Problems in Catalytic Oxidation of Hydrocarbons and Detailed Simulation of Combustion Processes

Yuxuan Xin

A Dissertation
Presented to the Faculty of Princeton University
in Candidacy for the Degree of Doctor of Philosophy

Recommended for Acceptance
By the Department of
Mechanical and Aerospace Engineering

Advisor: Chung K. Law

September 2014
Abstract

This dissertation research consists of two parts, with Part I on the kinetics of catalytic oxidation of hydrocarbons and Part II on aspects on the detailed simulation of combustion processes.

In Part I, the catalytic oxidation of \( \text{C}_1 \text{–C}_3 \) hydrocarbons, namely methane, ethane, propane and ethylene, was investigated for lean hydrocarbon-air mixtures over an unsupported Pd-based catalyst, from 600 to 800 K and under atmospheric pressure. The wire microcalorimetry and the numerical simulation of the detailed surface kinetics were adopted in this thesis. In Chapter 2, the experimental facility of wire microcalorimetry and simulation configuration were described in details, and the physical morphology and chemical composition of the wire surface were characterized by Scanning Electron Microscopy (SEM), X-ray Photoelectron Spectroscopy (XPS), and Atom Force Microscopy (AFM), showing the presence of a porous PdO layer of 1 to 2 \( \mu \text{m} \) thickness on the Pd wire during the hydrocarbon oxidation.

In Chapter 3 and 4, Wire microcalorimetry was utilized to quantify the rate of hydrocarbon oxidation over PdO surface, from which the apparent kinetic parameters were extracted, showing unity reaction order with respect to the hydrocarbon concentration and decreasing global activation energies in the order of methane, ethane, propane and ethylene. Supported by the experimental observations and the calculations using density functional theory, it is demonstrated that the oxidation of \( \text{C}_1 \text{–C}_3 \)
hydrocarbons over a PdO surface proceeds with a similar mechanism: they undergo
dissociative adsorption followed by the conversion of surface fragments to final products.
The rate of this process is determined by the dissociative adsorption of hydrocarbons but
is also influenced by the equilibrium of oxygen adsorption/desorption. Accordingly, a
detailed surface kinetics model is proposed for this process, which estimates the
equilibrium constant of O$_2$ adsorption from the thermodynamic properties of adsorbed
oxygen atoms, and derives the rate coefficient of hydrocarbon dissociative adsorption
from the wire microcalorimetry data.

In Part II, four fundamental studies were conducted through detailed combustion
simulations. In Chapter 5, self-accelerating, expanding, cylindrical, stoichiometric
hydrogen-air flames at eight atmospheres are studied via two-dimensional detailed
numerical simulation (DNS) of the compressible Navier-Stokes equations with detailed
chemistry. The flame morphology and propagation are finely resolved by the application
of a small time step and grid size. Temporally, the intermittent, pulsating propagation of
the flame front is captured by examining its propagation velocity. Spatially, the flame
front is found to comprise of segments exhibiting similar propagation properties, and the
intermittent instantaneous propagation of the flame front is attributed to the development
of cellular structures induced by hydrodynamic instability. The long-term average
propagation velocity of the flame front is described by a power law, with a self-
acceleration exponent of 1.22 for the flame radius with respect to time. The increase in
the global flame velocity is shown to be primarily a consequence of increased flame surface area, with the local front propagation velocity remaining largely at the constant laminar flame speed for the near-unity Lewis number mixture studied herein. The fractal structure is demonstrated for the flame front by the box-counting method, with a fractal dimension around 1.07±0.02.

In Chapter 6, skeletal reaction models for \( n \)-butane and \( iso \)-butane combustion are derived from a detailed chemistry model by using directed relation graph (DRG) and DRG-aided sensitivity analysis (DRGASA) methods. It is shown that the accuracy of the reduced models can be improved by optimization through the method of uncertainty minimization by polynomial chaos expansion (MUM-PCE). The dependence of model uncertainty on the model size is also investigated by exploring skeletal models containing different number of species. It is shown that the dependence of model uncertainty is subjected to the completeness of the model. In principle, the uncertainty of a complete model is convergent with respect to the model size while an incomplete model may display behavior that is difficult to predict.

In Chapter 7, diffusion models for multicomponent mixtures are investigated in a variety of flame configurations including the planar premixed flames, counterflow diffusion flames, and droplet flames. Discernable discrepancies are observed in the simulated flames with the mixture-averaged and multicomponent diffusion models, respectively, while the computational cost of the multicomponent model is significantly
higher than that of the mixture-averaged model. A systematic strategy is proposed to reduce the cost of the multicomponent diffusion model by accurately accounting for the species whose diffusivity is important to the global responses of the combustion systems, and approximating those of less importance. The important species in the reduced model are identified with sensitivity analysis and are found to be typically those in high concentrations with the exception of a few radicals, e.g., H and OH, which are known to participate in critical reactions. The reduced model is validated in simulating the candidate flames. The reduced model is shown to feature similar accuracy to that of the multicomponent model while the computational cost is reduced by a factor of approximately five for an n-heptane mechanism with 88 species.

In Chapter 8, the influence of Soret diffusion on the structure and response of n-heptane/air flames is investigated numerically with a detailed reaction mechanism and transport. Unstretched freely-propagating planar premixed flames as well as stretched counterflow premixed and diffusion flames are studied, with emphasis on the separate and combined Soret effects of n-heptane and species H₂ and H resulted from the decomposition of n-heptane, as well as those of the major species O₂, N₂, CO₂ and H₂O. Results show that, in the unstretched case for which the flame temperature remains at its adiabatic value, Soret diffusion primarily affects the chemical kinetics embedded in the flame structure and the net effect is small; while in the stretched cases, its impact is mainly through those of n-heptane and the secondary fuel, H₂, in modifying the flame
temperature, with substantial effects. Furthermore, H₂ and H also affect the chemical
kinetics especially when the active reaction zone is localized. The dilution/enrichment of
the reactant concentrations in the flame through the Soret diffusion of the major species
O₂, N₂, CO₂ and H₂O further exert finite effects on the flame burning intensity.
Acknowledgements

It is pleasant at this stage to look back on my journey in Princeton and how I have matured over the past seven years. At this rewarding time, I would like to express my gratitude to all those who have guided, helped and encouraged me along the way.

The first person I wish to express my gratitude to is my advisor, Professor Chung K. Law. He has not only taught me almost every piece of knowledge that I know about combustion, but he has also educated me on how to think properly. I sincerely appreciate his great mentorship, which has nourished my intellectual growth, sharpened my personality and will undoubtedly influence me for my entire life.

In addition to my advisor, I have also been fortunate to receive advice and assistance from a number of fabulous scholars. Professor Hai Wang of Stanford University guided me on the kinetic study of the catalytic hydrocarbon oxidation and model development, which constitute the major components of this dissertation. Professor Tianfeng Lu of the University of Connecticut introduced me to academic life and took care of me as his younger brother in more personal matters. Dr. Jacqueline H. Chen of the Sandia National Laboratories offered me the great opportunity to conduct the state-of-the-art direct numerical simulation and shared her expertise throughout my time as a graduate student. Last but not least, like every student graduating from Law’s group, I owe a big “thank you” to Mr. Delin Zhu, who built my facility from scratch and supported all my experimental studies.
I have also collaborated with many outstanding researchers during my Ph. D. program. Without their helps, I would not have been able to accomplish this dissertation. They include Professor Chih-Jen Sung, University of Connecticut; Professor Chunsang Yoo, Ulsan National Institute of Science and Technology; Dr. Nan Yao, the director of the PRISM Imaging and Analysis Center at Princeton University; Professor Taichang Zhang, Chinese Academy of Sciences; Professor Bin Yang, Tsinghua University, Dr. David Sheen, National Institute of Standards and Technology, and Professor Zhuyin Ren, Tsinghua University.

I appreciate the precious opportunity to pursue my Ph.D. degree in the MAE department of Princeton, and I would like to thank all the faculty members of the department, from whom I have been learning throughout the years. Particularly, I am grateful to Professors Yiguang Ju and Alexander Smits for serving as my committee members and providing support and assistance in my academic growth. I would also like to thank Professor Frederick L. Dryer for the invaluable discussions, and Professor Michael Mueller for reviewing this dissertation and offering many helpful comments which have greatly improved its presentation.

I am grateful to have the following fantastic colleagues as my lab-mates in Professor Law’s group: Sili Deng, Andrew Kelley, Jeremy Koch, Wenkai Liang, Wei Liu, Samuel Nackman, Xiaoyu Tang, Fujia Wu, Sheng Yang, Peng Zhang and Peng Zhao; V’yacheslav Akkerman, Swetaprovo Chaudhuri, Abhishek Saha, Andrew Smallbone,
Hongyan Sun; Shuiqing Li and Yun Huang, Yuyang Li, Jiaying Pan, Chenglong Tang, Hui Wang, Yao Wang, Ning Wu, Taichang Zhang and Xin Hong; and in Professor Hai Wang’s group: Joaquin Camacho, Dexing Du, Shaokai Gao, Sydnie Lieb, Shaodong Niu Yujie Tao, and Erik Tolmachoff. Their friendship will be a treasure for my family forever.

I want to specially thank my parents for their love and support, the energy source for my journey across half of the earth. I reserve my most heartfelt expression of gratitude to my wife, Shanshan Ming, the partner of my life journey. With you, good times, hard times, but never bad times.

This research was supported by the Air Force Office of Scientific Research through a MURI program on Nano-catalysts in Propulsion under the technical monitoring of Dr. Michael R. Berman. This dissertation carries the number of 3263-T in the records of the Department of Mechanical and Aerospace Engineering.
Contents

Abstract ......................................................................................................................................... iii
Acknowledgements ................................................................................................................ viii
Contents ........................................................................................................................................ xi
Chapter 1 Introduction .................................................................................................................. 1

1.1 Catalytic Combustion of Light Hydrocarbons ................................................................. 4
    1.1.1 Utilization of Natural Gas by Catalytic Combustion .............................................. 4
    1.1.2 Kinetic Study on Catalytic Combustion of Light Hydrocarbons ....................... 6
    1.1.3 Catalytic Combustion Assisted by Freely Suspended Nanoparticles ................. 8
    1.1.4 Research Methodology and Outline of Part I ....................................................... 10

1.2 Numerical Studies on Fundamental Combustion ............................................................ 12
    1.2.1 Direct Numerical Simulation of Self-accelerating Hydrogen-air Flame .......... 12
    1.2.2 Optimized Model Reduction Strategy ................................................................. 15
    1.2.3 Reduced Maxwell-Stefan Diffusion Model ......................................................... 16
    1.2.4 Thermal Diffusion in n-heptane-air Flames ....................................................... 18

1.3 List of Publications ........................................................................................................ 19

References ............................................................................................................................. 21

Chapter 2 Experimental Setup and Computational Configuration ......................................... 29

2.1 Experimental Setup .......................................................................................................... 29
    2.1.1 Wire Microcalorimetry ...................................................................................... 29
    2.1.2 Mass Spectrometry ......................................................................................... 30

2.2 Computational Configuration .......................................................................................... 31
    2.2.1 Specifics of Computation ............................................................................... 31
    2.2.2 Validation of Flow Model .............................................................................. 33
7.3 Methodology for Multicomponent Diffusion Reduction

7.3.1 Review of the multicomponent diffusion model

7.3.2 A reduced multicomponent diffusion model

7.3.3 Species bundling for further reduction

7.3.4 Correction of the diffusive velocity

7.4 Implementation of RM Model in Heptane-Air Flames

7.4.1 Identification of the Reduced Multicomponent Model

7.4.2 Validation of the Reduced Multicomponent Model

7.5 Conclusions

References

Table and Figures

Chapter 8 A Mechanistic Evaluation of Soret Diffusion in Heptane/Air Flames

8.1 Introduction

8.2 Specification of Flames

8.3 Unstretched Planar Premixed Flames

8.4 Counterflow Premixed Flames

8.5 Counterflow Diffusion Flames

8.6 Conclusions

References

Figures

Chapter 9 Summary and Future Work

9.1 Summary

9.2 Future Work

References
Chapter 1 Introduction

The utilization of fire was a milestone in the evolution of the human race. The brain of the *Homo erectus* was nourished by the cooked food, allowing man to occupy the highest link of the biological chain. The second major development in the peaceful use of fire for the service of mankind is that associated with the industrial revolution. At present, over 80% of the world’s energy need is met by a variety of combustion devices [1], such as the reciprocating internal combustion engines, gas turbines and burners, with each burning its own kind of fuel.

To make the burning stronger, and the fire cracker louder and brighter, the human tinkerer has conducted and conceptualized endless real and thought experiments. In recent decades such “combustion research” has evolved from one largely based on empirical observation to a rigorous scientific discipline. Currently laser-based diagnostics and advanced numerical simulations are routinely used to acquire the knowledge of complex combustion systems involving wide ranges of time and length scales; equally important, the theoretical framework of combustion science is now elegantly anchored in the foundations of fluid mechanics and fuel chemistry. Combining the efforts of experimental, simulation and theoretical studies, combustion scenarios can be well interpreted from fundamental physical principles. Consequently, we are living in an era in which the study of combustion has the most potential to flourish.
It is therefore an entirely fortunate development that this empowerment of combustion knowledge is now taking place when it is needed the most – to tackle the twin challenges of energy sustainability and environmental degradation that threaten the smooth functioning of the modern society. To wit, the matrix of fuel supply is expected to drastically change in that the anticipated depletion of the crude petroleum oil reserve in the next decades will lead to the corresponding emergence of other forms of fuels such as natural gas, coal, and the various biofuels [2]. Furthermore, the average global temperature has been rising steadily since the early 19th century, coinciding with the start of large scale energy generation through the burning of fossil fuels, which is indisputably the source of anthropogenic greenhouse gas emissions [3]. Consequently, the development of combustion technologies, for more efficient and cleaner energy production, constitutes an immense challenge for the human society.

Based on the above considerations, an appropriate goal for frontier combustion research needs to satisfy two criteria: namely it has to be novel and it has to be deep. The first criterion calls for studies on non-petroleum fuels and novel combustion processes, while the second criterion demands the comprehensive and profound understanding of combustion for better control.

Having been stimulated by the above considerations, the writer of this thesis commenced his dissertation research with the following goals: be broad, be deep, be novel, and be useful. This is a tall order to fill, yet the chase has been fun and fulfilling.
In order to accomplish the goal of breadth, he has tackled several problems which, while generally considered to be within the realm of combustion, are quite phenomenologically diverse, and require different scientific tools for investigation. The goal of depth is a must, and its attainment is supported by publications in leading journals. The goals of novelty and usefulness are somewhat subjective, and are perhaps to be judged by the extent of follow-on work in the future.

In order to account for the topical breadth of the problems investigated, the dissertation is divided into two parts. Specifically, Part I, consisting of Chapters 2 to 4, is an extensive undertaking to investigate the chemical kinetics of light hydrocarbon combustion over unsupported Pd-based catalyst, serving as a novel system to facilitate ignition of lean and/or hard-to-ignite mixtures. Part II consists of several topics covering a diverse arena in fundamental combustion, namely the self-acceleration of flames due to the continuous generation of cell over its surface as a consequence of inherent flamefront instabilities, in Chapter 5; the systematic reduction of complex reaction mechanisms and the associated uncertainty analysis, in Chapter 6; the systematic reduction of multicomponent diffusion coefficients in gas mixtures, in Chapter 7 and a mechanistic evaluation of the influence of Soret diffusion in flames, in Chapter 8.

Essence of the above components will be briefly introduced in the following sections, and reported in detail in the rest of the dissertation.
1.1 Catalytic Combustion of Light Hydrocarbons

Natural gas is a mixture of hydrocarbons, which mainly consists of methane, ethane, propane and ethylene, referred to as the light hydrocarbons within the scope of this dissertation. Natural gas is a desirable source of energy because of its abundant reserve and clean burning. For the utilization of natural gas, Part I investigates the catalytic combustion of light hydrocarbons, as briefly introduced in this section. Section 1.1.1 first compares the approaches to generate energy from natural gas, thermal combustion and catalytic combustion, and then presents the advantages of catalytic combustion such as low operation temperature and operation flexibility. Afterward, Section 1.1.2 reviews the literature on the catalytic combustion of light hydrocarbons with the emphasis on supported catalysts, and indicates the shortcomings of supported catalysts such as transport limitation and stability of the catalyst. These problems may be resolved by adopting freely suspended nanoparticles in catalytic combustion, as discussed in Section 1.1.3. Therefore, Part I conducts fundamental studies for this novel process by the research methodology described in Section 1.1.4.

1.1.1 Utilization of Natural Gas by Catalytic Combustion

On average, light hydrocarbons account for more than 98% effective component of natural gas by volume, and methane accounts for about 95% effective component of natural gas by volume [4]. Therefore properties of natural gas are largely determined by that of methane. Methane is a tetrahedral molecule with four equivalent C–H bonds and
only one carbon atom. Since methane has the smallest C/H ratio compared with other hydrocarbons, it has the lowest carbon dioxide emission as per unit energy released, implying that natural gas burns more cleanly than other fuels. On the other hand, the symmetrical structure of methane leads to strong C–H bond with the bond dissociation energy (BDE) of 104 kcal mol⁻¹[5], which precludes the homogeneous oxidation of methane at low temperatures. Consequently, most current power plants using natural gas employ thermal combustion within the temperature range of 1,500 to 2,000 °C [6, 7]. The high operating temperature significantly enhances the formation of oxides of nitrogen, which are undesirable byproducts. Consequently, much effort has been extended to reduce the temperature of methane oxidation, and catalytic combustion has been demonstrated to be a promising solution [6, 7].

Historically, Sir Humphry Davy published the first scientific paper of catalytic combustion in 1817 [8], which reported the work on the combustion of coal gas enhanced by preheated platinum wires. Currently, catalytic combustion is widely adopted in numerous applications, such as gas turbines, aircraft afterburners, domestic heaters and exhausted-gas treatment for automobiles [9-11]. The contemporary concept of catalytic combustion was described by Pfefferle [12], and the differences between catalytic combustion and thermal combustion were reviewed in [13, 14], indicating several advantages of catalytic combustion. First, catalytic combustion is typically operated below 1300 K, and hence reduces NOₓ emission substantially. Second, catalytic
combustion can be carried out over a wider range of temperatures and fuel/air ratios. Consequently, catalytic combustors are robust to the fluctuation of operation temperature and feed composition, which are liable to cause unstable flames in thermal combustors. However, catalytic combustion involves complex surface reactions of hydrocarbon oxidation, requiring a large number of kinetic studies, as reviewed in the next section.

