \text{Re}(\lambda_1(J)) \) as indicated in Eq. (5-9), it is expected that \( E_2 \) instead of \( E_2' \) separates the stable and unstable branches on the “S”-curve for \( n \)-heptane.
To verify this point, two steady state solutions were selected between E$_2$ and E$_2'$ on different sides of I$_1$. A small perturbation, $\Delta T = -10$ K, was made to the temperature of the steady state solutions, and the unsteady PSR was integrated in time to show the response of the system to the perturbations. It is seen in Fig. 5-4a that the small perturbation for the point on the right side of I$_1$ increases with time and evolves to a nonlinear oscillation with finite amplitude. Nevertheless, the solution for the other point on the left side of I$_1$ extinguishes after a few oscillations and the solution jumps to the lower branch with the inlet temperature of 700 K, as shown in Fig. 5-4b. Since the point in Fig. 5-4b has a residence time larger than that at the turning point E$_2'$, it is clear that E$_2'$ is indeed not a physical extinction point, i.e. the system extinguishes prior to E$_2'$ when marching down the “S”-curve from E$_2$. In this case, the point E$_2$ can be regarded as the physical extinction point for the cool flame branch since a stable cool flame cannot sustain itself beyond E$_2$ with further reduced residence time. This phenomenon was also observed in the study of “S”-curves for oxidation of DME in PSRs as shown in Chs. 2-3.

To extend CEMA for PSRs to other systems with more complex mixing terms, the residence time in Eqs. 5-(9-10) can be replaced by a mixing timescale defined as:

$$\tau_s = -\frac{1}{b_e \cdot J_s \cdot a_e}.$$  \hspace{1cm} (5-11)

A Damköhler number can then be defined for the CEM as

$$Da = Re(\lambda_e) \cdot \tau_s.$$  \hspace{1cm} (5-12)

If $Da \gg 1$, the mixture is auto-igniting since the mixing terms are significantly slower compared with the chemical explosive mode. If $Da \ll -1$, CEM is not present in the mixture. The post-ignition mixture features short chemical timescales and is rate-limited by mixing, similar to the
conditions in the reaction zone of a strongly burning diffusion flame. Note that, to further extend CEMA for diagnostics of turbulent flows, the scalar dissipation rate can be used to approximate the reciprocal mixing timescale as studied in Refs. [81, 106].

5.5 Diagnostics of 1-D Steady State Laminar Premixed Flames

5.5.1 Location of premixed flame fronts

As discussed in [81, 106], premixed flame fronts of hydrogen–air and ethylene–air are thin surfaces that propagate through fresh mixtures and convert the fresh mixtures with CEM to post-ignition mixtures without CEM. The zero-crossing of the CEM can therefore be utilized to accurately locate premixed flame fronts. Figure 5-5 shows the temperature profiles of 1-D steady state freely propagating laminar premixed flames of n-heptane–air, with different equivalence ratios at atmospheric pressure. In the high temperature zone shown in Fig. 5-5, the CEM becomes fast as the mixtures enter the preheat zones, as indicated by the progressively darker red color. Zero-crossings of CEM then occur near the reaction zones where large curvatures are observed on the temperature profiles. CEM is absent in the post-ignition mixtures as indicated by the blue colors. Therefore the zero-crossings of the CEM accurately indicate the locations of the reaction zones in the high temperature range of premixed flames. In contrast with the hydrogen–air and ethylene–air premixed flames which exhibit only a single zero-crossing point [81, 106], there are two additional zero-crossing points in the cool flame temperature range. It is seen in Fig. 5-5 that the fresh mixtures are only weakly reacting upstream of the flame where the temperature is low, as indicated by the green color, i.e. \( \text{Re}(\dot{\lambda}_c) \to +0 \). Then the CEM becomes faster as the mixture approaches the cool flame. The zero-crossing point occurs when the red colors turn to cyan colors, indicating the location of the reaction zone in the low temperature
range. Therefore, while the premixed flames for small hydrocarbons are characterized by a single-layered surface for CEM zero-crossing, those of larger hydrocarbons may be characterized by triple surfaces due to the cool flame chemistry.

5.5.2 Propagation of premixed flame vs. auto-ignition reaction front

Premixed reaction front propagation can be controlled either by auto-ignition or diffusion. While steady state premixed flame propagation through cold frozen mixtures is known to be controlled by back diffusion of energy and radicals, a burner stabilized premixed flame with high inlet temperatures can be stabilized by auto-ignition when the reaction front is sufficiently distant from the burner. It nevertheless can be difficult to distinguish between these two types of reaction front propagation mechanisms at intermediate conditions in complex 3-D flow fields. In such cases, a criterion based on CEMA can be employed to distinguish between auto-igniting reaction fronts and diffusion controlled flame propagation.

In a steady state premixed flame, the effects of convection and diffusion in causing the ignition of a local fluid particle can be measured by the following quantities:

\[ l_c = u \tau_e, \quad \tau_e = \left| \text{Re}(\lambda_e) \right|^{-1}, \quad (5-13) \]

\[ l_\alpha = \sqrt{\alpha \tau_e}, \quad (5-14) \]

where \( u \) is the local flow velocity, and \( \alpha \) is the thermal diffusivity. Since \( \tau_e \) is the characteristic time for local ignition, \( l_c \) and \( l_\alpha \) are the local characteristic lengths over which convection and diffusion can result in significant changes, respectively, in the temperature distribution during a time period of \( \tau_e \). The relative strength of the local convection and diffusion terms can then be measured by a Nusselt number defined as:
Note that $Nu_e$ is a function of $u$, $\alpha$, and $\lambda_e$. If $Nu_e \gg 1$ within the entire preheat zone, convection, or the flow residence time effect, dominates diffusion in causing the ignition of the fluid particle, and thus the reaction front propagation is primarily caused by auto-ignition rather than back diffusion. If $Nu_e \ll 1$ at the location of maximum $Re(\lambda_e)$, diffusion is important in forcing the particle to ignite prior to the reaction zone, and the flame propagation is controlled by back diffusion. To demonstrate the utility of $Nu_e$ in determining the dominant mechanism for flame front propagation, structure of two premixed flames for ethylene–air is shown in Fig. 5-6.

Figure 5-6a shows the temperature profile and the spatial distribution of $Nu_e$ for a 1-D freely propagating premixed flame through a cold stoichiometric ethylene–air mixture with free-stream temperature $T_0 = 300$ K. It is seen that $Nu_e < 1$ where $Re(\lambda_e)$ is large. As such, back diffusion is important for the flame propagation. Figure 5-6b shows the structure of a burner-stabilized premixed flame for lean ethylene–air with equivalence ratio $\phi = 0.2$, inlet temperature $T_0 = 1200$ K, and inlet flow velocity $u_0 = 17.1$ m/s. It is seen that $Nu_e \gg 1$ within the entire domain, and thus diffusion is not important for ignition of the mixture. As such, the burner-stabilized flame in Fig. 5-6b is an auto-igniting reaction front, in which a fluid particle auto-ignites as it travels downstream. To verify this point, the flame was re-computed using the same inlet conditions while the mixture-averaged diffusivity of each species and the mixture’s thermal conductivity were reduced by a factor of 1000. The resulting temperature profile is shown by the dashed line in Fig. 5-6b. It is observed that the substantial reduction in diffusivities has negligible effects on the reaction front and flame structure.
5.6 2-D DNS for n-Heptane at HCCI Conditions

The utility of CEMA in DNS data mining will next be demonstrated with a 2-D DNS dataset for n-heptane–air under HCCI conditions [173]. In this simulation, the compressible Navier–Stokes equations were solved using Sandia’s DNS code, S3D [179]. A 4th order explicit Runge–Kutta method was used for time integration and an 8th order central differencing scheme was used for spatial differentiation [179].