1.1.2 Kinetic Study on Catalytic Combustion of Light Hydrocarbons

The kinetic study on the catalytic combustion of light hydrocarbons has been well reviewed [5, 15-21]. The investigated catalysts include both noble metals, such as Pt, Pd and Rh, and metal oxides, such as Co3O4, CuO, Mn2O3 and Cr2O3. Among the different catalysts, Pt generally has the highest activity for all the hydrocarbons except methane, whose combustion is facilitated the most by Pd. These observations can be explained by the Sabatier principle [22]: the catalyst-oxygen bond should be “just right”, neither too weak nor too strong. On one hand, a weak catalyst-oxygen bond cannot bind enough oxygen on the catalytic surface and hence cannot result in significant number of reactions. On the other hand, a strong catalyst-oxygen bond will induce oxygen to block surface sites, which prevents the adsorption of hydrocarbons and reduces the activity of the catalysts as well.

Pd-based catalysts have been the subject of many investigations, as reviewed in [16, 23-27], and they fall into two categories, specifically unsupported and supported.
The unsupported catalysts only include the active component of Pd material in the form of wire and foil of the size above millimeters, while the supported catalysts are prepared by dispersing Pd particles, with a diameter of a few to hundreds nanometers, on the surface of the supports, e.g., Al₂O₃ and ZrO₂. The supported Pd-based catalysts offer larger surface-to-volume ratio but has several problems for adoption in practical applications. First, the activity of supported Pd-based catalysts can hardly be predicted because it is determined by the micro-structure of the local Pd nanoparticles, which is sensitive to the interaction with supports and cannot be well controlled at the molecular level.

Consequently, the design of supported Pd-based catalysts is an empirical practice. In addition, the performance of supported Pd-based catalysts is also subject to other factors in combustion applications [7, 23, 27], such as transport limitation and stability of the catalyst. Specifically, when catalytic combustion occurs above 800 K, the rate of combustion is usually limited by the gas-phase transport of fuel and air to the catalyst surface. For applications above 1000 K, thermal stability of supported catalysts becomes a serious problem. The high temperature and oxidative environment attacks the weak binding between the Pd nanoparticles and the support, and hence may destroy the mechanical structure and reduce the chemical activity of the catalyst. To solve the limitations of supported catalysts, the use of freely suspended nanoparticles are proposed for catalytic combustion, which is discussed in the next section.
1.1.3 Catalytic Combustion Assisted by Freely Suspended Nanoparticles

Recently, there is increasing interest in applying freely suspended nanoparticles in catalytic combustion, with the nanoparticle diameter ranging from a few to tens of nanometers. This concept was originally proposed to overcome the ignition difficulty in hypersonic flight, in which the residence time within the combustor can be as short as a few milliseconds and hence cannot be satisfied by the homogeneous ignition of hydrocarbons. By injecting freely suspended nanoparticles into the combustor, catalytic combustion can be initialized at low temperatures. The corresponding heat generation increases the system temperature and shortens the ignition delay of combustion. Flow reactor experiments and simulation studies [28, 29] have shown that the inclusion of Pd nanoparticles can reduce the ignition delay of stoichiometric methane-air mixtures up to two orders of magnitude.

Freely suspended nanoparticles hold substantial potential to solve the problems of supported catalysts. First, the activity of freely suspended nanoparticles is easier to be predicted and controlled because they do not involve the complex interaction with supports. Moreover, freely suspended nanoparticles do not have transport limiting and stability issue. The reaction rate over freely suspended nanoparticles is solely determined by surface kinetics, without complications from the gas-phase transport, because the diameter of freely suspended nanoparticles is substantially smaller than the mean free path of the gas molecules. Furthermore, since freely suspended nanoparticles avoid
support-particle binding, they are resistant to high temperature and oxidative environments.

Catalytic combustion assisted by freely suspended nanoparticles has a promising future but is rarely studied at present. Consequently, I have conducted fundamental studies on this novel process, more specifically, on the combustion of light hydrocarbons assisted by Pd-based catalysts. Historically, pioneered by Kemball and Patterson in the early 1960s [30], the oxidation of light hydrocarbons over Pd wires [31-33] and foils [30, 34-35] have been examined for decades. There is general agreement that, under fuel lean conditions, the oxidation rate is first-order with respect to the fuel concentration, suggesting the adsorption of hydrocarbon as the rate-limiting step. This hypothesis is confirmed by subsequent studies using advanced surface detection techniques [36-38], which further reveals the details of hydrocarbon adsorption. Specifically, during the adsorption process, a hydrocarbon molecule breaks a C–H bond through the interaction with surface oxygen, and the remaining fragment occupies the active site of the Pd surface. The rate coefficient of hydrocarbon adsorption is crucial to model the combustion of light hydrocarbons over Pd-based catalysts as the rate-limiting step, but it has not been quantitatively studied over the temperature range of combustion interests at present. Although several theoretical studies of density functional theory (DFT) have been employed for this issue [39-47], these calculation results must be properly verified against the experimental data. Therefore, Part I of this dissertation is devoted to
quantifying the rate coefficient of hydrocarbon adsorption from experimental measurements and numerical simulations, by the research methodology introduced in the next section.

1.1.4 Research Methodology and Outline of Part I

Part I proposes a detailed kinetic model for the combustion of light hydrocarbons over unsupported Pd-based catalysts for experimental and computational studies. For the experimental study, the method of wire microcalorimetry is employed to quantify the rate of surface reactions from the corresponding heat generation rate, which has been widely employed in surface kinetic studies [30-31, 48-49]. For the computational study, the wire microcalorimetry is simulated by using a Computational Fluid Dynamics (CFD) code with detailed gas-surface kinetic model developed in this dissertation. The rate coefficient of each elementary reaction in the kinetic model is independently verified by experimental observations or ab initio calculations.

Part I consists of three chapters. Chapter 2 introduces the research methodology, and Chapters 3 and 4 present the kinetic studies on methane and the C2-C3 hydrocarbons, respectively. Chapter 2 first presents the experimental specifications of wire microcalorimetry as well as the configuration for the numerical simulation, and then illustrates the physical morphology and chemical composition of the catalyst surface, detected with Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM),
and X-ray Photoelectron Spectroscopy (XPS). In Chapter 3, the reaction rates of methane combustion over Pd-based catalysts are measured by wire microcalorimetry at different surface temperatures and methane concentrations, yielding the global kinetic parameters of unity reaction order in methane concentration and the apparent activation energy. The catalytic combustion of methane is simulated at the same conditions as the experiment, and the rate coefficient of methane adsorption is determined from the comparison between the experimental observation and simulation results. Chapter 4 extends the similar strategy of kinetic study from methane to C₂-C₃ hydrocarbons. The combustion rates of these heavier hydrocarbons are measured by wire microcalorimetry, from which the global kinetic parameters are extracted. For each hydrocarbon fuel, the rate coefficient of hydrocarbon adsorption is identified from the experimental data and numerical simulations. As a major achievement of Part I, a detailed kinetics model has been developed for the combustion of light hydrocarbons over unsupported Pd-based catalysts. This model provides an intrinsic and comprehensive description of the elementary surface processes, and as such it does not require parameter-tuning for specific simulations and can be employed in a wide range of CFD applications with high fidelity.
1.2 Numerical Studies on Fundamental Combustion

Part II adopts state-of-the-art detailed simulations to study the fundamental aspects of combustion scenarios. The fluid dynamics is simulated with the compressible Navier-Stokes equations. The chemistry is described by detailed mechanisms, which consist of elementary reactions of hydrocarbon oxidation. Diffusion is characterized by the Maxwell-Stefan multicomponent model, which considers the interaction between every species as well as the mass diffusion caused by the temperature gradient, i.e., thermal diffusion. These detailed simulations, obtained with substantial computation cost, have generated a large amount of information from which useful physical insights have been extracted, as reported in Chapters 5 and 8 on the impact of hydrodynamic instability and thermal diffusion on the fine structure of flames. In addition, we have also proposed strategies to reduce the cost of these detailed simulations in terms of chemistry and multicomponent diffusion, which will be reported in Chapters 6 and 7.

1.2.1 Direct Numerical Simulation of Self-accelerating Hydrogen-air Flame

When a spherical flame radially propagates outward in a uniform and quiescent reactive mixture, the density difference across the flame front generates hydrodynamic instability [5]. Accordingly, the flame surface becomes wrinkled and possesses more area per unit volume, and the flame burns stronger and propagates faster. This flame is therefore self-accelerating. From experimental observations, Gostintsev et al. [50] recorded the evolution of flame radii with time and correlated them by a power law with an exponent
of 1.5, which is defined as the acceleration factor. Moreover, they hypothesized that the wrinkled flame had a fractal character, and, based on the acceleration factor of 1.5, they estimated the flame fractal excess, i.e., the fractional portion of fractal dimension, as 0.33. This number is intriguing because the Kolmogorov turbulence has been demonstrated to have a fractal excess of 0.33 as well [51-52]. This implies the possible occurrence of self-turbulization, which has prompted numerous further experimental and numerical studies [53-70]. The experimental studies measured the acceleration factors of flame propagations in different reactive mixtures and pressures, with reported results scattered in a broad range of 1.1 to 1.5 [53-59]. The numerical studies simulated self-accelerating flames and resolved flame fronts to investigate the fractal structures. These simulations adopted the Sivashinsky equation [60-67], potential flow model [68] and level-set formulation [69], which are simplified models, compared to DNS with detailed chemistry mechanisms. Although these studies reported fractal-like patterns generally, the involved approximations lower the simulation fidelity inevitably. It is important to caution that in practically all these investigations there were considerable latitude and uncertainty in the exponent determined, some of them ostensibly motivated by the goal to demonstrate the specific exponent of 1.5. Consequently, a definitive investigation of the possible existence of the fractal structure of self-accelerating flames has not been conducted. This dissertation therefore attempts to bring closure to this question by state-of-the-art numerical simulation, which performs DNS with detailed chemistry and diffusion to
simulate self-accelerating flames. Mixtures of hydrogen and air are used because of the relative simplicity and fidelity of the reaction mechanism.

DNS is widely adopted in turbulence simulations by numerically solving the Navier-Stokes equations without any turbulence model, and as such resolving the entire range of spatial and temporal scales. The foundations of DNS were laid at the National Center for Atmospheric Research [71]; a short review of the history of DNS is given in [72]. For the combustion community, with the development of high performance computation, DNS has been advanced in pursuing critical information of turbulence combustions, as reviewed in [73-76].

In the present study flame propagation in the stoichiometric hydrogen-air mixture is simulated in the two dimensional domain in Chapter 5. The compressible Navier-Stokes equations, species equations and energy equation were solved with the advanced numerical scheme and small grid size and short time step, while the chemistry of hydrogen combustion is described by the well-validated mechanism developed by Li et al. [77]. From the simulation results, we identify the flame front by contours of species concentration and extract the flame radius and propagation velocity accordingly. It will be shown that the flame propagation is intermittent in nature, while the flame front is demonstrated to have a fractal character.
1.2.2 Optimized Model Reduction Strategy

Detailed chemistry models are required to describe complex and nonlinear combustion processes, e.g., the Z-shaped explosion limit of hydrogen-air flames and the negative temperature coefficient (NTC) in the auto-ignition of hydrocarbons. Detailed models have been developed for many combustion systems, as reviewed in [78-85]. The establishment of a detailed chemistry model involves compiling a set of elementary reactions and determining reaction rate coefficients from experimental measurements, theoretical calculations or estimates from analogous reactions. Furthermore, the rate coefficients of detailed models are always optimized to better reproduce the data from experiments.

Detailed models of practical fuel molecules are usually sizable, in the order of hundreds to thousands of species and thousands to tens of thousands of reactions [86]. They are however rarely utilized, or even utilizable, in large-scale CFD simulations because of the prohibitive computational cost. Consequently, detailed models must be properly reduced [86], and different strategies have been proposed to do so [87-108]. Model reduction strategies can be characterized in two categories: skeletal reduction to eliminate unimportant species and time scale analysis to eliminate species of short time scales. The current model reduction strategies do not compensate the accuracy loss of reduced model caused by reduction. Therefore, as more species are eliminated during the reduction process, the accuracy of the reduced model correspondingly decreases. The
reduction terminates when the accuracy of reduced model reaches a user-specified threshold value, constituting the minimum size of the reduced model.

To generate reduced models of good accuracy and smaller sizes, this dissertation proposes to compensate the accuracy loss due to reduction by optimizing the reduced models. As a prototype study, this strategy is applied to the detailed model of USC Mech II [109] for butane combustion. The reduced model is first determined by the Directed Relation Graph (DRG) [93] and DRG-Aided Sensitivity Analysis (DRGASA) [97] algorithms, and is then optimized by using the Model Uncertainty Minimization-Polynomial Chaos Expansion (MCM-PCE) [110]. Significant improvement in the performance of reduced models is demonstrated.

### 1.2.3 Reduced Maxwell-Stefan Diffusion Model

In mixtures of multiple components, mass diffusion is caused by collisions between different molecules. Therefore, rigorous modeling of diffusion coefficients must consider interactions between each species pair, such as the Maxwell-Stefan model derived by Curtiss and Hirschfelder [111] from the Boltzmann equation. For an $N$ component mixture, the Maxwell-Stefan model represents interactions of species by a diffusion matrix of dimension $N$, and calculates the diffusion coefficients from matrix inversion. This model has great accuracy and ensures mass conservation, and hence it is desired for high-fidelity combustion simulations [112-123]. However, this model requires prohibitive
computational expense because the cost of exact matrix inversion scales cubically with the matrix dimension. As such, Chapter 7 develops a strategy to reduce the cost of the Maxwell-Stefan model; the rationale is briefly discussed next.

We first note that flames are considered to be sensitive to the diffusivity of only a few species, which are termed as critical-diffusivity species. They include species of large concentrations and several highly reactive radicals that dominate the diffusion process and participate in crucial reactions. The diffusion coefficients of these species are calculated by the reduced Maxwell-Stefan model, which applies the Maxwell-Stefan model to the system of only critical-diffusivity species. Since the number of critical-diffusivity species is less than the number of species in the original multicomponent mixture, the reduced Maxwell-Stefan model involves less expensive matrix inversion operations and hence achieves significant computational saving. In the prototype study of \( n \)-heptane-air mixtures of 88 species, Chapter 7 simulates the propagation of planar premixed flames, the extinction of counterflow diffusion flames, and the ignition of droplet flames with various diffusion models of the Maxwell-Stefan model, the mixture-averaged model and the reduced Maxwell-Stefan model. The mixture-averaged model leads to noticeable deviations at conditions of elevated pressure and large strain rate, while the reduced Maxwell-Stefan model achieves the accuracy close to that of the Maxwell-Stefan model with reducing the computational cost by a factor of approximately five in all cases.
1.2.4 Thermal Diffusion in \textit{n}-heptane-air Flames

Thermal diffusion, which describes mass diffusion caused by a temperature gradient, was first observed by Carl Ludwig in 1856 [124] and named after Charles Soret for the first explanation on this phenomenon in 1879 [125]. The Soret effect causes species of small molecular weights to diffuse towards high temperature regions, and species of large molecular weights to diffuse towards low-temperature regions. Soret diffusion could potential modify the concentrations and consequently processes related to them of species of extreme molecular weights such as those in hydrogen and sooting flames [112-128], but is believed to be unimportant in other cases. However, from the study of thermal diffusion in \textit{n}-heptane-air flames in Chapter 8, the Soret effect is shown to present notable influences in combustion systems in general.

For \textit{n}-heptane-air mixtures, propagation of planar premixed flames and the extinction of counterflow flames are simulated in Chapter 8, with and without activating thermal diffusion. Simulation results show that, while Soret diffusion has negligible impact on unstretched planar flames, it becomes significant in stretched counterflow flames. For the burning intensity of flames, the Soret effect perturbs the flame speed of planar flames by 1%, while it can change the extinction strain rate of counterflow flames by up to 20%. For the detailed flame structure, the Soret effect is identified to influence the flame temperature and chemical kinetics through two mechanisms. First, in concert with flame stretch, Soret diffusion affects the diffusive flux of \textit{n}-heptane, thereby the
total energy entering flames, which is represented by the flame temperature. Second, Soret diffusion alters the diffusive flux of H radicals and thereby the rates of crucial chain-branching reactions. In general, the first effect has a stronger impact since the flame temperature is of leading-order importance in the flame response. This effect is absent in unstretched planar flames, for which the flame temperatures is decoupled from the diffusion flux of species. This therefore explains the small influence of Soret diffusion on planar flames.

1.3 List of Publications

A good part of the dissertation research have been either published or submitted for publication. The materials contained in them are distributed in the dissertation, as follows.


References


Part I

Kinetics of Catalytic Oxidation of Hydrocarbons
Chapter 2 Experimental Setup and Computational Configuration

2.1 Experimental Setup

2.1.1 Wire Microcalorimetry

Chapter 2 specifies the experimental setup and computational configuration for the study of hydrocarbon oxidation over Pd-based catalyst, followed by the analysis revealing the physical morphology and chemical component of catalytic surface. In this dissertation, wire microcalorimetry [1-7] identifies the rate of surface reaction by measuring the heat release rate. A metallic wire of the catalytic material, specifically a palladium wire 10 cm in length and 0.1 mm in diameter (99.99%, Aldrich), forms the essential component of wire microcalorimetry. Mechanically, the wire is suspended in a closed chamber by two copper columns and connected to direct current (DC) electrical power. For a given gas-phase composition, wire microcalorimetry places the wire in a steady, low-speed gas flow in the cross-stream orientation. By passing an electric current through it, the wire is heated and its temperature \( T \) is determined through a balance between Joule heat generation and heat loss due to radiation, conduction, and convection to the gas stream. Therefore by passing a certain current \( I \) through the wire and also by measuring its resistance \( R \), the power required to maintain the wire at temperature \( T \) as \( P = I^2 R \) can be evaluated, with \( T \) simultaneously determined by the property relation \( R(T) \) [8].

Figure 2-1 illustrates the methodology of wire microcalorimetry. The wire is first
heated up in a non-reactive gas such as nitrogen to a certain temperature. When the system reaches steady state, the power input compensates the heat loss from the wire to the environment, and is recorded as the reference value. Afterwards, the test reactive mixture is introduced in the chamber, and the wire is heated to the same temperature, resulting in the same amount of heat loss. However, the occurrence of surface reaction diminishes the demanding of power input, while the difference in these cases quantifies the heat release rate ($\Delta P$) of the surface reaction, which is further converted to the reaction rate by considering the corresponding enthalpy change.

2.1.2 Mass Spectrometry
The concentrations of gas-phase species around the Pd wire are analyzed by an electron ionization mass spectrometer, as shown in Fig. 2-2. The apparatus consists of the wire microcalorimetry chamber, a three-stage differentially pumped sampling system, and an RGA 300 mass spectrometer. The gaseous sample close to the Pd wire (2 mm) is withdrawn through a nozzle 0.1 mm in diameter and a 10-cm long inlet tube. The gases exit the inlet tube then expand into the first differential region, and the central part of the expansion is collimated by a skimmer (1 mm diameter orifice), passing through the open grids of the mass spectrometer ion source as a molecular beam, and finally passing into a turbomolecular pump. The pressure is around $1, 2\times10^{-3}$ and $10^{-7}$ Torr in the three pumping stages with the mass spectrometer housed in the last stage. All mass spectrometric analyses are carried out with the use of a 70 eV electron energy, and an
electron multiplier gain of 1000. The resolution ($\Delta m = 10\%$) is 1 amu, and the minimum detectable partial pressure is around $10^{-11}$ Torr.

2.2 Computational Configuration

2.2.1 Specifics of Computation

The experiment of wire microcalorimetry involves a weakly buoyant flow field, which is sufficiently simple and well defined. The simulation was performed by using the commercial software package FLUENT with detailed gas-surface kinetic models, to determine the surface heat release rate of a horizontal cylinder maintained at a given temperature. Figure 2-3 presents the schematic of the computational domain. In particular, since the ratio of the wire length to its diameter is large, the flow around the heated wire can be approximated as a 2D natural convection problem. Furthermore, because of symmetry, only half of the cylinder was simulated. The mesh was created by the software GAMBIT, with a maximum cell squish index of 0.13. Quadrilateral instead of triangle meshes were used for increased accuracy with fewer cells. The area external to the cylinder covering the bulk flow was also resolved with fine meshes because of the importance and complication of the flow around the cylinder. The laminar, viscous flow was solved using pressure-based solver at steady-state conditions. Radiation was not considered because the highest wire temperature was less than 800 K and the wire was very thin. For pressure–velocity coupling, the SIMPLE (Semi-Implicit Method for Pressure Linked Equations) algorithm [9] was used. The discretization scheme was least squares cell based for the gradient, standard for the pressure, and second order upwind for
the momentum, energy and species concentrations. Since the velocity in the present natural convection flow is very low, the residue values for continuity and momentum were taken as $10^{-6}$ while that for energy as $10^{-10}$. The boundary conditions are as follows: the cylinder was defined as a wall with the surface reaction mechanism at constant temperature; bottom, top and side surfaces were defined as the pressure-inlet type and taken as equal to the ambient temperature; the mole fraction of each component in the fuel/air mixture was defined as constant at bottom, top and side surfaces, with ignoring the concentrations of combustion products at boundaries. The height of the mesh domain was twice its width. With increasing width of the mesh, the influence of the mesh domain on the heat flux rate of the cylinder was studied. The result shows that the heat flux rate becomes independent of the domain size when the ratio of the domain width and cylinder diameter is larger than 60. Thus the ratio was set at 70. Gas phase chemistry is generally unimportant for the present experiments, but its effect is nevertheless considered in the detailed simulation. The reaction model is described by the 111-species and 784-reaction USC Mech II [10]. The surface kinetic model is developed in the following chapters of this dissertation. The thermodynamic and transport properties of the gas-phase and surface species are taken from Ref. [11] and derived from the vibrational frequencies of surface species [12, 13].
2.2.2 Validation of Flow Model

The model without considering surface reaction was validated by the relation of Rayleigh number \( (Ra) \) and Nusselt number \( (Nu) \).

\[
Ra = Gr Pr = \frac{g \beta}{\nu \alpha} (T_s - T_\infty) D^3
\]

\[
Nu = \frac{hD}{\kappa} = \frac{q}{A\Delta T} \frac{D}{\kappa}
\]

where, \( Gr \) is the Grashof number, \( Pr \) the Prandtl number, \( g \) the gravitational acceleration, \( \beta \) the thermal expansion coefficient, \( \nu \) the kinetic viscosity, \( \alpha \) the thermal diffusivity, \( T_s \) the surface temperature, \( T_\infty \) the environment temperature, \( D \) the diameter of the cylinder, \( h \) the convective heat transfer coefficient, \( \kappa \) the thermal conductivity, \( q \) the heat flow, \( A \) the heat transfer surface area, and \( \Delta T \) the difference in temperature of the wire surface and ambient gas. The fluid properties \( Pr, \beta, \nu, \alpha \) and \( \kappa \) were evaluated at the film temperature \( (T_f) \), which is defined as \( T_f = (T_s + T_\infty)/2 \). In our case, \( T_\infty \) is the room temperature, and \( T_s \) varies in the range of 500-1200 K. Correspondingly, \( Ra \) is in the range of \( 1.5 \times 10^{-3} \) to \( 5 \times 10^{-3} \), implying low Rayleigh number flows. The ratio \( q/A \) was calculated, from which \( Nu \) was determined.

As shown in Fig. 2-4, the black blocks represent the calculated relation between \( Ra \) and \( Nu \), while the red circles and blue triangles denote the relation of \( Ra \) and \( Nu \) calculated by using the following two expressions for free-convection heat transfer [14],
\[ Nu^{0.5} = 0.6 + \frac{0.39Ra^{0.16}}{1 + (0.56 \cdot Pr)^{0.29}} \quad 10^{-5} \leq Ra \leq 10^{12} \quad (2-2a) \]

\[ Nu = 0.675Ra^{0.052} \quad 10^{-10} \leq Ra \leq 10^{-2} \quad (2-2b) \]

It is seen that the values determined by the calculation are consistent with those given by the correlations, hence substantiating the adequacy of the computational simulation. It is noted that since the two correlations were obtained by fitting the experimental data in different ranges, they do not overlap in their respective ranges of correlation.

2.3 Surface Characterization

In an oxidizing environment at the temperature of interest, the oxidized state of Pd is thermodynamically favored the metallic phase [15]. The oxidation process leads to a significant change in the morphology and composition of the wire surface. To conduct our experiment in a reproducible manner, the Pd wire was pretreated with a standard procedure [16] that led to the formation of a stable PdO layer at the wire surface. In this procedure, the wire was heated first at 900 K in N2 for one hour and then exposed to a 2% CH4/air mixture for another hour. The surface composition and morphology of the treated wire was probed by Scanning Electron Microscopy (SEM) and X-ray Photoelectron Spectroscopy (XPS). The SEM analysis was carried out using a XL300 FEG SEM, and the XPS measurement was accomplished with a VG Scientific ESCALAB MKII, showing a 1~2 μm, porous PdO layer over the bulk polycrystalline Pd in Fig. 2-5. By
analyzing the SEM pore image in Fig. 2-6, the pore size is distributed log-normally and has a median radius $\langle r \rangle = \sim 0.5 \, \mu m$, geometric standard deviation of 1.62 and length $L = 10 \, \mu m$. The number density of the pore is approximately $0.1 \, \mu m^{-2}$. The actual wire surface differs from the smooth cylinder assumed in the simulation, yielding the large surface area. The specific surface area ratio will be quantified in the kinetic study of CH$_4$ catalytic combustion in Chapter 3.
References

**Figure 2-1.** Principle of wire microcalorimetry. Symbols are experimental data; lines are drawn to guide the eye. The difference in the power input $p$ with and without methane is directly proportional to the surface heat release rate.
Figure 2-2. Schematic diagram of the experimental setup with the RGA 300 mass spectrometer. Region I, II and III are the three-stage differentially pumped chambers. The RGA 300 mass spectrometer is stalled in the chamber III.
Figure 2-3. Schematic of the computational domain. Boundary conditions: $T = 300$ K, $P = 1$ atm and fresh reactant mixture.
Figure 2-4. Dependence of $Nu$ on $Ra$ given by expressions in the literature and determined through the present simulation.

\[
Nu = 0.675 + 0.058 
\]

\[
Nu = 0.6 + 0.387 \{Ra/[1+(0.559/Pr)^{0.56}]^{1.78}\}^{0.16} 
\]

\[
Nu = 0.6 + 0.387 \{Ra/[1+(0.559/Pr)^{0.56}]^{1.78}\}^{0.16} 
\]
Figure 2-5. Scanning electron microscopy images of the wire cross sections before (left panel) and after (middle panel) exposing the wire in a 2% CH₄-air mixture, scanning from 500 to 800 K, at 1 atm for ~1 hour. XPS spectrum of the wire (right panel).
Figure 2-6. Scanning electron microscopy (SEM) image (left panel), pore radius distribution (right panel, line is a lognormal fit to data) of a PdO surface having been exposed to a 2% CH₄-air mixture at 923 K and 1 atm for 1 hour.
Chapter 3 Kinetics of Catalytic Oxidation of Methane over Palladium Oxide

3.1 Introduction

Catalytic combustion of methane over palladium oxide (PdO) catalyst has been studied extensively over the past few decades [1]. As an efficient low-temperature reaction process, catalytic combustion serves as a promising alternative to converting energy from natural gas with minimal soot and NOx emission. It is known that the heterogeneous reaction occurs around and above the temperature of 550 K [2-5]. Towards higher temperatures, the catalytic activity is impacted by Pd/PdO phase equilibrium. PdO was identified as the stable phase below 1070 K in air under atmospheric pressure [6].

Heterogeneous reaction kinetics of methane oxidation over PdO have been examined over supported catalysts [2,5,7] and on wires [4]. The apparent activation energy was reported to be in the range of 46 to 105 kJ/mol, while the reaction orders are close to unity and zero for methane and oxygen, respectively. A Mars-van Krevelen type mechanism has been widely accepted. Methane interacts with the lattice oxygen on a PdO surface, thus forming adsorbed methyl radicals. Further dissociation of the C-H bonds proceeds rapidly on the catalyst surface, eventually leading to the formation and desorption of CO2 [8,9]. The resulting oxygen vacancy is re-occupied by the oxygen from gas-phase or support [10], which completes the catalytic cycle.

Initial C-H bond breaking in methane has been proposed as a rate-limiting step in the
overall catalytic oxidation process [11-13]. Fujimoto et al. [14] suggested that methane undergoes physic-adsorption on the surface first and interacts with neighboring oxygen vacancies, producing surface CH$_3$ and OH species. This mechanism is challenged by the low probability of physi-adsorption to account for the surface reaction rates observed experimentally [2-5]. Rather, the initial reaction of methane with the surface probably proceeds through dissociative adsorption on a Pd-O dimer, generating CH$_3$ and OH species bound to the neighboring Pd centers [1,15].

Direct observation of dissociative adsorption is difficult to make, for the products react with the neighboring surface oxygen rather rapidly. Theoretically, Density Functional Theory (DFT) has been used to probe the reaction mechanism. Interaction of methane with a single PdO dimer was examined [16,17], and the energy barrier was calculated to be 102.4 kJ/mol. Recently, methane adsorption over a PdO(101) surface was examined. The energy barrier to dissociative adsorption was found to be 64.2 kJ/mol [18].

Oxygen adsorption and desorption is another critical process to methane oxidation. The sticking coefficient of O$_2$ was determined over various single and polycrystalline Pd/PdO surfaces [19-23]. Engel [19] studied the adsorption of O$_2$ on Pd (111) by a molecular beam technique, and identified the temperature and coverage dependency of this process. The sticking coefficient on a bare Pd surface was found to decrease from 0.5 to 0.25 over the surface temperature from 300 to 800 K. At certain temperatures the
sticking coefficient can decrease notably with an increase in surface coverage. Goschnick et al. [20] examined the oxygen adsorption on Pd (110) by low energy electron diffraction (LEED) and mass spectrometry (MS) with surface temperature ranging from 100 to 600 K. They observed a constant initial sticking coefficient of 0.5 above room temperature. Jones et al.[21] reported similar results by X-ray photoelectron spectroscopy (XPS) and molecule beam experiments. Matsuchima et al.[22] conducted auger electron spectroscopy (AES) on O₂ adsorption on a polycrystalline palladium surface. They reported an initial sticking coefficient of 0.8 at 463 K. Carstens et al.[23] examined methane adsorption of methane with PdO supported on zirconia as a function of temperature and reported an apparently lower binding energy for oxygen atoms on a crystalline surface of PdO than on a metallic Pd surface.

Recently, catalytic combustion of methane has attracted a renewed attention for high-speed combustion. In hypersonic combustion, the local residence time in an engine can be as short as a few milliseconds, which approach the time scale of combustion reactions [24]. Depending on local thermodynamic conditions, this extremely short residence time can be significantly less than the time needed to initiate gas-phase radical processes during the induction time to flame ignition. Nanocatalysis, an approach by which freely suspended nanoparticles induce catalytic surface reaction and local heat release, was proposed to address this problem [25]. The concept shares the chemical considerations of traditional catalysis functionalized on a wall, but it differs in the physical aspects of the
problem. The catalyst size is substantially smaller than the mean free path of the gas. Hence, the oxidation reaction rate is limited by gas-surface reaction kinetics without complications from mass and heat transfer. In that context, Shimizu et al. [25,26] studied the catalytic combustion of methane in a flow reactor by generating PdO nanoparticles in-situ from a soluble precursor. They examined the heterogeneous reaction kinetics of methane oxidation over the surfaces of palladium nanoparticles and demonstrated that it is possible to reduce the ignition delay time by one to two orders of magnitude compared to the homogeneous ignition. Zhang et al.[27,28] measured the heat release rate of methane oxidation over a PdO surface by wire microcalorimetry and extracted kinetic parameters from experimental observations. In these earlier studies, a gas-surface reaction model was proposed [25] and improved subsequently based on experimental observations [26-28]. Analysis of the data again shows that in the realm of nanocatalysis, the oxidation rate of methane is largely limited by two principal kinetic processes: the adsorption and desorption of O$_2$ and the dissociative adsorption of CH$_4$.

In the present work, it is shown that the wire microcalorimetry experiments are able to produce fundamental gas-surface reaction rate coefficients when they are properly designed and conducted. It is investigated the oxidation of lean CH$_4$-air mixture over a PdO surface, with the equivalence ratio of 0.1-0.3 under atmospheric pressure. The rate constant of dissociative adsorption of CH$_4$ was obtained over the temperature range of 600 to 740 K.
3.2 Surface Area of Real Wire

The surface of the catalyst wire undergoes chemical and morphological changes when it was exposed to oxygen or mixtures of methane and oxygen. Figure 3-1 shows SEM images of the cross sections of a Pd wire before and after it was employed in a wire microcalorimetry experiment, which used a 2% CH₄-air mixture scanning from 500 to 800 K over a one-hour period. Morphologically, the wire surface evolved from a polycrystalline structure to a porous layer 1-2 μm in thickness. XPS analysis in that surface region shows both Pd and PdO crystal structures. Because of the reactive mixture examined in this work is extremely fuel-lean, there is a sufficient amount of gas-phase molecular oxygen in constant contact with the surface. The reaction oxidized the surface to form PdO, as expected from thermodynamic considerations [6].

The modification of the surface resulting in an increase in the surface area poses a notable challenge in data interpretation. In a previous study [27], the surface area was only estimated on the basis of an experimental work reported by Rieo et al. [4]. Using Scanning Tunneling Microscopy and ¹⁸O isotope exchange, they observed a fact of 2 to 3 increase in the surface area upon oxidation of a Pd surface to PdO. In the current work, however, the surface area change was carefully determined in a two-step procedure. As shown in Fig. 3-2, SEM analysis shows that the wire as received (wire a) has a polycrystalline surface that is smooth at the micron level, but at a finer scale AFM probing shows ~100-nm surface islands and ~10-nm crystal grains and steps. The surface
area of the untreated wire was determined by integrating the locally rough surfaces as determined by AFM, which gives a value 1.7 times that of an ideal cylinder. Unfortunately, SEM is not able to determine the surface area of the wire treated in CH$_4$-air mixtures. Figure 3-2 shows surface pores that were formed during wire treatment in a 2% CH$_4$-air mixture (wire b). The wire pretreated in 6% CH$_4$ in air at 900 K for 1 hour has an even greater porosity and surface area (wire c). The surface pores have a feature size around 100 nm, but the depth and distribution of the pores under the surface is difficult to determine. Therefore, the surface area has to be measured indirectly using an alternative method.

A comparison of the specific heat release rates for 2% CH$_4$ oxidized in air using wires (a) and (b) reveals the surface area difference between them. For wire (a), the microcalorimetric data can be obtained reliably only under 650 K. Above this temperature, drastic surface morphological change accompanies the catalytic reaction and the surface sub layer undergoes oxidation in addition to surface reactions leading to methane oxidation. As shown in Fig 3-3, in the temperature range of 600 to 670K the ratio of wire (b) to wire (a) is around 2 for the specific heat release rates measured. This difference can only be attributed to an increase in the surface area. Within the same temperature range, the reaction is expected to be kinetically limited. Evidence supporting this fact comes from experiments with 2% CH$_4$ oxidized over the surface of wire (c) at 900 K for 1 hour. Such a surface is expected to cause greater diffusional resistance to
reaction. Yet, over the 600-670 K temperature range the ratio of specific heat release rates of wire (c) to wire (b) is a constant (cf, the inset of Fig. 3-3). Had the reaction limited by mass transport or heat transport, one would expect the heat release rate to decrease as the temperature is increase, as is the case for observations made above 670 K. The above analyses allow us define the surface area by combining the AFM measurement with the result of reactive area measurements, leading to a surface area enhancement of 3.5 for wire (b) compared to an ideal cylinder.

### 3.3 Apparent Kinetic Study

Based on the surface area of the real wire, the apparent kinetic study is conducted for the 1-3% CH₄-air mixture with the equivalence ratios of 0.1 to 0.3, which are premixed from CH₄ (99%, Airgas) and high purity air (21% O₂ + 79% N₂, Airgas). Figure 3-4 shows the variations of the specific heat release rate and the apparent reaction rate ω_app as a function of the temperature for 1, 2 and 3% of CH₄ oxidized over the surface of wire (b) in air. The apparent reaction rate may now be defined as

\[
ω_{\text{app}} = \frac{Δp}{3.5ΔH_r(T)} = k_{\text{app}}[\text{CH}_4]^n
\]

(3-1)

where \(ΔH_r(T)\) is the enthalpy of combustion of methane (lower heating value). Hence, a measurement of the apparent reaction rate allows us to determine the apparent rate
constant $k_{\text{app}}$ and the overall reaction order $n$ with respect to the concentration of CH$_4$.