The 2-D DNS of n-heptane–air combustion under HCCI conditions was simulated with a 58 species non-stiff reduced mechanism and the mixture-averaged transport model [173]. As a brief description, the mechanism was derived using a suite of methods reviewed in [3]. The number of species in the detailed mechanism was first reduced using DRG, DRGASA and isomer lumping. Chemical stiffness induced by fast species with timescales shorter than 10 ns was removed on-the-fly by assuming that the fast chemical processes are exhausted [45]. Species with similar diffusivities were then bundled to 14 groups to reduce the computational cost in evaluating mixture-averaged diffusion coefficients. More detailed description of the reduced mechanism can be found in [173]. The domain of the DNS is 3.2 mm by 3.2 mm in the x- and y-directions, respectively, uniformly discretized with 2.5 μm grid spacing in each direction. Periodic boundary conditions were imposed on all four boundaries. The initial equivalence ratio, $\phi$, pressure, $p_0$, and mean temperature, $T_0$, are 0.3, 40 atm, and 900 K, respectively. A temperature fluctuation with a root mean square value of 100 K and isotropic turbulence with a velocity fluctuation of 0.5 m/s were prescribed for the initial flow and temperature fields. A more detailed description of the 2-D DNS parameters is provided in Ref. [173].

Figure 5-7 shows the spatial distribution of $\lambda_e$, normalized OH concentration, and temperature at different times. The initial states in the flow field are shown in the top row. It is
seen that CEM is present in the entire initial mixture as indicated by the red colors on the $\lambda_e$ plot. At $t = 0.35$ ms, the $\lambda_e$ plot shows narrow strips of cool flames (cyan color) that correspond to the mixtures immediately after the first stage ignition. Note that the timescales of the CEMs for the cool flames are similar to those shown in Figs. 5-(1, 3b, 5). The cool flames are however difficult to observe on the OH and temperature plots, in which the white isolines indicate the zero-crossing of CEM, i.e. Re($\lambda_e$) = 0. At $t = 1$ ms and 1.7 ms, substantial portions of the mixture have passed the second stage ignition as indicated by the blue colors on the $\lambda_e$ plot. Significant increases in OH concentration and temperature can also be observed such that the ignited mixtures can also be readily identified on the temperature and OH plots. Nevertheless, the identification of ignited mixtures based on OH concentration involves an arbitrary threshold concentration, which depends on local mixture composition and the thermodynamic state and frequently needs to be empirically determined. At $t = 2$ ms, all of the mixture in the flow field has ignited as indicated by the blue colors on the $\lambda_e$ plot, while a large degree of scatter in OH concentration can still be observed in the flow field. Therefore, using arbitrary isolines of OH concentration may readily result in false identification of flame fronts, while CEMA is a universal and more reliable approach to identify different flame zones.

5.7 Reduced Descriptions of CEMA

The above CEMA results are based on a detailed chemical Jacobian requiring the information of the full set of reactions and species in the detailed chemistry. Although the chemistry in the DNS is already highly reduced, CEMA is still computationally expensive due to the need to perform the grid-wise eigen-decomposition. In addition, CEMA requires the fully detailed information on the entire species set and thermodynamic state variables, as such has been only applied to numerically solved flow fields. To extend the application of CEMA in
experimental combustion with information only on a subset of species, a reduced description of CEMA is proposed in the present study by using a semi-analytic expression involving only a few dominant reactions and species to approximate the full description of CEMA.

To identify the dominant species and reactions for the eigenvalue $\lambda_e$ of the CEM in Eq. (5-3), the chemical Jacobian $J_\omega$ can be decomposed to the contribution from each reaction and each species as

$$J_\omega = \sum_{r=1}^I \left( S_r \cdot \frac{\partial \omega_r}{\partial C} \right), \quad C = [C_1, C_2, \ldots, C_{KK}, T]^T,$$