The overall reaction order $n$ with respect to the CH$_4$ concentration may be obtained from the slope in a plot of $\log \omega_{\text{app}}$ versus $\log[\text{CH}_4]$. Figure 3-5 shows the $n$ values as a function of wire surface temperature. We found $n = 1.01 \pm 0.03$, independent of temperature over its range tested. Since O$_2$ concentration in the unreacted mixture is substantially higher than that of CH$_4$, the heterogeneous reaction occurs as a pseudo-first order reaction. The apparent rate constant $k_{\text{app}}$ may be obtained as the intercept by fitting the measured reaction rate as $\log \omega_{\text{app}} = \log k_{\text{app}} + \log[\text{CH}_4]$, as shown in Fig. 3-6. The resulting rate constant value is plotted as an Arrhenius plot as seen in Fig. 3-7. The rate constant may be in the range of 600 to 740 K of expressed as

$$k_{\text{app}} \text{ (cm/s)} = (3.2 \pm 0.8) \times 10^4 e^{-(62.8 \pm 1.6) \text{ (kJ/mol)}/RT} \tag{3-2}$$

where $R$ is the universal gas constant. The value of the apparent activation energy is consistent with those reported in previous studies [2-5]. Though it is measurable, the amount of heat release below 600 K is too small to obtain an accurate rate constant. Above 740 K, the rate constant appears to fall off as the temperature increases, which is indicative of the mass transport limitation.
3.4 Development of Detailed Surface Kinetic Model

The surface reaction model developed in this work is largely derived from that in Ref. 26 and 28, as shown in Table 3-1. The model is established based on experiments conducted on the surfaces of nanoparticles and wires, for which the support effect cannot be taken into account. Consequently the model is not applicable to supported catalysts. As in previous studies, critical reactions were identified by a sensitivity analysis. The overall oxidation rate was found to be sensitive to the reversible $O_2$ adsorption, as well as desorption, and methane dissociative adsorption

$$O_2 + 8\text{Pd(S)} \xrightleftharpoons[k_{2b}]{k_{2a}} 2\text{O}^4(S)$$ (R2)

$$\text{CH}_4 + \text{O}^4(S) + \text{Pd(S)} \xrightarrow{k_{16}} \text{CH}_3(S) + \text{OH}^4(S)$$ (R16)

The sensitivity coefficients of these reactions are more than an order of magnitude greater than those of other reactions over the entire range of temperature and methane concentration considered. We focus on deriving the rate parameters of R2f, R2b and R16. In the current model, the rate coefficient of $O_2$ adsorption is described in the form of sticking coefficient $\gamma$:

$$k_{2f} = \gamma \sqrt{\frac{kT}{2\pi m_{O_2}}}$$ (3-3)
where $m_{O_2}$ is the molecular mass of $O_2$ and $k$ is the Boltzmann constant. Based on previous studies [19-23], the sticking coefficient on a bare Pd surface is close to 0.5 at room temperature, which decreases with an increase in surface temperature and coverage. The current model considers the influences of both the surface temperature and coverage on the sticking coefficient as the product of two functions:

$$\gamma = \gamma_0(T) F(\theta)$$

(3-4)

where $\gamma_0(T)$ is the sticking coefficient on a bare Pd surface and $F(\theta)$ accounts for the dependency on coverage. From a molecule beam experiment of $O_2$ adsorption on a Pd (111) surface [19], $\gamma_0(T)$ may be given as

$$\gamma_0(T) = e^{-T/540}$$

(3-5)

The surface coverage dependency is attributable to the fact that each O atom occupies four surface Pd sites [1]. Therefore the adsorption of each $O_2$ requires at least four adjacent sites that are available. The number of these adjacent sites decreases exponentially as the surface coverage increases. The function $F(\theta)$ was computed here by a Monte Carlo simulation, in which O atoms are randomly distributed over a surface. The number density of four empty adjacent sites is counted and normalized by that of a
bare Pd surface. The results are shown in Fig. 3-8. The correlation may be described quantitatively as

$$F(\theta) = e^{-8.8\theta}$$  \hspace{1cm} (3-6)

The desorption of $O_2$ from a PdO surface may be determined from the adsorption rate constant and the equilibrium constant of reversible reaction R2. The enthalpy of reaction R2 was taken to be 230 kJ/mol [29]. The heat capacity $c_p$ and entropy $s$ of surface oxygen may be derived from [30]

$$\frac{c_p}{R} = \sum_{i=1}^{3N-6} \left( \frac{\hbar v_i}{kT} \right) e^{(\hbar v_i/kT) \left[ e^{(\hbar v_i/kT)} - 1 \right]}^{-2}$$  \hspace{1cm} (3-7)

$$\frac{s}{R} = \sum_{i=1}^{3N-6} \left[ \left( \frac{\hbar v_i}{kT} \right) \left[ e^{(\hbar v_i/kT)} - 1 \right]^{-1} - \ln \left( 1 - e^{-(\hbar v_i/kT)} \right) \right]$$

where $N$ is the number of atoms in a species, $h$ is the Planck constant, and $v_i$’s are the vibrational frequencies taken from refs. 31 and 32. Figure 3-9 shows the equilibrium constant computed in this work. A comparison with the earlier work of Deutschmann et al. [33] shows a reasonably good agreement between the two studies. The discrepancy is the result of a somewhat larger enthalpy of adsorption used in ref. 33 and to a lesser extent, updated vibrational frequency values used in the present work.
Calculation of the equilibrium constant just discussed ignores the impact from surface coverage, and thus is valid for a bare Pd surface only. With an increase in coverage, the adsorbed oxygen becomes less stable leading to a significantly reduced enthalpy of adsorption. In the gas-surface reaction model proposed by Wolf et al. [34], the enthalpy of oxygen adsorption on a Pd/PdO surface is linearly proportional to surface oxygen coverage, and the adsorption enthalpy of O\(_2\) on a fully covered surface was chosen to be 110 kJ/mol. The same value was used in the current work. As in a previous study [26], the variation of the enthalpy of O\(_2\) adsorption was assumed to be a linear function with respect to the coverage, using the value just mentioned as the limit for a fully covered surface and 230 kJ/mol for a bare surface.

The rate expression for reaction R16 was determined from the experimental heat release rates observed for 2% CH\(_4\) in air, in the range of 600 to 740 K, to be

\[
k_{16} \text{ (cm/s)} = (7.7 \pm 1.6) \times 10^4 e^{-(59.9 \pm 1.2 \text{ (kJ/mol)})/RT}
\]  

(3-8)

The results are plotted in Fig 3-10. The above rate expression is subject to uncertainties in the equilibrium constant and the rate constant of O\(_2\) adsorption and to an extent, the surface area discussed earlier. We note that the activation energy is consistent with the DFT energy barrier of 64.2 kJ/mol for the CH\(_4\) dissociative adsorption over a PdO (101) surface [18].
The above rate expression, along with the reaction model of Table 3-1, gives heat release rates closely matching the experimental observation for all three CH₄ concentrations, as seen in Fig. 3-11. Analysis of the computational results suggests that under the experimental conditions tested the reaction is largely kinetically controlled without complications from buoyancy-induced natural convection or gas-phase species concentration gradients near the surface of the catalyst wire. Under this condition, the overall rate of methane oxidation over a PdO surface is governed by the dissociative adsorption of methane, as expected, with the reaction rate given by

\[ \frac{d[\text{CH}_4]}{dt} = k_{16}[\text{CH}_4] \theta_{\text{O}^4} \theta_{\text{pdS}} \]  

(3-9a)

Neglecting surface species other than O⁴(S), this expression can be simplified to

\[ \frac{d[\text{CH}_4]}{dt} = k_{16}[\text{CH}_4] \theta_{\text{O}^4} \left(1 - \theta_{\text{O}^4}\right) \]  

(3-9b)

With or without reaction (R16), the \( \theta_{\text{O}^4} \) value changes by < 0.1%. In addition, O₂ adsorption and desorption is in equilibrium, consequently, the methane adsorption affects surface oxygen coverage to only a minor degree. Hence, \( k_{16} \) may be derived from the apparent rate constant \( k_{\text{app}} \) determined earlier as
\[ k_{16} = \frac{k_{app}}{\theta_{O^*(S)} \left(1 - \theta_{O^*(S)}\right)} \]  

(3-9c)

Since \( \theta_{O^*(S)} \) is determined by equilibrium oxygen adsorption and desorption, the uncertainty of its equilibrium constant directly impact the accuracy of the \( k_{16} \) expression. Unfortunately, there is little to no direct measurements available to verify the accuracy of the equilibrium constant experimentally. Hence, the \( k_{16} \) expression derived here is implicitly coupled with and must be used together with the specific equilibrium constant shown in Fig. 3-9.

### 3.5 Conclusions

Catalytic oxidation of CH\(_4\) diluted in air was investigated over a PdO surface at atmosphere pressure by microcalorimetry. Under the conditions considered, the catalytic reaction is pseudo first-order with respect to the methane concentration, and is due to a lack of buoyancy induced natural convection or gas-phase species concentration gradients near the surface of the catalyst wire. The global kinetic parameters were extracted from experimental data, which yielded unity reaction order in methane and an activation energy 62.8±1.6 kJ/mol. Over the examined temperature range of 540 to 800 K, the oxidation rate of methane is determined by its dissociative adsorption on a PdO surface, which combines the effects of surface oxygen coverage and the intrinsic rate of methane
dissociative adsorption on a vacant Pd site surrounded by PdO. The apparent rate constant for the overall oxidation rate was obtained as

\[ k_{\text{app}} \left( \text{cm/s} \right) = \left( 3.2 \pm 0.8 \right) \times 10^4 e^{-\left( 62.8 \pm 3.6 \right) \text{[kJ/mol]} / RT} \] for 600 < T < 740 K. The intrinsic rate constant of the dissociative adsorption of methane was derived to be

\[ k_{16} \left( \text{cm/s} \right) = \left( 7.7 \pm 1.6 \right) \times 10^4 e^{-\left( 59.9 \pm 1.2 \right) \text{[kJ/mol]} / RT} \] from the oxygen adsorption/desorption equilibrium constant estimated here and the apparent rate constant over the same temperature range.
References

**Table 3-1.** Surface reaction model of methane oxidation over PdO above 450 K.

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction $^a$</th>
<th>Rate Parameters $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1f</td>
<td>$\text{H}_2 + 2\text{Pd(S)} \rightarrow 2\text{H(S)}$</td>
<td>$A = 1.0^c$, $\beta = -0.5$, $E = 0$</td>
</tr>
<tr>
<td>1b</td>
<td>$2\text{H(S)} \rightarrow \text{H}_2 + 2\text{Pd(S)}$</td>
<td>$A = 5.33 \times 10^{16}$, $\beta = 0.992$, $E = 87.4$</td>
</tr>
<tr>
<td>2f</td>
<td>$\text{O}_2 + 8\text{Pd(S)} \rightarrow 2\text{O}^4\text{(S)}$</td>
<td>$A = 0.0$, $\beta = 0.0$, $E = 0$</td>
</tr>
<tr>
<td>2b</td>
<td>$2\text{O}^4\text{(S)} \rightarrow \text{O}_2 + 8\text{Pd(S)}$</td>
<td>$A = 3.01 \times 10^{26}$, $\beta = -0.5$, $E = 230.0-120\theta^d$</td>
</tr>
<tr>
<td>3f</td>
<td>$\text{H(S)} + \text{O}^4\text{(S)} \rightarrow \text{OH}^4\text{(S)} + \text{Pd(S)}$</td>
<td>$A = 2.39 \times 10^{18}$, $\beta = 1.156$, $E = 120.3-30\theta^d$</td>
</tr>
<tr>
<td>4f</td>
<td>$\text{H}^+ + \text{Pd(S)} \rightarrow \text{H(S)}$</td>
<td>$A = 1.0^c$, $\beta = 0$, $E = 0$</td>
</tr>
<tr>
<td>4b</td>
<td>$\text{H}^+ + \text{Pd(S)} \rightarrow \text{H(S)} + \text{Pd(S)}$</td>
<td>$A = 1.0^c$, $\beta = 0$, $E = 0$</td>
</tr>
<tr>
<td>5f</td>
<td>$2\text{OH}^4\text{(S)} \rightarrow \text{H}_2\text{O}^4\text{(S)} + \text{O}_2\text{(S)}$</td>
<td>$A = 1.40 \times 10^{19}$, $\beta = 1.1$, $E = 40.7+60\theta^d$</td>
</tr>
<tr>
<td>5b</td>
<td>$\text{H}_2\text{O}^4\text{(S)} \rightarrow \text{H}^+ \text{+ Pd(S)}$</td>
<td>$A = 1.32 \times 10^{10}$, $\beta = 1.1$, $E = 261.7$</td>
</tr>
<tr>
<td>6f</td>
<td>$\text{H}_2 + \text{Pd(S)} \rightarrow \text{H}^+ \text{+ Pd(S)}$</td>
<td>$A = 1.64 \times 10^{10}$, $\beta = 1.1$, $E = 369.7-60\theta^d$</td>
</tr>
<tr>
<td>6b</td>
<td>$\text{OH}^4\text{(S)} \rightarrow \text{OH}^+ \text{+ Pd(S)}$</td>
<td>$A = 1.60 \times 10^{10}$, $\beta = 1.1$, $E = 227.5-30\theta^d$</td>
</tr>
<tr>
<td>7f</td>
<td>$\text{O}^4\text{(S)} \rightarrow \text{O}^+ \text{+ Pd(S)}$</td>
<td>$A = 1.0^c$, $\beta = 0$, $E = 0$</td>
</tr>
<tr>
<td>7b</td>
<td>$\text{OH}^4\text{(S)} \rightarrow \text{OH}^+ \text{+ Pd(S)}$</td>
<td>$A = 1.60 \times 10^{10}$, $\beta = 1.1$, $E = 227.5-30\theta^d$</td>
</tr>
<tr>
<td>8f</td>
<td>$\text{H}^+ + \text{Pd(S)} \rightarrow \text{H(S)}$</td>
<td>$A = 1.0^c$, $\beta = 0$, $E = 0$</td>
</tr>
<tr>
<td>8b</td>
<td>$\text{H}^+ + \text{Pd(S)} \rightarrow \text{H(S)} + \text{Pd(S)}$</td>
<td>$A = 1.62 \times 10^{10}$, $\beta = 1.1$, $E = 43.8$</td>
</tr>
<tr>
<td>9f</td>
<td>$\text{CO}_2 + 5\text{Pd(S)} \rightarrow \text{CO(S)} + \text{H}_2\text{O}(S)$</td>
<td>$A = 1.00 \times 10^{19}$, $\beta = 1.115$, $E = 59.8$</td>
</tr>
<tr>
<td>9b</td>
<td>$\text{CO}_2 + 5\text{Pd(S)} \rightarrow \text{CO(S)} + \text{H}_2\text{O}(S)$</td>
<td>$A = 1.00 \times 10^{19}$, $\beta = 1.115$, $E = 59.8$</td>
</tr>
<tr>
<td>10f</td>
<td>$\text{CO}^+ + \text{O}^4\text{(S)} \rightarrow \text{CO}_2 + 5\text{Pd(S)}$</td>
<td>$A = 1.00 \times 10^{19}$, $\beta = 1.115$, $E = 59.8$</td>
</tr>
<tr>
<td>10b</td>
<td>$\text{CO}^+ + \text{O}^4\text{(S)} \rightarrow \text{CO}_2 + 5\text{Pd(S)}$</td>
<td>$A = 1.00 \times 10^{19}$, $\beta = 1.115$, $E = 59.8$</td>
</tr>
<tr>
<td>11f</td>
<td>$\text{CO} + \text{Pd(S)} \rightarrow \text{CO}_2 + \text{H}_2\text{O}(S)$</td>
<td>$A = 1.0^c$, $\beta = 0$, $E = 0$</td>
</tr>
<tr>
<td>11b</td>
<td>$\text{CO} + \text{Pd(S)} \rightarrow \text{CO}_2 + \text{H}_2\text{O}(S)$</td>
<td>$A = 1.0^c$, $\beta = 0$, $E = 0$</td>
</tr>
<tr>
<td>12f</td>
<td>$\text{C(S)} + \text{O}^4\text{(S)} \rightarrow \text{CO}_2 + 5\text{Pd(S)}$</td>
<td>$A = 1.00 \times 10^{19}$, $\beta = 1.115$, $E = 59.8$</td>
</tr>
<tr>
<td>12b</td>
<td>$\text{C(S)} + \text{O}^4\text{(S)} \rightarrow \text{CO}_2 + 5\text{Pd(S)}$</td>
<td>$A = 1.00 \times 10^{19}$, $\beta = 1.115$, $E = 59.8$</td>
</tr>
<tr>
<td>13f</td>
<td>$\text{CH}_4 + 3\text{Pd(S)} \rightarrow \text{C(S)} + 3\text{H}_2\text{(S)}$</td>
<td>$A = 1.07 \times 10^{19}$, $\beta = 1.1$, $E = 85.1$</td>
</tr>
<tr>
<td>13b</td>
<td>$\text{CH}_4 + 3\text{Pd(S)} \rightarrow \text{C(S)} + 3\text{H}_2\text{(S)}$</td>
<td>$A = 1.07 \times 10^{19}$, $\beta = 1.1$, $E = 85.1$</td>
</tr>
<tr>
<td>14f</td>
<td>$\text{CH}_4 + 3\text{O}^4\text{(S)} \rightarrow \text{CO}_2 + 5\text{Pd(S)}$</td>
<td>$A = 4.00 \times 10^{19}$, $\beta = 0$, $E = 196.0$</td>
</tr>
<tr>
<td>14b</td>
<td>$\text{CH}_4 + 3\text{O}^4\text{(S)} \rightarrow \text{CO}_2 + 5\text{Pd(S)}$</td>
<td>$A = 4.00 \times 10^{19}$, $\beta = 0$, $E = 196.0$</td>
</tr>
<tr>
<td>15f</td>
<td>$\text{CH}_4 + \text{Pd(S)} \rightarrow \text{C(S)} + \text{H}_2\text{(S)} + \text{OH}^4\text{(S)}$</td>
<td>$A = 7.70 \times 10^{10}$, $\beta = 0$, $E = 59.9$</td>
</tr>
<tr>
<td>15b</td>
<td>$\text{CH}_4 + \text{Pd(S)} \rightarrow \text{C(S)} + \text{H}_2\text{(S)} + \text{OH}^4\text{(S)}$</td>
<td>$A = 7.70 \times 10^{10}$, $\beta = 0$, $E = 59.9$</td>
</tr>
</tbody>
</table>

$^a$ Pd site occupancy of O(S), OH(S) and H2O(S) is set to 4. Surface site density is $1.95 \times 10^{-9}$ mol/cm$^2$.

$^b$ Rate constant is written in the form $k = AT^a e^{-E/RT}$. Unit of $A$ are given in terms of mol, cm and s. $E$ is in kJ/mol.

$^c$ Sticking coefficient.