(5-16)

where $\omega_r$ is the reaction rate of the $r$th reaction, and $I$ is the total number of reactions. It is noted that the forward and reverse directions of a reversible reaction are regarded as two different reactions. $C$ is the vector consisting of species concentrations and temperature and $KK$ is the total number of species. $S_r$ is the vector of stoichiometric coefficients for the $r$th reaction with the last entry corresponding to heat release. Based on a dot product of the eigenvectors $b_e$ and $a_e$ on the chemical Jacobian $J_\omega$, the eigenvalue $\lambda_e$ can be subsequently decomposed as

$$\lambda_e = b_e \cdot J_\omega \cdot a_e = \sum_{r=1}^I \left( \frac{\partial \omega_r}{\partial C} \cdot (b_e \cdot S_r \cdot a_e) \right) = \sum_{r=1}^I \sum_{i=1}^{KK+1} \left( \alpha_{r,i} \cdot \frac{\partial \omega_r}{\partial C_i} \right),$$

(5-17a)

$$\alpha_{r,i} = b_e \cdot S_r \cdot a_{e,i}.$$

(5-17b)

$\alpha_{e,i}$ is the coefficient corresponding to the $r$th reaction and $i$th species. It is seen in Eq. (5-17a) that the eigenvalue $\lambda_e$ is comprised of $(I \times (KK + 1))$ entries, each of which is the product of the coefficient $\alpha$ and the derivative of the reaction rate to a species concentration or temperature, and can be normalized as
where CI\(_{r,i}\) indicates the importance of the \((r, i)\)-th entry to the eigenvalue \(\lambda_e\). Once the importance of each entry is obtained, the entries with negligible CI values can be ignored in the evaluation of \(\lambda_e\) while the limit phenomena associated with the eigenvalue zero-crossing can still be captured. A reduced formula of CEMA is consequently obtained. This method is demonstrated with PSRs in the following to identify the extinction states for three types of fuels, including methane, ethylene and \(n\)-heptane.

Methane is first studied over a wide range of equivalence ratios and pressures using the GRI1.2 mechanism [180, 181]. Through imposing an error threshold on the predicted extinction temperature, e.g. \(\varepsilon_T = 60\) K in the present study, the eigenvalue \(\lambda_e\) for the reduced description of CEMA can be approximated by only two entries in Eq. (5-17), which are relevant to the chain-branching reaction R1: \(\text{H} + \text{O}_2 \rightarrow \text{O} + \text{OH}\),

\[
\lambda_e = k_1 \cdot \left( \alpha_{r,H} \cdot C_{O_2} + \alpha_{r,O_2} \cdot C_H \right),
\]

(5-19)

where \(k_1 = AT^n \exp\left(-\frac{E_a}{RT}\right)\) is the reaction rate of R1. The extinction state identified with Eq. (5-19), as the approximation of the zero-crossing of \((\lambda_e - 1/\tau)\) discussed in Section 5.4, is shown in Fig. 5-8 for the “S”-curves of methane–air in PSRs at inlet temperature of 1000 K, pressures of 1 and 30 atm, and equivalence ratios of 0.5, 1 and 2, respectively. The reduced description of CEMA marked with red circles closely agrees with the turning points that are the actual extinction states. To further demonstrate the effectiveness of the reduced description of CEMA
in identifying the extinction of PSRs at different conditions, Fig. 5-9 presents the extinction temperature and extinction residence time as functions of equivalence ratio at different pressures, calculated by the detailed and reduced descriptions, respectively. It is seen that the reduced description captures the extinction residence time very accurately and the extinction temperature with a worst-case error of approximately 37 K.