$^d$ $\theta$ is the total occupied site fraction, i.e., $\theta = 1 - \theta_{\text{Pd}}$. 
Figure 3-1. Scanning electron microscopy images of the wire cross sections before (left panel) and after (middle panel) exposing the wire in a 2% CH$_4$-air mixture, scanning from 500 to 800 K, at 1 atm for ~1 hour. XPS spectrum of the wire (right panel).
Figure 3-2. Atomic force microscopy of untreated Pd wire surface (upper left panel) and scanning electron microscopy images of (a): untreated Pd wire surface; (b) and (c): wire surfaces treated in 2% CH₄ and 6% CH₄-air, respectively, at 900 K and 1 atm for approximately 1 hour.
Figure 3-3. Specific heat release rates measured for the oxidation of 2% CH$_4$ in air over several wire surfaces. The wire surface area is assumed to be that of a perfect cylinder. Symbols are experimental data; lines are drawn to guide the eye. The measurements over the untreated Pd wire are unstable above 650 K. Inset: ratios of specific heat release rates.
Figure 3-4. Heat release (top) and surface reaction (bottom) rates determined for the oxidation of CH₄ in air over PdO surface. Symbols are experimental data; lines are drawn to guide the eye.
Figure 3-5. Reaction order $n$ determined for CH$_4$ oxidation in air over a PdO surface. Symbols are experimental data determined at each temperature; the line represents the average of the data over the temperature range shown.
Figure 3-6. Apparent specific reaction rate versus methane concentration. Symbols are experimental data; lines are fits to data assuming the reaction order $n = 1$ with respect to methane concentration.
Figure 3-7. Arrhenius plot for the global oxidation reaction of CH$_4$ in air over a PdO surface. Symbols are experimental data; the line represents a simple Arrhenius fit to data.
Figure 3-8. Surface coverage dependency of O₂ on a Pd/PdO surface. Symbols are results of Monte Carlo simulation; the line is a fit to data.

\[ F = e^{-8.8\theta} \]
Figure 3-9. Equilibrium constant of $O_2$ adsorption on a bare Pd surface. Solid line: current work; dash line: ref. 33
Figure 3-10. Arrhenius plot of $k_{16}$ measured in this work. Symbols are experimental data; the line is an Arrhenius fit to the data.
Figure 3-11. Heat release rates measured (symbols) and predicted (lines) for the oxidation of 1-3% CH$_4$ in air.
Chapter 4 Kinetics of Catalytic Oxidation of C$_2$-C$_3$ Hydrocarbons over Palladium Oxide

4.1 Introduction

Chapter 4 extends the kinetic study from methane (CH$_4$) to C$_2$-C$_3$ hydrocarbons of ethane (C$_2$H$_6$), propane (C$_3$H$_8$) and ethylene (C$_2$H$_4$). The catalytic oxidation of ethane and propane has been examined over a Pd foil [1] and supported Pd catalysts [2]. The reaction rates generally exhibit approximately zeroth and first order dependency with respect to the partial pressures of oxygen and the hydrocarbon, respectively, especially under fuel-lean conditions. Moreover, a series of Density Functional Theory (DFT) studies were reported by Weaver et al. [3-5] on the reactions of methane, ethane and propane over a PdO (101) surface. They identified a similar precursor-mediated mechanism and confirmed that dissociative adsorption is the rate-determining step. The energy barriers of this reaction step were reported to be 64.2 and 51.8 kJ/mol for methane and propane, respectively. Compared to methane, the reduced energy barrier to the dissociative adsorption of propane is consistent with its smaller C-H bond energies than that in methane. Kinetic [1, 2] and DFT [3-5] studies on ethane and propane oxidation over PdO consistently suggest a reaction mechanism similar to methane, that is, the activation of the hydrocarbon reactant over the catalyst acts as the rate-determining step. However, the rate coefficients for the activation of ethane and propane remain unavailable.
The oxidation of $C_2H_4$ on Pd/PdO surfaces has been studied below 600 K. Gas-phase ethylene oxidation over palladium is an industrial process for vinyl acetate synthesis [6]. Over the temperature of 323 to 413 K, ethylene oxidation over evaporated films of palladium produces carbon dioxide and water directly [7], and the reaction was zeroth order with respect to oxygen and first order with respect to ethylene at low pressures but evolved to zeroth order at high pressures. Minor products of the reaction include mainly acetic acid and acetate anhydrate. Furthermore, ethylene oxidation over a Pd/$\gamma$-Al$_2$O$_3$ catalyst at around 600 K [8] was found to have a global activation energy of 13.8 kcal/mol and is inhibited by water in a manner similar to methane oxidation (see, e.g., [9,10]). Studies on the kinetics of vinyl acetate synthesis from ethylene on bulk Pd(100) and Pd nanoparticles supported on silicate showed quite strong dependence of the reaction rate on the particle size [11].

Studies have also shown that the initial adsorption of ethylene on Pd(111) surfaces yields a di-$\sigma$ bond [12,13]. On oxygenated, Pd(111)$_{2\times2}$-O surfaces, both ethylidyne (– CH–CH$_3$) and a $\pi$-bonded configuration are formed at room temperature, but the $\pi$-bonded ad-species desorbed completely as the surface is heated [14]. Reaction pathways of $C_2H_4$ decomposition over a PdO surface were investigated recently by density functional theory (DFT) [15-18]. These studies depicted a relatively clear picture of $C_2H_4$ interaction with Pd surfaces: $C_2H_4$ adsorbs on the Pd surface followed by the conversion
of the ad-species to ethylidyne. Dehydrogenation follows, sequentially converting the ad-species to surface carbon. Under reduced pressure or vacuum-like conditions (a few bars), the oxidation of ethylene on Pd(111) surface forms dissolved carbon up to 650 K, above which CO is formed as the main product, along with CO₂ [19, 20]. While there is a significant body of work for the catalytic oxidation of C₂H₄ at low temperatures or low pressures, kinetic investigations at high temperatures are clearly needed for combustion applications.

We present herein the hierarchical kinetic investigation for the catalytic oxidation of C₂-C₃ hydrocarbons over a PdO surface. Specifically, the overall reaction order with respect to the hydrocarbon reactant concentration and the apparent oxidation rates were determined within the pseudo-first order regime and under dilute conditions where the diffusion limitation is negligible and the overall reaction is controlled by the concentration of the hydrocarbon reactant and its surface reactions. The rate coefficient for the elementary dissociative adsorption of ethane, propane and ethylene were also derived from the experimental data at the ambient pressure and over the temperature range of 620 and 740 K and compared to that of methane under similar conditions.
4.2 Apparent Kinetic Study

4.2.1 Catalytic Oxidation of C₁-C₃ Alkanes

Figure 4-1 presents the heat release rates measured for the oxidation of methane, ethane and propane, over the temperature range of 540 to 800 K. Within this temperature range, the surface reaction rates are large enough to be probed by wire microcalorimetry while gas-phase reactions are suppressed. For each hydrocarbon reactant, three equivalence ratios were investigated. Figure 4-1 provides also a comparison of the reactivity of the three hydrocarbons with a similar carbon concentration. Clearly, the reaction rates decrease in the order of propane, ethane to methane. Figure 4-2 shows the reactant consumption rates, \( \omega \), derived from the measured heat release rate, \( \Delta p \), the surface area ratio of 3.5 and the enthalpy of combustion, \( \Delta_r H_m \). For the hydrocarbons tested, the onset of heat release was observed to occur at the same temperature (550 K). Above this temperature the heat release rates rise quickly.

Apparent kinetic parameters of the overall oxidation process can be derived from the surface reaction rates observed above 620 K. The unity reaction order has been observed in previous studies [1, 2] and verified in this work, as shown in Fig. 4-3. The results are presented in Fig. 4-4 as a function of temperature. As expected, the reaction order of the hydrocarbon reactant was found to be 1.0±0.1, independent of the fuel type or temperature. The apparent, pseudo first-order rate constant, \( k_{app} \), is defined as

\[
\omega = k_{app} [RH] \tag{4-1}
\]
where \([\text{RH}]\) is the concentration of the hydrocarbon reactant. \(k_{\text{app}}\) can be derived by fitting the surface reaction rates with respect to fuel concentrations in a log-log scale, as shown in Fig. 4-5, while the Arrhenius plot of the results are presented in Fig. 4-6. The activation energies of the apparent rate constants are derived over the temperature range of 620 to 740 K, which are equal to \(48.2 \pm 3.5\) to \(57.6 \pm 2.0\) and \(62.3 \pm 2.0\) kJ/mol for propane, ethane and methane, respectively. Here, all uncertainty values are reported as one-standard deviation. The kinetic parameters obtained experimentally are summarized in Table 4-1.

The apparent rate constant \(k_{\text{app}}\) begins to level off above 740 K, implying the onset of decreased activity with increased temperature. The phenomenon has been noted frequently in earlier studies [21-23], and is typically attributed to the presence of intermediate \(\text{PdO}_x\) states between the \(\text{Pd/PdO}\) phase transition. More detailed discussions are available in ref. [21-24]. A Thiele modulus analysis is conducted for 1\% \(\text{C}_3\text{H}_8\)-air mixture at 800 K, where pore diffusion should be the most pronounced. The pore is modeled here as a cylinder of radius \(<r>\) and length \(L\). The effectiveness factor \(\eta\), namely the ratio of reaction rates w/o diffusion being the limiting process, is given by

\[
\eta = \frac{\tanh h_r}{h_r} \quad (4-2a)
\]
where the Thiele modulus $h_T$ for a first-order reaction is [25]

$$h_T = \sqrt{\frac{2kL^2}{\langle r \rangle D}} \quad (4-2b)$$

with $k$ being the rate constant and $D$ the diffusion coefficient. In evaluating $h_T$ at 800 K, $k$ is quantified to be 6 cm/s by extrapolating the apparent rate constant in Fig. 4-6 using a simple Arrhenius expression, and $\langle r \rangle$ and $L$ are adopted as 0.5 and 10 $\mu$m. The gaseous diffusion coefficient $D = 0.67$ cm$^2$/s was obtained from the ChemKin package [26]. Here we note that the pore diameter is at least an order of magnitude larger than the mean free path of the gas and thus Knudsen diffusion is negligible. The above analysis yields a Thiele modulus $h_T$ value of 0.57 and an effectiveness factor $\eta$ of 0.9. Clearly, diffusion process plays a role around 800 K, and such an effect could be coupled with changes in the intrinsic chemistry, leading to the apparent activity drop observed at and above 760 K.

### 4.2.2 Catalytic Oxidation of Ethylene

Figure 4-7 presents the heat release rate for the catalytic oxidation of 0.3-0.6% C$_2$H$_4$/3.75% O$_2$/N$_2$ from 400 to 800 K. Heat release is discernible above an onset temperature of 440 K. Below 560 K, the heat release rate is seen to be independent of temperature and only mildly dependent on the ethylene concentration. The observation is
in agreement with the previous observation of C$_2$H$_4$ oxidation on a Pd film [7], in which the reaction was found to be of zeroth order with respect to C$_2$H$_4$ under similar conditions. Above 560 K, the heat release rate increases with the surface temperature and becomes a function of the C$_2$H$_4$ concentration.

The catalytic combustion of ethylene presents a distinctive different scenario compare to the alkanes, with the low temperature plateau. The mass spectrum was employed to explore the reaction pathways and identify the products. Species were extracted at a position 2 mm from the wire and analyzed by a mass spectrometer for experiments using a mixture containing 0.5% C$_2$H$_4$/3.75% O$_2$/1% He/Ar. Helium was used as the internal standard and N$_2$ was replaced by Ar because of its interference with the crucial peak at $m/z = 28$; recognizing nevertheless that a trace amount of N$_2$ was always present in the system. The measurement was performed over the temperature range of 400 to 800 K. The spectrum generated was normalized by the intensity of the He peak ($m/z=4$). The reproducibility of the normalized intensities is within ±5%.

Figure 4-8 shows a sample mass spectrum recorded at 600 K. The peaks at $m/z = 14$, 27, 28 have major contributions from ionization and dissociative ionization of C$_2$H$_4$; those at $m/z = 14$, 28 also have contributions from N$_2$, those at $m /z = 28$, 44 from CO$_2$ and those at $m/z = 20$ and 40 result from Ar$^{2+}$ and Ar$^+$. No notable $m/z$ values were observed above 44, indicating the absence of acetic acid or acetate anhydride as the major
products of the current catalytic experiments. To discern the level of CO produced from catalytic experiments, the peak at $m/z = 28$ was analyzed in detail. Specifically, spectra of pure C$_2$H$_4$, N$_2$, and CO$_2$ were measured and adopted as the internal standard. Calibration was also made using a mixture containing 5% CO and 5% CO$_2$ diluted in a mixture of Ar and He. Each spectrum collected under the catalytic reaction condition was processed to subtract the contributions from C$_2$H$_4$, N$_2$ and CO$_2$ at $m/z = 28$ by considering the intensities at $m/z = 27$, 14 and 44, respectively. Figure 4-9 plots the residual signal intensities at $m/z = 28$. It is seen that there is no discernible correlation between the residue intensity and temperature. Based on this observation, it is concluded that the level of CO is below the background noise. The upper limit of the CO/CO$_2$ ratio may be estimated by assuming the residual signal intensity at $m/z=28$ to be solely from CO. The maximum CO/CO$_2$ ratio is smaller than 10% at 400 K owing to the weak signal of CO$_2$, and zero at higher temperatures.

The mole percentages of the species measured are shown in Figure 4-10. At 400 K, appreciable amounts of CO, H$_2$ and H$_2$O were measured even though the heat release rate is below the sensitivity of wire microcalorimetry. Towards the high temperatures, the dominant product is CO$_2$, followed by H$_2$. The carbon balance is excellent as seen in Fig. 4-11, which confirms that CO$_2$ is the dominant product at 800 K. The missing hydrogen and oxygen from the elemental balance at 700 and 800 K is caused by water
condensation in the sampling line. Two pieces of evidence support this assertion. First, the missing hydrogen is almost exactly two times the missing oxygen. Second, when the actual H$_2$O mole percentage is inferred from the missing hydrogen and the as-measured H$_2$O data of Fig. 4-10, the mole percentage of H$_2$O follows closely that of CO$_2$ at and above 600 K, as shown by the solid circle and dashed line in the same figure. Therefore, the analysis suggests that the surface reactions yield predominantly CO$_2$ and H$_2$O above 600 K. Below 600 K, both H$_2$ and H$_2$O are produced and their concentrations can be similar. In fact, the temperature at which H$_2$O dominates over H$_2$ coincides with the onset temperature of rapid heat release beyond the plateau regime, as seen in Fig. 4-7.

The MS analysis suggests that above 600 K the surface reaction produces predominantly CO$_2$ and H$_2$O as for the combustion. The apparent rate constant $k_{app}$ and the reaction order with respect to ethylene $n$ were extracted from the measured heat release rate using Eq. 4-1. A plot of $\omega_{app}$ as a function of $c$, shown in Fig. 4-12, yields $k_{app}$ as the intercept and $n$ as the slope. Figure 4-13 plots the resulting $n$ value as a function of temperature. Clearly the current experiment indicates that the reaction order is unity with respect to ethylene concentration, a conclusion identical to the studies on C$_1$-C$_3$ alkanes.

The apparent reaction rate coefficient $k_{app}$ corresponding to a unity reaction order is shown as an Arrhenius plot in Fig. 4-14 and can be expressed by

$$
 k_{app} \text{(cm/s)} = (1.9 \pm 0.1) \times 10^4 \exp \left[ \frac{48.2 \pm 1.4 \text{ kJ/mol}}{RT} \right]
$$

(4-3)
over the temperature range of 620 to 740 K. Keeping in mind that the $\Delta H_r$ value used does not consider $H_2$ as a minor product, the above expression probably represents the upper limit for ethylene oxidation over a Pd surface. In comparison, the apparent activation energies are 62.3, 57.6 and 48.2 kJ/mol for methane, ethane and propane, respectively, under comparable conditions. Clearly the reactivity of ethylene is closer to propane than to methane.

The apparent rate coefficient is shown to level off above 740 K as for the case of C$_1$-C$_3$ alkanes. To assess the impact of diffusion, Thiele modulus was calculated as Eq. (4-2) with the diffusivity and reactivity of ethylene. At 800 K, $k_{app}$ is 13.50 cm/s, obtained by extrapolating the apparent rate constant of Fig. 4-14 to that temperature, and $D$ is 1.08 cm$^2$/s for C$_2$H$_4$ in the 0.5% C$_2$H$_4$/3.75% O$_2$/N$_2$, by the CHEMKIN package [26]. The Thiele modulus $h_T$ was found to be 0.71. The corresponding effectiveness factor $\eta$ is 0.86, which clearly suggests that diffusion limitation plays an important role at that temperature. In comparison, the $\eta$ value is 0.94 at 700 K, indicating a drastically reduced pore diffusion effect below that temperature.
4.3 Development of Detailed Kinetic Model

4.3.1 Catalytic Oxidation of C₁-C₃ Alkanes

The similarity of the global reaction behavior observed for three alkanes considered suggests that the surface reaction mechanism is similar for the three reactants. This observation is indirectly supported by the DFT studies of Weaver et al. [3-5]. In the present work, a surface reaction model is proposed for the oxidation of ethane and propane on the basis of methane oxidation. The reaction model, presented in Table 4-2, is comprised of three components: the adsorption of the hydrocarbon molecule, the adsorption and desorption of molecular oxygen, and reactions describing the oxidation of surface intermediates, which lead to the formation of the final products, CO₂ and H₂O. As the sensitivity analysis shown in Fig. 4-15, predictions of the catalytic activities are largely sensitive to only three reactions, oxygen adsorption/desorption and dissociative adsorption of the hydrocarbon molecule.

The elementary reactions of the oxygen adsorption/desorption inherit the rate coefficients from the methane oxidation model in chapter 3. Wire microcalorimetry experiment was then used to determine the rate constant for the dissociative adsorption of the hydrocarbon molecules. The rate of oxidation over the PdO surface is controlled by C-H bond breaking through dissociative adsorption,

\[
R-H + O^4(S) + Pd(S) \xrightarrow{k_{ads,nt}} R(S) + OH^4(S)
\]

(4-4)
The rate of this reaction, \( r_{\text{ads}} \), can be expressed as

\[
r_{\text{ads}} = k_{\text{ads,RH}} [\text{RH}] \theta_{\text{O}_2(S)} \theta_{\text{Pd(S)}}
\]  

(4-5)

The diffusion limitation is not to be important below the surface temperatures of 740 K.

The reactant concentration, [RH] at the wire surface is accordingly given by that in the bulk unreacted gas. Furthermore, since \([\text{O}_2] >> [\text{RH}]\) and under the temperature of interest, \(\theta_{\text{O}_2(S)} + \theta_{\text{Pd(S)}} \approx 1\). We have

\[
\theta_{\text{O}_2(S)} \theta_{\text{Pd(S)}} = \theta_{\text{O}_2(S)} \left(1 - \theta_{\text{O}_2(S)}\right)
\]  

(4-6)

In the study on methane catalytic oxidation, \(\theta_{\text{O}_2(S)}\) was shown to be determined largely by the competition between \(\text{O}_2\) adsorption and desorption equilibrium and hence the equilibrium constant. The coverage of surface oxygen is hardly affected by the presence of methane because the rates of \(\text{O}_2\) adsorption and desorption are much larger than that of methane adsorption. The same observation holds for ethane and propane. Figure 4-16 shows that the rates computed for ethane and propane dissociative adsorption is nearly three orders of magnitude lower than that of \(\text{O}_2\) adsorption.

Assuming that the subsequent reaction leading to the formation of \(\text{CO}_2\) on the surface
and its desorption is fast compared to the initial dissociative adsorption of the hydrocarbon reactant, the heat release rate is basically controlled by the rate of reaction (4-5). Its rate coefficient may be determined by

\[ k_{\text{ads,RH}} \equiv \frac{k_{\text{app}}}{\theta_{O^*(S)}(1-\theta_{O^*(S)})} \] (4-7)

where \( \theta_{O^*(S)} \) may be determined by the equilibrium constant of \( O_2 \) adsorption/desorption.

Figure 4-17 presents the Arrhenius plot for the above rate constants determined for 1-3\% CH\(_4\), 0.5-1.5\% C\(_2\)H\(_6\) and 0.4-1.0\% C\(_3\)H\(_8\) mixtures. The rate expressions may be extracted from the plot over the linear regime:

\[
\begin{align*}
\text{CH}_4 & : k_{16} \ (cm / s) = (5.7 \pm 0.2) \times 10^4 \ \exp(-\frac{58.0 \pm 2.5 \ \text{kJ/mol}}{RT}) \\
\text{C}_2\text{H}_6 & : k_{19} \ (cm / s) = (4.5 \pm 0.2) \times 10^4 \ \exp(-\frac{53.3 \pm 2.5 \ \text{kJ/mol}}{RT}) \\
\text{C}_3\text{H}_8 & : k_{21} \ (cm / s) = (1.6 \pm 0.1) \times 10^4 \ \exp(-\frac{44.0 \pm 3.3 \ \text{kJ/mol}}{T})
\end{align*}
\] (4-8)

all of which were fitted to the temperature range of \( 620 \leq T \leq 740 \) K. Above 740 K, the overall heat release rate is influenced by finite-rate diffusion, and the rate coefficient determined starts to level off towards higher temperatures.
The proposed surface reaction model is applied to various hydrocarbon/air mixtures. Figure 4-18 shows the comparison between the experimental data and model prediction. It is seen that, below 740 K, good agreement is achieved for all gas phase compositions. Above this temperature, the model predicts larger heat release rates in all cases, as expected. The discrepancy is attributed to potential pore diffusion effects and/or intrinsic surface kinetics change due to Pd/PdO phase transition. The presented results are subject to the uncertainty in the mechanism of subsequent reactions of \( R(S) \) and their rate coefficients assumed, *i.e.*, reactions 17, 18 and 20 of Table 4-2. If the oxidation of \( R(S) \) is fast, neither the exact mechanism nor the rates is critical to the determination of dissociative adsorption rate coefficients and the overall heat release rate observed.

This work explains the increasing reactivity from methane to propane by their ability to undergo adsorption - an issue that has also been investigated by Weaver *et al.* [3-5]. The dissociation of alkanes on PdO(101) occurs through a precursor-mediated mechanism. Upon adsorption, an alkane molecule forms dative bonds with coordinatively unsaturated Pd atoms. A kinetic competition between dissociation and desorption of the precursor determines the net probability for dissociation. The energy barriers of methane and propane dissociation have been reported as 64.2 and 51.8 kJ/mol [3,5], respectively. These are consistent with the order of reactivity observed for these fuels. In fact, these energy barriers are quite close to the activation energies measured in the present work.
4.3.2 Catalytic Oxidation of Ethylene

For the catalytic combustion of ethylene above 600 K, it is noted that no direct and detailed mechanistic information about CO₂ and H₂O production can be deduced from the current experiment. For the C₁-C₃ alkanes, the overall rate of catalytic reaction over Pd is decided by the dissociative adsorption of the hydrocarbon. We assume it also holds for the ethylene oxidation, partly supported by the unity apparent reaction order. Here we postulate that the initial reaction of ethylene with a PdO surface may be described by reactions R22 and R23 of Table 4-2. Along with reaction steps proposed for methane oxidation, we find the value of \( k_{23} \) iteratively by fitting the microcalorimetry data at each temperature and gas composition. The results are shown in Fig. 4-19 and are fitted to an Arrhenius expression:

\[
C_2H_4 : k_{23} (cm/s) = (2.5 \pm 0.1) \times 10^4 \exp\left(-\frac{43.1 \pm 0.8 \text{kJ/mol}}{RT}\right)
\]  

(4-9)

over the temperature range of 620 and 740 K. Sensitivity analysis was performed again identifying the adsorption/desorption of O₂ and the dissociative adsorption of C₂H₄ to be the critical reaction steps. Compared to the activation energies of methane, ethane and propane oxidation under comparable conditions (58, 53 and 44 kJ/mol, respectively), the activation energy of ethylene dissociative adsorption is the lowest. The pre-exponent
factor lies between those of ethane \((4.5\times10^4\ \text{cm/s})\) and propane \((1.6\times10^4\ \text{cm/s})\). Below 600 K, \(\text{C}_2\text{H}_4\) undergoes dehydrogenation reaction on the PdO surface. No detailed analysis is conducted here because of the detailed reaction mechanism needed to describe the overall heat release rate is currently unavailable. In any case, the temperature regime is too low to have any practical implication for combustion applications.

### 4.4 Conclusions

Catalytic oxidation of methane, ethane and propane in air was investigated over a PdO surface by wire microcalorimetry over the surface temperature range of 600 to 800K and equivalence ratio from 0.1 to 0.3 at atmospheric pressure. The global reaction order was found to be close to unity with respect to the hydrocarbon reactant concentration, which indicates the dissociative adsorption of the hydrocarbon molecule on the catalyst surface to be the rate determining-step. The oxidation rate was observed to increase with an increase in the carbon number of the reactant. The activation of the hydrocarbon molecule on the catalyst surface is described by dissociative adsorption, and their rate coefficients are determined from the experimental data over the temperature range of 620 and 740 K. The kinetic data are found to be consistent with earlier DFT calculations.

Catalytic oxidation of 0.3-0.6%C\(_2\)H\(_4\)/3.75%O\(_2\)/N\(_2\) mixtures was studied over PdO surface by wire microcalorimetry and mass spectrometry over the temperature range of
400 to 800 K and under atmospheric pressure. Heat release was observed starting from 450 K. From this temperature and below 580 K, the heat release rate was found to be independent of temperature and only mildly dependent on the ethylene concentration. The primary reaction products include CO$_2$, H$_2$ and H$_2$O. Above 580 K, the heat release rate increases drastically as a function of temperature and the primary reaction products are CO$_2$ and H$_2$O. The heat release rates were analyzed, which yielded a global activation energy of 48.2 ± 2.5 kJ/mol and a reaction order of unity over the temperature of 620 to 740 K. A surface chemistry model was proposed for reaction above 600 K. The rate coefficient of ethylene dissociative adsorption on Pd surface was proposed by fitting the microcalorimetry data.
References


Table 4-1. Kinetic parameters of C$_2$-C$_3$ hydrocarbons oxidation over PdO $620 \leq T \leq 740$ K.

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Reaction order</th>
<th>Activation energy (kJ/mol)</th>
<th>Pre-exponential factor $\times 10^4$ (cm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>1.01±0.03</td>
<td>62.8±2.0</td>
<td>3.2±0.8</td>
</tr>
<tr>
<td>Ethane</td>
<td>0.99±0.06</td>
<td>57.6±2.0</td>
<td>2.3±0.1</td>
</tr>
<tr>
<td>Propane</td>
<td>0.98±0.07</td>
<td>48.2±3.5</td>
<td>0.8±0.1</td>
</tr>
<tr>
<td>Ethylene</td>
<td>1.02±0.09</td>
<td>48.2±1.4</td>
<td>0.9±0.1</td>
</tr>
</tbody>
</table>
### Table 4-2. Surface reaction model of C₁-C₃ hydrocarbons oxidation over PdO.

<table>
<thead>
<tr>
<th>No</th>
<th>Reaction</th>
<th>Rate Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H₂+2Pd(S)=2H(S)</td>
<td>A=1.0&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>2f</td>
<td>O₂+8Pd(S)=2O₄(S)</td>
<td>e&lt;sup&gt;(P/540+8.8θ)&lt;/sup&gt;</td>
</tr>
<tr>
<td>2b</td>
<td>2O₄(S)=O₂+8Pd(S)</td>
<td>3.0×10&lt;sup&gt;36&lt;/sup&gt;</td>
</tr>
<tr>
<td>3f</td>
<td>H(S)+O₄(S)=OH₄(S)+Pd(S)</td>
<td>2.9×10&lt;sup&gt;18&lt;/sup&gt;</td>
</tr>
<tr>
<td>3b</td>
<td>OH₄(S)+Pd(S)=H(S)+O₄(S)</td>
<td>2.3×10&lt;sup&gt;19&lt;/sup&gt;</td>
</tr>
<tr>
<td>4f</td>
<td>H(S)+OH₄(S)=2H₂O₄(S)+Pd(S)</td>
<td>6.6×10&lt;sup&gt;15&lt;/sup&gt;</td>
</tr>
<tr>
<td>4b</td>
<td>H₂O₄(S)+Pd(S)=H(S)+OH₄(S)</td>
<td>2.1×10&lt;sup&gt;18&lt;/sup&gt;</td>
</tr>
<tr>
<td>5f</td>
<td>2OH₄(S)=H₂O₄(S)+O₄(S)</td>
<td>3.9×10&lt;sup&gt;17&lt;/sup&gt;</td>
</tr>
<tr>
<td>5b</td>
<td>H₂O₄(S)+O₄(S)=2OH₄(S)</td>
<td>1.4×10&lt;sup&gt;19&lt;/sup&gt;</td>
</tr>
<tr>
<td>6</td>
<td>H+Pd(S)=H(S)</td>
<td>1.0&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>7</td>
<td>O+Pd(S)=O₄(S)</td>
<td>1.0&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>8</td>
<td>OH+Pd(S)=OH₄(S)</td>
<td>1.0&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>9</td>
<td>H₂O+Pd(S)=H₂O₄(S)</td>
<td>1.0&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>10</td>
<td>CO(S)+O₄(S)=CO₂+5Pd(S)</td>
<td>1.0×10&lt;sup&gt;19&lt;/sup&gt;</td>
</tr>
<tr>
<td>11</td>
<td>C(S)+O₄(S)=CO(S)+4Pd(S)</td>
<td>1.0×10&lt;sup&gt;19&lt;/sup&gt;</td>
</tr>
<tr>
<td>12</td>
<td>CO=Pd(S)=CO(S)</td>
<td>1.0&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>13</td>
<td>CH₃(S)+3Pd(S)=C(S)+3H(S)</td>
<td>1.1×10&lt;sup&gt;19&lt;/sup&gt;</td>
</tr>
<tr>
<td>14</td>
<td>CH₄(S)+3O₄(S)=C(S)+3OH₄(S)</td>
<td>1.1×10&lt;sup&gt;19&lt;/sup&gt;</td>
</tr>
<tr>
<td>15</td>
<td>CH₂=2Pd(S)=CH₂(S)+H(S)</td>
<td>4.0×10&lt;sup&gt;5&lt;/sup&gt;</td>
</tr>
<tr>
<td>16</td>
<td>CH₂+Pd(S)+O₄(S)=CH₃(S)+OH₄(S)</td>
<td>5.7×10&lt;sup&gt;4&lt;/sup&gt;</td>
</tr>
<tr>
<td>17</td>
<td>CH₃(S)+2O₄(S)=C(S)+2OH₄(S)</td>
<td>1.1×10&lt;sup&gt;19&lt;/sup&gt;</td>
</tr>
<tr>
<td>18</td>
<td>C₂H₆(S)+Pd(S)=C₂H₅(S)+CH₂(S)</td>
<td>1.1×10&lt;sup&gt;19&lt;/sup&gt;</td>
</tr>
<tr>
<td>19</td>
<td>C₂H₅+Pd(S)+O₄(S)=C₂H₅(S)+OH₄(S)</td>
<td>4.5×10&lt;sup&gt;4&lt;/sup&gt;</td>
</tr>
<tr>
<td>20</td>
<td>C₂H₅(S)+2Pd(S)=C₂H₄(S)+2CH₂(S)</td>
<td>1.1×10&lt;sup&gt;19&lt;/sup&gt;</td>
</tr>
<tr>
<td>21</td>
<td>C₂H₅+Pd(S)+O₄(S)=C₂H₅(S)+OH₄(S)</td>
<td>1.6×10&lt;sup&gt;4&lt;/sup&gt;</td>
</tr>
<tr>
<td>22</td>
<td>C₂H₆(S)+O₄(S)=CO(S)+CH₃(S)</td>
<td>1.07×10&lt;sup&gt;19&lt;/sup&gt;</td>
</tr>
<tr>
<td>23</td>
<td>C₂H₄(S)+Pd(S)+O₄(S)=C₂H₃(S)+OH(S)</td>
<td>2.5×10&lt;sup&gt;4&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

---

*<sup>a</sup> Pd site occupancy of O(S), OH(S) and H₂O(S) is set to 4. Surface site density is 1.95×10<sup>−9</sup> mol/cm<sup>2</sup>.

*<sup>b</sup> Rate constant is written in the form $k=A\theta^β\exp(−E/RT)$. Unit of $A$ are given in terms of mol, cm, and s. $E$ is in kJ/mol.

*<sup>c</sup> $θ$ is the total site fraction, i.e., $θ=1−θ_{Pd}$.

*<sup>d</sup> Sticking coefficient.
Figure 4-1. Heat release rates measured for the oxidation of methane, ethane and propane in air over PdO surfaces. Symbols are experimental data; lines are drawn to guide the eye.
Figure 4-2. Specific oxidation rates determined for methane, ethane and propane in air over PdO surfaces (see text). Symbols are experimental data; lines are drawn to guide the eye.
Figure 4-3. Overall reaction order observed for methane, ethane and propane at 700 K. Symbols are experimental data; lines are Arrhenius fits to data.
Figure 4-4. Overall reaction order with respect to the fuel concentration over a PdO surface.

\[
n = 1.0 \pm 0.1
\]

\[
\begin{align*}
& n_{CH_4} = 1.00 \pm 0.08 \\
& n_{C_2H_6} = 0.99 \pm 0.06 \\
& n_{C_3H_8} = 0.98 \pm 0.07 \\
\end{align*}
\]

\[P = 1 \text{ atm} \]
Fuel-air mixtures of \( \Phi = 0.1 \sim 0.3 \)
Figure 4-5. Apparent specific reaction rates versus methane, ethane, propane concentration. Symbols are experimental data; lines are fits to data assuming the reaction order $n = 1$ with respect to methane, ethane and propane concentration.
Figure 4-6. Apparent rate coefficient of methane, ethane and propane oxidation over a
PdO catalyst. Symbols are experimental data; lines are Arrhenius fits to data. The units
for the rate expressions shown are cm/s.
Figure 4-7. Heat release rates observed for the oxidation of C₂H₄/O₂/N₂ mixtures over a PdO surface. Symbols are experimental data; lines are drawn to guide the eye.
Figure 4-8. A typical mass spectrum of gas sampled at 600 K.
Figure 4-9. Residual peak intensities at $m/z=28$. Mean residue values are $5 \times 10^{-13}$ at 400 K, $-2 \times 10^{-13}$ at 500 K, and $-2 \times 10^{-12}$ at 600 and 700 K.
Figure 4-10. Mole percentage of major species C$_2$H$_4$, O$_2$, CO$_2$, H$_2$ and H$_2$O sampled near the wire surface. Symbols are experimental data; solid lines are drawn to guide the eye. The solid circle and dashed line indicates the mole percentages of water inferred from the missing hydrogen element above 600 K (see text).
Figure 4-11. Mole percentage of H, O, C elements in gas sampled. Symbols are experimental data; solid lines are drawn to guide the eye. The dashed lines indicate inferred mass conservation if all missing H element is attributed to H₂O (see text).
Figure 4-12. Apparent reaction rates as a function of molar concentration of ethylene observed for the oxidation of 0.3-0.6% C$_2$H$_4$/3.75% O$_2$/N$_2$ mixtures over a PdO surface. Symbols are experimental data; lines are fits to data, where the slopes yield the values of the reaction order with respect to C$_2$H$_4$ concentration.
Figure 4-13. Overall reaction order with respect to C$_2$H$_4$ over a PdO surface. Symbols are experimental data; line represents the average over 600 to 780 K.
Figure 4-14. Apparent rate coefficients for the oxidation of 0.3-0.6% C₂H₄/3.75% O₂/N₂ over a PdO surface from 600 to 740 K. Symbols are experimental data; the line is the Arrhenius fit to the data.

\[ k_{\text{app}} \text{ (cm/s)} = (1.9 \pm 0.1) \times 10^4 \exp \left( \frac{-5800 \pm 200}{T} \right) \]

\[ 620 \leq T \leq 740 \text{ K} \]
Figure 4-15. Sensitivity spectrum of selected reactions computed for methane, ethane and propane oxidation over a PdO surface.
Figure 4-16. Adsorption rates of molecular oxygen compared to those of the hydrocarbon fuels. Symbols are simulated results; lines are drawn to guide the eye.
Figure 4-17. Rate coefficient of methane, ethane and propane dissociative adsorption on Pd(s) over a PdO surface. Symbols are experimental data; lines are Arrhenius fits to data. The units for the rate expressions shown are cm/s.

\[
\begin{align*}
620 \leq T & \leq 740 \, K \\
k_{\text{ads,C}_3\text{H}_8} & = (1.6 \pm 0.1) \times 10^4 \exp\left(-\frac{5300 \pm 400}{T}\right) \\
k_{\text{ads,C}_2\text{H}_6} & = (4.5 \pm 0.2) \times 10^4 \exp\left(-\frac{6400 \pm 200}{T}\right) \\
k_{\text{ads,CH}_4} & = (5.7 \pm 0.2) \times 10^4 \exp\left(-\frac{7000 \pm 300}{T}\right)
\end{align*}
\]
Figure 4-18. Measured (symbols) and predicted (lines) the oxidation rates of 1-3% CH₄, 0.5-1.5% C₂H₆, and 0.4-1.0% C₃H₈ in air over a PdO surface.
Figure 4-19. Rate coefficients of C₂H₄ adsorption over PdO surface for mixtures of 0.3-0.6% C₂H₄/3.75% O₂/N₂. Symbols are derived by fitting the wire microcalorimetry data through detailed modeling; the line is an Arrhenius fit to the data.

\[ k_{14} \ (\text{cm/s}) = (2.5 \pm 0.1) \times 10^4 \exp\left(-\frac{-5200 \pm 100}{T}\right) \]

\[ 620 \leq T \leq 780 \ K \]
Part II
Problems in Detailed Simulation of Combustion Processes
Chapter 5 A DNS Study of Self-Accelerating Cylindrical Hydrogen-Air Flames with Detailed Chemistry

5.1 Introduction

The celebrated analyses of Darrieus [1] and Landau [2] demonstrated that the propagation of a premixed flame of infinitesimally thin front is hydrodynamically unstable, characterized by the evolution of cells over the front due to the density jump across it. When the flame is in addition expanding, as in cylindrical and spherical flames, the continuously increasing flame dimension suggests the possible accommodation of progressively more cells. This could then lead to increased total flame surface as compared to that of the otherwise smooth flame, and hence the concomitant increase in the global flame propagation rate, resulting in the so-called self-acceleration of the global flame front. Consequently, if the instantaneous global flame radius is designated by a power law in time $t$ with an exponent $\alpha$, then the flame undergoes self-acceleration if $\alpha > 1$. Furthermore, if $\alpha$ is a constant over a period of time, then the propagation is self-similar within this period. It has also been suggested that, for non-integer values of $\alpha$ the wrinkled flame surface and thereby the propagation phenomenon could assume a fractal character. If $\alpha$ in addition assumes the particular value of 1.5 [3], which has been shown to be the fractal dimension of Kolmogorov turbulence [4-5], then it has been further suggested that the flame has undergone self-turbulization, assuming the characteristics of
a turbulent flame. This last observation is particularly intriguing and has generated considerable interest to experimentally or computationally demonstrate that such a value can indeed be attained. A definitive verification however has not been demonstrated.