The above approach is applied to ethylene–air [106] and \textit{n}-heptane–air [173], and a similar reduced formula for the eigenvalue is obtained:

$$
\lambda_c = k_i \cdot \left( \alpha_{i,H} \cdot C_{O_2} + \alpha_{i,O_2} \cdot C_H + \alpha_{i,T} \cdot \left( \frac{n}{T} + \frac{E_n}{R_i T^2} \right) \cdot C_H \cdot C_{O_2} \right).
$$

(5-20)

It is seen that the only difference between Eqs. (5-19) and (5-20) is the last term in Eq. (5-20) that is related to heat release. Figure 5-10 shows the “S”-curves for ethylene–air with the extinction states predicted by the reduced formula in Eq. (5-20) marked with red circles. Figure 5-11 further compares the extinction temperature and extinction residence time calculated by the detailed and reduced CEMA descriptions, respectively, over a wide range of equivalence ratios and pressures. It is seen that the extinction residence time is accurately captured and the worst-case error in extinction temperature is approximately 64 K, being comparable to that of methane–air. Similar results are also observed for \textit{n}-helptane–air as shown in Figs. 5-12 and 5-13, with the worst-case error being about 50 K in extinction temperature.

The utility of reduced CEMA description is hereby demonstrated. It is expected that the current methods can also be extended to larger hydrocarbons featuring NTC chemistry and cool flame behaviors.
5.8 Concluding Remarks

The versatility of CEMA for CFLD was demonstrated using n-heptane and ethylene for a variety of flame configurations. The utility of CEMA is primarily based on the observation that CEM plays a critical role in many combustion problems such as ignition, extinction and premixed flame propagation.

Based on the definition of CEM in Eq. (5-3), CEM is purely a chemical property of the local mixture since it is determined only by the local temperature and species mole concentrations. Since the mixing term is not required in evaluating the local chemical Jacobian, CEMA can be performed independently at each grid point of a large flow field. Thus it can be readily implemented for parallel computing with high efficiency. It is emphasized that the exclusion of transport in the definition of CEM should not be confused with the obviously incorrect assumption that the effect of diffusion is negligible in flames. This is because while chemical reactions are strongly coupled with transport in many flames, the complex chemistry–transport interactions will eventually result in changes in the chemical properties of the mixtures. In many cases, critical flame features can be effectively detected based on such changes in the chemical properties without the need to resolve the chemistry–transport couplings. CEM was found to be an important chemical property, of which the zero-crossing is closely related to many near-limit flame behaviors. Therefore, CEM can be utilized as a quantitative diagnostic technique for many complex combustion problems.

In the present study, the detection of auto-ignition using CEMA is based on the observation that CEM is present in preheated mixtures prior to ignition and is absent once the mixture has ignited. The detection of premixed flame fronts using CEMA is based on the similar observation while tracking a fluid particle in the Lagrangian system. In PSRs, it was shown that
the competition between the CEM and mixing is the primary reason in causing ignition and extinction of the system. It is noted that a local mixing timescale is involved in CEMA for limit phenomena detection in steady state systems. The application of CEMA on DNS results for HCCI shows that CEMA is advantageous for flame diagnostics compared with other methods based on individual scalars such as temperature and a species concentration. First, this is because arbitrary thresholds are needed to mark the flames with such scalars. Second, the variation of temperature and species concentrations across a flame may be difficult to observe at extreme conditions, e.g. when the mixtures are extremely lean or rich or when significant spatial fluctuations are present.

The cool flame chemistry is important for ignition and extinction at low temperatures for large hydrocarbons as shown by the CEMA results for \( n \)-heptane flames. When two-stage ignition is involved, e.g. as shown in Figs. 5-(1, 2, 5, 7), the EI data for temperature and species can be employed together with the timescale of CEM to distinguish the different ignition stages which are attributed to different controlling species at different ignition stages. Furthermore, it is shown that the stabilities of steady state flames can be rather complex when multiple turnings are present in the “S”-curves. In such cases the conventional definition of ignition and extinction based on the turning points may be unphysical.

For fuels without NTC behaviors such as ethylene, only a single CEM has been observed in the present and previous studies of CEMA [81, 106] when Eq. (5-1) was formulated with temperature and species mole concentrations as dependent variables. Two CEMs with distinctive eigenvalues, which are not a complex conjugate pair, have been observed for \( n \)-heptane in Fig. 5-3b in the present work. If complex CEMs are present for other fuels or at other flame conditions,
CEMA is formulated with the real parts of the eigenvalues and eigenvectors only, as shown in Eqs. 5- (3-5).

It is noted that CEMA can be extended as a computational diagnostic technique for many other combustion problems, e.g. ignition and extinction in steady state diffusion flames, classification of local premixed flame fronts and auto-ignition fronts in unsteady flows, and the effects of differential diffusion on near-limit flame behaviors. Furthermore, once the information for the CEM is calculated, that for other modes also becomes available. The information of other chemical modes may also be useful for flame diagnostics. Such topics are more involved and merit further study.

A reduced description of CEMA is further investigated through decomposing the eigenvalue of the CEM, such that a reduced formula with only very few terms can be used to approximate the eigenvalue of the CEM. Reduced CEMA descriptions are obtained for three fuels, namely methane, ethylene and n-heptane, and are validated in PSRs over a wide range of conditions. It is found that, the reduced CEMA descriptions for flame extinction primarily involve only temperature, two species concentrations, namely H and O₂, and a single reaction R1, H + O₂ → O + OH. Such highly reduced descriptions can significantly reduce the cost and improve the applicability of CEMA for on-the-fly computational diagnostics of numerical simulations. It also renders it possible to apply CEMA based criteria in experimental diagnostics where only a limited amount of information is available on the temperature and species concentration fields.
Figure 5-1: Time dependence of temperature and $\lambda_c$ in auto-ignition under constant pressure at different initial temperatures for $n$-heptane. The color at each data point indicates the value of $\text{sign(Re}(\lambda_c)) \times \log_{10}(1+|\text{Re}(\lambda_c)|)$. “sign()” denotes the signum function; “Re()” denotes the real part of a complex number.
Figure 5-2: Temporal evolvement of a) $\lambda_e$ and temperature, and b) EI for different species for auto-ignition of a lean $n$-heptane–air mixture under constant pressure and initial temperature of 800K. Lines with symbols in panel (b) indicate EI data.
Figure 5-3: “S”-curves of PSR for a) ethylene–air and b) n-heptane–air. The colors superposed to the data points on the “S”-curves indicate the values of $\text{sign}(\text{Re}(\lambda_2 - 1/\tau)) \times \log_{10}(1 + |\text{Re}(\lambda_2 - 1/\tau)|)$. “sign()” denotes the signum function; “\text{Re}()” denotes the real part of a complex number.
Figure 5-4: Temperature evolution in unsteady PSR of $n$-heptane–air after a small initial perturbation ($\Delta T = -10$ K) to the steady state solutions, at a) a point between $E_2$ and $E_2'$ in Fig. 5-3b with a residence time larger than that at $I_1$, and b) a point between $E_2$ and $E_2'$ with a residence time shorter than that at $I_1$. The values of temperature in the titles indicate the steady state solutions without the perturbation.
Figure 5-5: Temperature profiles of 1-D planar freely propagating laminar $n$-heptane–air premixed flames with different equivalence ratios at atmospheric pressure. The color superposed to each data point indicates the value of $\text{sign}(\text{Re}(\lambda_c)) \times \log_{10}(1+|\text{Re}(\lambda_c)|)$. “sign()” denotes the signum function; “Re()” denotes the real part of a complex number.
Figure 5-6: Profiles of temperature and $Nu_e$ for ethylene–air for a) 1-D steady state freely propagating laminar premixed flame with equivalence ratio of 1.0 and free stream temperature of 300 K, and b) 1-D steady state burner stabilized flame with equivalence ratio of 0.2 and inlet temperature of 1200 K. The color superposed to each data point indicates the value of $\text{sign}(\text{Re}(\lambda_e)) \times \log_{10}(1 + |\text{Re}(\lambda_e)|)$. “$\text{sign}()$” denotes the signum function; “$\text{Re}()$” denotes the real part of a complex number.
Figure 5-7: Spatial distribution of $\lambda_e$ (left column), OH concentration (middle column) and temperature (right column) for 2-D n-heptane–air mixture with an equivalence ratio, $\phi = 0.3$, initial pressure, $p_0 = 40$ atm, initial mean temperature, $T_0 = 900$ K with a RMS fluctuation of $T' = 100$ K. The rows from top to bottom correspond to the time instants: $t = 0$, 0.35 ms, 1 ms, 1.7 ms, and 2 ms, respectively. The white isolines denote $\text{Re}(\lambda_e) = 0$. 
Figure 5-8: “S”-curves of PSR for methane–air at a) pressure $p = 1$ atm, and b) pressure $p = 30$ atm, under equivalence ratio $\phi = 0.5, 1$ and 2, and inlet temperature $T_{in} = 1000$ K. The symbols denote the extinction states identified from the reduced CEMA description based on Eq. (5-19).
Figure 5-9: (a) Extinction temperature and (b) extinction residence time as functions of equivalence ratio calculated with the full and reduced CEMA descriptions, respectively, for methane–air in PSRs at inlet temperature $T_{\text{in}} = 1000$ K and pressure $p = 1$ and 30 atm.
Figure 5-10: “S”-curves of PSR for ethylene–air at a) pressure $p = 1$ atm, and b) pressure $p = 30$ atm, under equivalence ratio $\phi = 0.5$, 1 and 2, and inlet temperature $T_{\text{in}} = 1000$ K. The symbols denote the extinction states identified from the reduced CEMA description based on Eq. (5-20).
Figure 5-11: (a) Extinction temperature and (b) extinction residence time as functions of equivalence ratio calculated with the detailed and reduced CEMA descriptions, respectively, for ethylene–air in PSRs at inlet temperature $T_{in} = 1000$ K and pressure $p = 1$ and 30 atm.
Figure 5-12: “S”-curves of PSR for $n$-heptane–air at a) pressure $p = 1$ atm, and b) pressure $p = 30$ atm, under equivalence ratio $\phi = 0.5, 1$ and 2, and inlet temperature $T_{in} = 1000$ K. The symbols denote the extinction states identified from the reduced CEMA description based on Eq. (5-21).
Figure 5-13: (a) Extinction temperature and (b) extinction residence time as functions of equivalence ratio, calculated with the detailed and reduced CEMA descriptions, respectively, for \( n \)-heptane–air in PSRs at inlet temperature \( T_{in} = 1000 \) K and pressure of 1 and 30 atm.
Chapter 6  Summaries and Future Perspectives