To substantiate the last statement in terms of computational investigation, which is the present approach, we first note that because of the prohibitive computational cost, previous investigations have invariably adopted the 2D, cylindrical instead of the 3D, spherical configuration. While such an approach is meaningful, some studies using cylindrical flames have however incorrectly claimed the $\alpha = 1.5$ value, which is relevant only for spherical flames. As pointed out in [6], this is conceptually inappropriate in that a 2-D cylindrical flame intrinsically undergoes less pronounced acceleration than a 3-D spherical flame. Furthermore, most of these studies used the Sivashinsky equation or a modified form of it [7-11], while Ashurst [12] conducted 2-D Lagrangian simulations with a potential flow model, and Aldredge and Zuo [13] used a level-set formulation and Euler equation. Only Liberman et al. [6] performed 2-D simulations by direct numerical simulation (DNS) of the Navier-Stokes equations, with one-step overall chemistry.

The above discussion demonstrates that, in spite of the fundamental and practical importance of the phenomenon of interest and the fact that the fluid mechanical, transport, and reaction components governing it are well defined, a detailed, rigorous study based on DNS of the fluid flow down to the fine scales needed to resolve the flame
structure, together with a detailed reaction mechanism to properly describe the chemistry, has not been performed. Furthermore, there has also been considerable latitude in the extraction of the acceleration exponent in previous studies, which has led to substantial ambiguity in assessing the issues of self-acceleration, self-similarity and self-turbulization mentioned above.

In response to the above considerations, we have performed a DNS study of an expanding cylindrical hydrogen-air flame, with a detailed and largely validated chemistry. The DNS has allowed us to perform a detailed study of the morphology and propagation of the wrinkled flame front, providing insight into the relation between the dynamics of the local flame structure and the expanding global flame. The study unambiguously yields the self-acceleration exponent $\alpha$, allowing further exploration of this phenomenon with confidence.

The chapter is organized as follows. In the next section, the numerical method is specified. In Section 3, the instantaneous propagation of the simulated flame front is described and discussed. The self-acceleration exponent is extracted by various methods in Section 4, followed by the conclusions in Section 5.
5.2 Numerical Method

The study involves the DNS of the propagation of a globally cylindrical flame in a stoichiometric hydrogen-air mixture at eight atmospheres of pressure by using the Sandia S3D code, whose numerical scheme [14] is briefly specified as follows. The compressible Navier–Stokes, species continuity, and total energy equations were temporally integrated by a fourth-order explicit Runge–Kutta method [15]. The solution was spatially discretized using an eighth-order central differencing scheme, with a tenth-order filter to remove spurious high-frequency fluctuations in the solution.

The computational domain is a square box of 5 cm on each side, which is large enough for the full development of hydrodynamic instability determined from a complementary experimental study [16]. A uniform mesh with the grid size of 4 microns is applied to resolve the fine structure of the flame front, based on the 1-D unstrained planar stoichiometric hydrogen-air flame at eight atmospheres simulated by the PREMIX code [17]. The chemistry of the system is described by a detailed mechanism developed by Li et al. [18], while the reaction rates, thermodynamic and mixture-averaged transport properties are evaluated by the CHEMKIN and TRANSPORT libraries [19, 20] linked to S3D.

The pressure of the computational domain is set at the constant value of eight atmospheres. A 300 K stoichiometric hydrogen-air mixture is uniformly distributed
across the entire domain initially. The Lewis number of the mixture is near unity [21], and, as such, the mixture is largely diffusional neutral such that only hydrodynamic instability is activated. The high system pressure substantially reduces the flame thickness, which promotes the onset of hydrodynamic instability and is also expected to further suppress much of the residual unbalanced diffusional-thermal effects. A Gaussian high temperature profile is superposed at the domain center to mimic spark ignition of the mixture. Different peak values of the temperature profile were tested such that the selected one barely initiates flame propagation without affecting its subsequent dynamics. Improved non-reflecting inflow/outflow open boundary conditions were also applied [22]. A time step of 2.5 ns was adopted, and the solutions of flow velocity, temperature, species mass fraction at each grid were stored every 800 steps, which corresponds to a temporal frequency of 2 µs. The flame was simulated for 1.7 ms at which time the flame front reaches the boundary.

5.3 Instantaneous Propagation of Flame Front

For the self-accelerated propagation of spherical flames, experimental measurement typically yields the relationship between the global flame radius and the propagation time $R(t) \sim t$. However, the focus of the present study is also to determine the evolution of the propagation velocity $V(t)$. In experimental studies, since the propagation velocity is
derived from the flame radius through numerical differentiation, the experimental error is amplified in this process and can significantly affect the calculated propagation velocity. In contrast, since the present simulation has extremely fine temporal and spatial resolution, a more reliable propagation velocity can be deduced.

Figure 5-1 shows the evolution of the simulated flame front at specific time instants, with an interval of 0.2 ms. The flame front is identified as an iso-surface of the progress variable $c = 0.5$, where $c = \frac{Y_{H_2O}}{Y_{H_2O}^c}$ and $Y_{H_2O}^c$ is the equilibrium water mass fraction behind the flame front. It is seen that the global flame front exhibits a fractal-like structure: humps and cups of a smaller scale superimposed on those of a larger scale. Thus, the otherwise smooth flame front is wrinkled by the hydrodynamic instability, and a cascade of cells continuously develops in the course of the front expansion. That is, when the curvature of the expanding flame becomes large compared to the cutoff length scale, the flame front becomes unstable and breaks up into smaller cells, which subsequently grow until their length scale again becomes large enough to result in a new generation of cells.

We shall discuss the propagation of the flame front from three aspects defining the front: mean radius, propagation velocity and burning intensity. Furthermore, the mean radius of the flame front $R$ is evaluated by three different methods, as illustrated in Figures 5-2 (a-c). Here MD refers to the mean distance of the flame front from the
domain center, while AR and CR are derived from the area $A$ enclosed by the flame front, as $\sqrt{A/\pi}$, but with $A$ determined differently. Specifically, for AR, $A$ is simply counted as the number of grids enclosed by the flame front, while for CR, $A$ is determined from consumption of the fresh mixture. That is, the mass of the consumed fresh mixture at a specific time, $m'_u$, is computed through integrating the component change over the entire domain, and accordingly, $A$ is calculated as $m'_u/\rho_0$ by considering thermal expansion. Figure 2d shows that these three methods yield an identical result of $R \sim t$.

The instantaneous (downstream) propagation velocity $V$ is extracted from the correlation of $R \sim t$. At a certain time, $R$ is locally fitted by a polynomial with respect to $t$ over a range of 0.1 ms, which analytically yields the instantaneous propagation velocity. Figure 5-3 presents the instantaneous propagation velocities derived from the three sets of data. The solid line, labeled with “Full set”, is based on the simulation results of all $R \sim t$ with the time interval of 2 $\mu$s. The stars, labeled with “Quarter set”, adopt only 25% of the simulation results of $R \sim t$ with the fourfold time interval of 8 $\mu$s. The circle-solid line, labeled with “Half domain”, is generated from the simulation conducted in a 2.5×2.5 cm$^2$ domain. For the numerical noise, the stars closely distribute across the solid line, indicating that the recorded $R \sim t$ is dense enough to cancel out the numerical noise within the differentiation process. To understand the influence of the physical boundary, the solid and circle-solid line are shown to collapse onto a single curve before 0.7 ms.
corresponding to a flame diameter of 1.9 cm, or 75% of the domain length of 2.5 cm; hence, the regime is free of boundary effects.

It is further seen that the propagation velocity remains constant until 0.3 ms, at which time it quickly increases and indicates the onset of the hydrodynamic instability. Furthermore, the curve displays a wavy shape after 0.8 ms, demonstrating that cell formation leads to pulsating propagation of the global flame front. This feature was reported in previous simulations using the Sivashinsky equation [7, 10], but was not observed experimentally due to the much coarser temporal resolution of the experiment. To substantiate this assessment, we have conducted an independent experiment following the same procedure as that of [16] and measured the temporal variation of the mean radius of the expanding spherical flame. The instantaneous propagation velocity is then deduced through the same numerical procedure applied to the DNS results. Figure 5-4 shows the propagation velocity fitted from the experimental and DNS results with a typical experimental time resolution of 0.03 ms. It is then seen that these two propagation velocities scatter to a similar extent, and the fine-scale waviness is largely suppressed.

To understand the globally pulsating nature of the flame propagation, the propagation velocities of different segments of the flame front are spatially and temporally resolved. Figure 5-5 shows the local shape and propagation velocity of the
flame front at 1 ms, with every segment of the flame front indexed by its azimuthal angle with respect to the domain center. It is seen that the flame front is composed of various cells, and hydrodynamic instability causes different segments within the same cell to propagate at different velocities, which peak at the center and achieve local minima at the edge. Figure 5-6 shows the temporal evolution of the local propagation velocity at three different azimuthal angles, demonstrating that their behaviors are consistent with that of the global flame front, and hence implying that the flame front can be treated as an ensemble of flame segments with similar propagation characteristics. This observation is physically reasonable in that the flame front is surrounded by a uniform fresh mixture, and hence different segments would propagate into the same environment and as such should behave similarly. Results from Figures 5-5 and 5-6 therefore suggest that the flame front is synthesized from unit cell structures such that pulsation of the global flame is a consequence of the pulsation of the individual segments.

Figure 5-7 focuses on the propagation of a single segment, which correlates with the instantaneous shape and propagation velocity of a segment with an azimuthal angle of 1.35 radians. It is seen that pulsation in the propagation velocity coincides with the development of the cell structure. As illustrated in Figure 5-5, hydrodynamic instability imposes varied influence on the cell structure, accelerating the center but decelerating the edge. For the segment between the center and edge, the net effect depends on the relative
distance with respect to the center and edge. At an early stage of cell development, the cell length is small, and most segments within the cell structure are located close to the center. Conversely, at a late stage, the cell length is significantly enlarged, and most segments within the cell structure are distributed closer to the edge rather than the center. In a statistical sense, a segment typically initially accelerates and ends up decelerating. Eventually, when the cell length becomes larger than the cut-off length scale of the hydrodynamic instability, fast and slow segments cannot be maintained within the same cell structure. The cell breaks up into a few smaller cells of a new generation, and the process repeats anew.

The burning intensity of the flame front can be represented by the mean heat release rate, $\bar{hr_m}$, and is plotted in Figure 5-8 (a), with the values being properly normalized. A 1-D planar stoichiometric hydrogen-air flame at eight atmospheres is simulated by PREMIX, and the heat release rate at the location where the mass fraction of H$_2$O equals half of the equilibrium value is used in the normalization. It is seen that after 0.8 ms, the normalized burning intensity varies in a tight range of $1.00 \pm 0.01$. This fact substantiates the assumption that, for the present near-unity Lewis number mixture, the local burning rate is invariant, and hence identical to that of the planar flame. Consequently, the self-acceleration behavior is solely caused by the increased surface area density and therefore
is a geometrical property of the flame front. This statement is further scrutinized in Figure 5-8 (b), in which we have plotted the normalized flame speed,

\[
\bar{V} = \frac{V / FL}{s_L / 2\pi R}
\]

(5-1)
defined as the flame speed \(V\) divided by the length of the wrinkled surface \(FL\), normalized by the independently computed laminar flame speed \(s_L\) divided by the circumference of the global flame \(2\pi R\). It is seen that this parameter is almost unity, hence again substantiating the concept that the local burning intensity is not affected by the wrinkling and that the increase in the global flame speed is simply due to the increase in the flame surface through wrinkling. The slight reduction from unity, by \(\sim 2\%\), is likely caused by residual stretch effects. Indeed, an independent assessment of the mixture Lewis number [23, 24] yielded a value of 1.1, which is slightly larger than unity. Since the expanding global flame has a positive curvature, while the local flame fronts also tend to be dominated by positive curvature due to Huygens propagation [25], the net effect of positive curvature and \(Le > 1\) mixture is a reduction in the propagation velocity. Furthermore, an independent evaluation of the effect of stretch on the expanding flame before the onset of instability, using the expression of [24] with \(Le = 1.1\) and a global activation energy of 40 kcal/mol [25], yields a reduction in the flame speed of about 1\%,
which captures the same range of reduction shown in Figure 5-8. The relatively small stretch effect, for \( Le = 1.1 \), is amplified by the small flame thickness at the elevated pressure of eight atmospheres which reduces the unbalanced diffusional-thermal effects.

### 5.4 Extraction of Self-Acceleration Exponent and Fractal Dimension

The above results show that the instantaneous propagation of the flame front is not monotonically accelerating; rather the propagation is pulsating and as such a power-like formula only describes the long term average behavior of the propagation. Consequently, the self-acceleration exponent \( \alpha \) should be extracted from either the mean radius \( R \) or the mean propagation velocity \( V \). For the former, \( \alpha \) is fitted by the formula \( R = R_0 + A t^\alpha \) as in previous studies [7-13], while, for the latter, \( \alpha \) is defined by the formula \( \ln V = \ln(A \alpha) + (\alpha - 1) \ln(t) \). Mathematically, these two formulas are equivalent, but numerically the second correlation could be more reliable because it involves fewer parameters in the fitting. Furthermore, a linear fitting is easier achieved than a nonlinear one. It is then of interest to note from Figures 5-9 and 5-10 that nearly identical acceleration exponents of 1.220 and 1.216 are obtained from these distinct fitting formulas over 0.8 to 1.4 ms, for which the hydrodynamic instability is well established and simulation results are not contaminated by boundary effects. This observation therefore confirms that the information contained in the original flame front is well
preserved in the propagation velocity.

The methodology of box-counting [26] is applied to identify the fractal excess, $\Delta D$, of the flame front, and the representative result at $t=1\text{ms}$ is presented in Figure 5-11. The box-counting method measures the total length of the flame front, $l$, by the ruler of length $\varepsilon$, and the length of the flame front should increase with decreasing $\varepsilon$ since more fine structures are captured. Quantitatively, the fractal excess of the flame front is defined as the response of enlarged flame length with respect to the ruler shrinking,

$$\Delta D = -\lim_{\varepsilon \to 0} \frac{\ln(l)}{\ln(\varepsilon)}$$  \hspace{1cm} (5-2)

For a physically real object, the ruler length cannot approach infinitely small but has to be bounded by a certain threshold. In Figure 5-11, plotting $l$ and $\varepsilon$ on a log-log scale gives rise to an apparent linear regime, indicating well-defined fractal structure. The boundaries of this regime are decided by examining the quality of linear fitting, characterized by the coefficient of determination, $R^2$. The upper and lower boundaries are iteratively adjusted until achieving $R^2$ larger than 0.99. The lower boundary of the linear regime is around 50 flame thickness, $\delta$, which corresponds to the cut-off length scale of hydrodynamic instability [27]. The cell pattern fails to be established below such a threshold, and hence the fractal structure cannot be observed. The upper boundary is 10 times the lower one and about 20% of the flame radius, beyond which the detailed structure of flame front will not be resolved. The fractal dimension $D_f$ of the flame front
is presented in Figure 5-12. After 0.8 ms, the fractal dimension of the flame front periodically varies from 1.05 to 1.09, repeating the same pattern four times until 1.5 ms. The oscillation in the fractal dimension is consistent with the wavy shape of the instantaneous propagation velocity and is again attributed to the development of cell structures. The fractal dimension fluctuates around a value of 1.07, which could be estimated as the average fractal dimension D.

5.5 Conclusions

The self-accelerated propagation of a cylindrical stoichiometric hydrogen-air flame at eight atmospheres is studied by direct numerical simulation of the Navier–Stokes equations with detailed chemistry. The instantaneous propagation is shown to be intermittent and globally pulsating due to development of the cell structure caused by the hydrodynamic instability. The instantaneous burning intensity is demonstrated to be invariant after the hydrodynamic instability is established, which substantiates the hypothesis that the self-acceleration is solely a consequence of the increased surface area of the flame front due to the hydrodynamic wrinkling. The long-term average flame propagation is described by a power-law dependence, with an exponent of 1.22 extracted from the evolution of the flame radius and propagation velocity. The fractal structure of the flame front is well captured by the fractal analysis of the box-counting, yielding a fractal dimension around 1.07.
References


Figure 5-1. Flame front evolution at selected time instants simulated by direct numerical simulation.
Figure 5-2. Mean radius of flame front identified by different methods.
Figure 5-3. Instantaneous propagation velocity of the flame front fitted from full set, half domain and a quarter set of data.
Figure 5-4. Instantaneous propagation velocity of the flame front fitted from experimental and DNS data.
Figure 5-5. Local shape and propagation velocity of the flame front at 1 ms. Stage I and II: early and late stages of cell development.
Figure 5-6. Instantaneous propagation velocity of representative segments of the flame front.
Figure 5-7. Instantaneous shape and propagation velocity of a representative segment of the flame front.
Figure 5-8. Instantaneous burning intensity and normalized propagation velocity of the flame front.
Figure 5-9. Self-acceleration exponent extracted from the instantaneous mean radius.
Figure 5-10. Self-acceleration exponent extracted from the instantaneous propagation velocity.
Figure 5-11. Fractal analysis of the flame front by box-counting method.
Figure 5-12. Fractal dimension of the flame front estimated by box-counting method.
Chapter 6 Skeletal Reaction Model Generation, Uncertainty Quantification and Minimization: Combustion of Butane

6.1 Introduction

Detailed kinetic modeling is a useful tool to probe intricate fuel combustion and flame phenomena. The modeling approach usually involves the use of a detailed reaction model consisting of the relevant chemical species and elementary reactions that may participate in sequential and parallel kinetic processes of fuel oxidation. In such a model, the rate parameters are usually derived from experimental rate measurements, reaction rate theories, or, in many cases, estimations from analogous reactions. In all cases, the values of the rate parameters can be uncertain to various extents [1]. Together, the parameter uncertainty causes the prediction to be correspondingly uncertain—an issue that has received an increased attention and has been discussed in a variety of context in recent years (see, e.g., [2-25]).