The research in the present dissertation is motivated by the fact that the limit flame phenomena, such as ignition, extinction and onset of instabilities, have a significant impact on energy conversion systems, and have not been fully understood due to the complex flow–chemistry and chemistry–chemistry couplings. The present study is primarily focused to develop systematic approaches for computational flame diagnostics to understand the critical flame features in practical combustion systems. Approaches based on two levels of the Jacobian analysis of the reacting systems, namely the bifurcation analysis based on the full Jacobian and CEMA based on the chemical Jacobian, were introduced and applied in different combustion models to accurately and efficiently identify the limit flame phenomena and the controlling physicochemical processes.

The bifurcation analysis formulated on the full Jacobian of the governing equations was proposed in Ch. 2 and employed in steady state PSRs. Ignition and extinction associated with the zero-crossing of the real part of the eigenvalues of the Jacobian were identified and demonstrated with methane and DME, respectively. It is found that the turning points on the “$S$”-curve for methane–air are consistent with those on the canonical “$S$”-curves, and they indicate the physical ignition and extinction states and the change in combustion stability. However, for DME with NTC behaviors, it is found that the physical extinction and ignition may occur at the Hopf bifurcation points instead of the turning points. The bifurcation analysis was further applied to DME–air of different equivalence ratios. The results show that for the strongly burning flames, the discrepancy between the physical extinction states and the turning points occurs at very rich cases, while for the cool flames, it is observed for both lean and rich cases. Hence the bifurcation
analysis is necessary to rigorously identify the physical extinction and ignition states, and it may be erroneous to simply match the experimentally measured ignition and extinction states with the numerically-obtained turning points when practical fuels with NTC chemistry are involved. It is also worth mentioning that the Jacobian used in the bifurcation analysis is analytically evaluated to ensure adequate accuracy in capturing the zero-crossing of the eigenvalues associated with bifurcation points.

In addition to identifying the physical ignition and extinction states, the bifurcation analysis was further employed in Ch. 3 to understand the underlying chemical kinetics controlling the limit flame phenomena, and was demonstrated with DME–air mixtures in PSRs. A bifurcation index (BI) was defined through evaluating the contribution of each elementary reaction and the mixing process to the bifurcation points. The extinction states for strong flames and cool flames were analyzed based on the BI method. It is found that the extinction of strong flames is primarily controlled by the reactions involving small molecules, while that of cool flames is dominated by the reactions related to NTC chemistry. The BI results were further compared with, and found to agree with, that of sensitivity analysis for identification of the ignition and extinction states. The BI method is nevertheless more effective and efficient than, and thus can be used as a substitute of, the global sensitivity analysis. The BI method was then extended to develop a compact model through first eliminating the reactions with small BI values and then tuning the “A”-factors of the selected important reactions with large BI values to match the results of ignition and extinction predicted by the detailed chemistry. A compact model was obtained with tuned rate parameters and an almost halved reaction set. The tuned model is validated for identifying the ignition and extinction states of both the strong and cool flames in
both steady and unsteady PSRs, revealing its potential to be applicable in more complex flame configurations.

The bifurcation analysis is further employed in Ch. 4 to develop reduced mechanisms for jet fuel combustion at high-temperature conditions. A viable surrogate of jet fuels was first identified through investigating the compositional effects of a few major jet fuel surrogate components on ignition delay and ignition and extinction of PSRs. The results show that the high-temperature ignition and extinction properties of jet fuels can be represented by that of large \textit{n}-alkanes such as \textit{n}-dodecane, while the effect of a small amount of toluene addition is insignificant. Therefore, \textit{n}-dodecane can be used as a jet fuel surrogate for high-temperature combustion.

The bifurcation analysis was further applied to understand the underlying chemical kinetics behind the jet fuel surrogate selection through identifying the controlling reactions and species for the limit phenomena. The results show that both the extinction and ignition states at high temperatures for pure \textit{n}-dodecane and the binary mixtures of \textit{n}-dodecane and a small amount of toluene are mostly controlled by the same set of reactions involving small molecules ranging from \textit{C}_1 to \textit{C}_3. It indicates that the fuel cracking reactions associated with the large molecules are not rate-limiting at high-temperature conditions and thus can be lumped to a few semi-global steps by assuming that the intermediate species from fuel cracking are in quasi-steady state. A reduced mechanism generated at the University of Connecticut based on the lumped jet fuel model was employed for demonstration was further validated in the extinction of premixed and non-premixed counterflow flames over a wide range of conditions, showing that the reduction strategy based on the lumped fuel cracking reactions is applicable to both unstrained and strained flames.
Chapter 5 studies the CEMA method defined based on the Jacobian of the chemical
source term. CEMA was first applied to auto-ignition, steady state PSRs and laminar premixed
flames, for ethylene and \(n\)-heptane, respectively, and the results show that CEMA is effective in
the detection of the critical flame features, including ignition, extinction, and flame fronts.
CEMA was then applied to the DNS results of \(n\)-heptane under HCCI conditions and the results
show that it can effectively identify the flame fronts for both the strong and the cool flames.

Future work on the CEMA method can include the extension of CEMA from DNS-type
datasets to those of LES (filtered data) and RANS (averaged data) simulations. Another possible
extension is to derive analytic or semi-analytic criteria for efficient identification of ignition and
extinction in large flow fields through identifying the dominant species and reactions controlling
the zero-crossing of the eigenvalue associated with the chemical explosive mode. Preliminary
studies show that such reduced criteria can be obtained for different fuels over a wide range of
flame conditions, and it is possible to use as few as two species concentrations, in addition to
temperature, to capture the extinction states in PSRs.