Meanwhile, recent efforts directed at developing reaction models for practical liquid fuels and their surrogates have led to the emergence of large models, some of them may contain $O(10^{3-4})$ species and $O(10^{4-5})$ reactions (see, e.g., [26]). The use of these detailed models in computational fluid dynamics (CFD) introduces another problem. That is, they are too large to be practical for CFD applications and must be reduced in size and complexity before they can be used [27, 28]. Consequently, various model reduction
strategies have been proposed (see, e.g., [28-30]). In general, the methods of model reduction may be categorized into skeletal reduction and time scale analysis. Skeletal reduction eliminates unimportant species and reactions, which can be achieved by sensitivity analysis [30-33], principal component analysis [34], Jacobian analysis [32], optimization [3], detailed reduction [35], directed relation graph (DRG) ([36-38]), DRG with error propagation [39], and DRG-aided sensitivity analysis (DRGASA) [40, 41]. Time-scale analysis identifies fast species as well as reactions, and describes their time evolutions by algebraic equations. Methods of time-scale analysis are primarily based on quasi-steady-state (QSS) and partial equilibrium (PE) assumptions [42-46]. Several approaches to identifying the QSS species have been proposed [45-52]. Other, and perhaps more systematic approaches to time-scale analysis include intrinsic low-dimensional manifolds (ILDM) [53] and computational singular perturbation (CSP) [54-57].

In the present study, we propose an improved model reduction strategy by integrating the processes of skeletal reduction with model optimization and uncertainty quantification. Specifically, the derived skeletal model is subject to parameter optimization to improve its predictiveness. In addition, we explore the correlation of model size and uncertainty. Models of different sizes were generated from a detailed chemistry model, USC Mech II, [58] using n-butane and i-butane combustion as
examples. The uncertainties of the skeletal models are quantified by the spectral expansion technique [20] and correlated to model size.

6.2 Methodology
6.2.1 Skeletal Reduction
A detailed reaction model is composed of three types of species: critical ones, nonessential ones, and marginal ones. For a given simulation, critical species involve reaction channels sensitive to the simulation results, while nonessential species only participate in channels having little to no contribution. The category of species is conditional, subject to the specific simulation circumstance. A successful skeletal reduction retains all critical species, eliminates all nonessential species, and properly deals with the marginal ones. The importance of species can be assessed by two types of method, examining the species conversion flux (e.g., [36-39]) or sensitivity analysis [30-32, 41]. These two methods have their respective advantages and disadvantages. Flux analysis is affordable computationally and able to identify nonessential species efficiently. However, it can misestimate the importance of marginal and critical species. Sensitivity analysis quantifies the importance of species with better accuracy but it often requires prohibitive computational costs, hence preventing its application in reducing large models. Here, the skeletal model reduction adopts a two-stage procedure [41]: the detailed model is first reduced by flux analysis to an intermediate-size model from which
a final skeletal model is generated by sensitivity analysis. In the present study, this two-stage strategy is conducted by combining DRG with DRGASA.

Both DRG and DRGASA have been discussed in detail elsewhere [36-38, 41], and as such are presented here only briefly. DRG represents a chemistry model by a directed relation graph, whose nodes are species and the width of the edge from node $m$ to $n$, $r_{mn}$, is calculated as:

$$r_{mn} = \frac{\sum_{i=1}^{N_R} \nu_{i,m} \omega_i \delta_i}{\sum_{i=1}^{N_R} \nu_{i,m} \omega_i}$$

and the subscripts $m$ and $n$ identify the species. Additionally, $N_R$ is the total number of reactions, $\nu_{i,m}$ the stoichiometric coefficient of species $m$ in the $i^{th}$ reaction, and $\omega_i$ the net reaction rate of the $i^{th}$ reaction. The value of $r_{mn}$ quantifies the importance of species $n$ to the production of species $m$. For a given user-specified threshold $\epsilon$, skeletal reduction is conducted by truncating edges narrower than $\epsilon$. A species is eliminated when all edges linking to it are removed during this process. With increasing $\epsilon$, an increased number of species is removed. The critical $\epsilon$ value, corresponding to the reduction of a certain species, is utilized as the DRG index of this species. An intermediate-size skeletal model is generated by removing species with a small DRG index, typically less than 0.1, and the
remaining species are further examined in the subsequent sensitivity analysis through DRGASA. In DRGASA, species with a large DRG index, greater than 0.5 in this work, are considered to be critical and kept in the final skeletal model without sensitivity test. In contrast, the importance of a species with a marginal DRG index is quantified by computing the difference in model predictions with and without this species. The examined species are ranked by their importance, and model reduction is carried out by successively eliminating species of the least importance, until the resulting model cannot satisfy a prescribed accuracy requirement.

6.2.2 Model Optimization and Uncertainty Quantification

Removal of reaction pathways can lead to quantitative changes in the model prediction. Because the dimensionality of the reduced model generally remains to be large, it should be possible to constrain the reduced model against the detailed model by an error minimization procedure. Rate coefficients subject to the minimization procedure are selected using a one-at-a-time sensitivity analysis [20]. For each computational experiment the uncertainty-weighted sensitivity coefficient $S_{r,k}$ is defined as,

$$S_{r,k} = \frac{d \ln \eta_r}{d \ln A_i} \ln f_i$$  \hspace{1cm} (6-2)
where \( \eta_{\text{pr}} \) is the response, \( A_i \) and \( f_i \) are the Arrhenius pre-exponential factor and the uncertainty factor of the \( i^{\text{th}} \) rate parameter, respectively. The active rate parameters are selected here as those with \( S_{r,i} > \max(S_{r,i})/10 \).

For illustration purposes, the responses selected here are ignition delay time and laminar flame speed. Ignition delay time simulations were performed using a kinetic integrator based on the DVODE solver [59] and the chemical production terms provided by ChemKin II [60]. Laminar flame speed was computed using Sandia PREMIX [61] and TRANSPORT [62] with modifications from [63].

Model constraint adopts the method of uncertainty analysis using polynomial chaos expansions (MUM-PCE) [20], which is summarized here. It is assumed that the uncertain parameters in the model can be expressed as a random vector \( \mathbf{X} = \mathbf{x}^{(0)} + \xi \mathbf{x}^{(l)} \), where \( \mathbf{x}^{(0)} \) is the factorial variable vector whose elements are

\[
\ln \left( \frac{\theta_i / \theta_{i,0}}{\ln f_i} \right) = x_i^{(0)}
\]

where \( \theta_i \) is the \( i^{\text{th}} \) active parameter and \( \theta_{i,0} \) its nominal value. \( \xi \) is a vector of independent, identically distributed (i.i.d) normal random variables with mean 0 and variance 1. \( \mathbf{x}^{(l)} \) is a transformation matrix, so that \( \mathbf{X} \) follows a multivariate normal distribution with mean \( \mathbf{x}^{(0)} \) and covariance matrix \( \Sigma = \mathbf{x}^{(l)} \mathbf{x}^{(l)T} \).
MUM-PCE applies Bayes’ Theorem to determine the joint probability density function (PDF) of the active parameters, which results in the following PDF for the constrained rate parameters,

$$\ln P_x(x) \sim - \left[ \sum_{r=1}^{N_e} \left( \frac{\eta_r(x) - \eta^\text{det}_r}{\sigma_r^{\text{tol}}} \right)^2 + 4 \sum_{r=1}^{N_e} x_r^2 \right] \quad (6-4)$$

Here, $\eta_r(x)$ is the model prediction expressed as a function of the rate parameters $x$, $N_e$ the number of computational experiments, $N_r$ the number of active variables, $\eta_r^\text{det}$ the detailed model prediction, and $\sigma_r^{\text{tol}}$ the error tolerance between the detailed and reduced model predictions. For the present analysis, $\sigma_r^{\text{tol}}$ is taken to be 2 cm/s for laminar flame speeds and 0.2 in the natural logarithm of the ignition delay time in microsecond, which is comparable to the experimental uncertainty.

Equation 6.4 can be approximated by a multivariate normal distribution, which will then have an $x^{(0)}$ that best reproduces the detailed model, and a $\Sigma^*$ that best reproduces their uncertainty. $x^{(0)}$ is found by the mode of the PDF in Eq. (6-4), equivalent to the least-squares optimization problem

$$x^{(0)*} = \arg \max_x \ln P_x(x) \quad (6-5)$$

and solved using the LMDIF solver [64]. $\Sigma^*$ is identified by linearizing the model predictions in the vicinity of $x^{(0)*}$, which yields
\[
\Sigma^* = \left[ \sum_{i=1}^{M} J_r J_r^T (\sigma_r^{(0)})^{-1} + 4I \right]^{-1}
\]  

(6-6)

where \( J_r \) is the gradient of \( \eta_r(x^{(0)}) \). \( x^{(1)} \) is then determined through the Cholesky factorization of \( \Sigma^* \).

To reduce the computational complexity of Eqs. (6-5) and (6-6), the method of solution mapping \([1, 65]\) was used, in which model predictions are expressed as polynomials with respect to the reaction rate parameters, \( \eta_r(X) = X^T b_r + a_r^T X + \eta_r^{(0)} \), where \( a_r \) and \( b_r \) are the first and second derivatives of \( \eta_r \), and \( \eta_r^{(0)} \) is the nominal prediction of the model. The derivatives are calculated using a method based on sensitivity analysis \([66]\). For a given value of \( x^{(0)} \) and \( x^{(1)} \), the predictions \( \eta_r \) can be expressed in terms of the (i.i.d.) basis random variables \( \xi \), \( \eta_r(\xi) = \xi^T \hat{\beta}_r \xi + \hat{\alpha}_r^T \xi + \eta_r^{(0)}(x^{(0)}) \), with \( \hat{\beta}_r = x^{(0)T} b_r, x^{(1)} \), and \( \hat{\alpha}_r = x^{(1)T} J_r \). The uncertainty \( \sigma_r \) is calculated by taking the variance,

\[
\sigma_r^2 = E(\eta_r^2) - E^2(\eta_r) = \sum_{i=1}^{N_r} \hat{\alpha}_r^2 + 2 \sum_{i=1}^{N_r} \hat{\beta}_r^2 + \sum_{i=1}^{N_r-1} \sum_{j=i+1}^{N_r} \hat{\beta}_r^2
\]  

(6-7)

To calculate the uncertainty in the reduced models before optimization, \( x^{(0)} = 0 \) and \( x^{(1)} = I_{N_r} \), \textit{i.e.}, the \( N_r \)-dimensional identity matrix, and so \( \hat{\beta}_r = b_r \), \( \hat{\alpha}_r = a_r \). The prediction uncertainty is given by \( \sigma_r^2 = \sum_{i=1}^{N_r} a_r^2 + 2 \sum_{i=1}^{N_r} b_r^2 + \sum_{i=1}^{N_r-1} \sum_{j=i+1}^{N_r} b_r^2 \).
6.3 Results and Discussion

6.3.1 Skeletal Model Generation and Analysis

The auto-ignition and flame propagation of \( n \)-butane-air and \( i \)-butane-air mixtures were simulated using USC Mech II [58]. The model was developed for high-temperature oxidation of \( \text{H}_2 \), \( \text{CO} \) and \( \text{C}_1-\text{C}_4 \) hydrocarbons and consists of 111 species and 784 reactions. The thermodynamic and mixture conditions considered cover pressure in the range of \( 1 \leq p \leq 20 \text{ atm} \), initial temperature \( 800 \leq T_0 \leq 1500\text{K} \) for auto-ignition, inlet temperature \( T_{in} = 300 \text{ K} \) for laminar flame speed, and equivalence ratio \( 0.6 \leq \phi \leq 1.5 \).

The skeletal reduction was first conducted through the use of DRG, as discussed before. From detailed simulations, the temperature and species concentrations were sampled from typical temporal moments of the auto-ignition process as well as spatial locations within the laminar premixed flame. Figure 6-1 presents the correlation between the number of species, \( N_s \), in the resulting skeletal model and the threshold value \( \epsilon \). In previous DRG studies [36-38], a threshold value of 0.1 was shown to be a reasonable cutoff. In the current work, however, an \( \epsilon \) value of 0.1 can only remove around ten species, which indicates the compact nature of USC Mech II. As such, no species is directly eliminated by DRG in this work.

In the DRGASA process that followed, ignition delay times \( \tau \) and laminar flame speeds \( s_u^* \) predicted by the detailed model were taken as the reference values. Spanning all thermodynamic conditions considered, DRGASA calculates the maximum percentage
error, $err_{max}$, in computing these global responses caused by the removal of each species. Accordingly, a ranking list of species is decided by their impact on model predictions. Figure 6-2 correlates the error of model prediction to the model size. By combining the information from auto-ignition and laminar premixed flame, two sets of three skeletal models with different levels of accuracy are generated; one set each for $n$-butane and $i$-butane, as shown in Table 6-1. The $n$-1 and $i$-1 models are quite close to the detailed model in terms of their predictions for the conditions tested. In contrast, the inferior performance of the more reduced versions may be attributed to over-truncation and thus missing critical reaction pathways under certain circumstances.

The ranking lists of species demonstrate an important property of high-temperature hydrocarbon oxidation chemistry. A substantial fraction of the reactions and species identified as critical to flame propagation and induction zone of the ignition delay overlap. Take $n$-butane as an example. Figure 6-3 presents the number of retained species common to skeletal models obtained individually from ignition and flame targets ($N_{v,c}$). Independent of the model size, around 90% of the species are found to be critical to both combustion properties. For a model of 50 species, those that are unique to auto-ignition are CH$_3$CCH$_2$, $i$C$_3$H$_7$, $n$C$_4$H$_5$, $i$C$_4$H$_7$ and CH$_2$CHCHCHO and those to flames are CH, CH$_2$OH, C$_2$H, H$_2$CC and CH$_3$CO. The intersection of the ranking lists emphasizes the importance of the small molecule chemistry in both cases, and the species unique to the
auto-ignition process correspond to a particular set of C$_3$-C$_4$ fragments of importance to the initial fuel breakdown. Comparing n-butane with i-butane, around 77% of the species retained are identical, as shown in Figure 6-4. For a 50-species model, the species unique to n-butane are nC$_3$H$_7$, C$_3$H$_8$, nC$_4$H$_5$, iC$_4$H$_5$, C$_4$H$_8$-2, pC$_4$H$_9$, sC$_4$H$_9$, CH$_2$CHCHCHO, and n-C$_4$H$_{10}$ and those unique to i-butane are CH$_2$OH, CH$_3$CO, pC$_3$H$_4$, CH$_2$CHCO, CH$_3$COCH$_3$, iC$_4$H$_9$, tC$_4$H$_9$, C$_6$H$_5$, and i-C$_4$H$_{10}$. The two models share the same chemistry of small hydrocarbons C$_1$-C$_2$, CO and H$_2$, and differ in fuel-specific reaction kinetics especially for the ignition phenomenon.

6.3.2 Skeletal Model Optimization

Skeletal models n-1 and i-1 are constrained against the detailed model in 54 combustion targets, including 45 ignition delay times and 9 flame speeds. They span the same range of thermodynamic conditions and stoichiometry where these skeletal models are derived. The predictions of the unconstrained and constrained skeletal models are compared to those of the full model, as shown in Figure 6-5. Clearly, the performances of the skeletal models are improved by the constraining process, which reduced the maximum error from around 25% to 6% for the ignition delay and 2 to 1% for the flame speed, as shown in Table 6-1. For n-butane and i-butane, the rate coefficients of 103 and 97 reactions are impacted by the constraining process, respectively. Figures 6-6 shows that most of the impacted $A$ factors are within 20% of the original value, well within their range of
uncertainty. Optimization of other skeletal models listed in Table 6-1 was not attempted, as these models can have missing reaction pathways, leading to a change in the underlying physics and thus reduced general predictability.

6.3.3 Size-Dependent Model Uncertainty

We take this opportunity to explore a related question concerning model uncertainty: the correlation between model size and uncertainty. Intuitively, the model uncertainty defined within the framework of MUM-PCE should increase with an increase in the model size, namely the number of model parameters. That is, the individual uncertainties of these parameters have a cumulative effect on the overall model uncertainty. This intuitive understanding is, in fact, only conditionally correct. The uncertainties of the sample skeletal models listed in Table 6-1 in predicting the ignition delay are shown in Figure 6-7. The uncertainties of models \( n-1 \) (without optimization) and \( n-2 \) are generally similar, and the same observation also holds for the \( i-1 \) (without optimization) and \( i-2 \) models. Yet for the skeletal model \( n-3 \) and \( i-3 \) with the smaller size, the model uncertainties can be both larger and smaller than those of the larger models, depending on the specific simulation scenarios. Similar observations can be made for the prediction of laminar flame speeds as well, as shown in Figure 6-8.

The non-monotonic size-dependent model uncertainty may be understood by considering an artificial model of \( N-1 \) parameters. This model gives some prediction \( \eta_{i,j} \),
with first and second derivative vectors $a'_r$ and $b'_r$. The uncertainty $\sigma'_r$, before optimization, in this prediction is given by

$$\sigma'^2_r = \sum_{i=1}^{N-1} a'^2_{r,i} + 2 \sum_{i=1}^{N-1} b'^2_{r,ij} + \sum_{i=1}^{N-2} \sum_{j=i+1}^{N-1} b'^2_{r,ij}$$  \hspace{1cm} (6-8)$$

If the model is enlarged by adding an $N^{th}$ parameter, it would now have a prediction $\eta_{r,0}$ and updated first and second derivative vectors $a_r$ and $b_r$. The updated model uncertainty $\sigma_r$ will be

$$\sigma^2_r = \sum_{i=1}^{N} a^2_r + 2 \sum_{i=1}^{N} b^2_r + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} b^2_{r,j}$$  \hspace{1cm} (6-9)$$

If the $N^{th}$ parameter does not influence the prediction and the sensitivity coefficients of the first through the $(N-1)^{th}$ parameters, $a_r$ and $b_r$ share the corresponding components with $a'_r$ and $b'_r$. The variance $\sigma'^2_r$ can be split into

$$\sigma'^2_r = \sigma'^2_r + a^2_{r,N} + 2b^2_{r,NN} + \sum_{i=1}^{N-1} b^2_{r,jN}$$  \hspace{1cm} (6-10)$$

which implies the model uncertainty must increase or at least remain constant with the model size, because of the non-negative term $a^2_{N,N} + 2b^2_{N,NN} + \sum_{i=1}^{N-1} b^2_{N,jN}$ . If the $N^{th}$ parameter is weakly coupled to the existing $N-1$ parameters, the model uncertainty will increase or at least remain constant. In contrast, if the $N^{th}$ parameter impact the sensitivities of the first through $(N-1)^{th}$ parameters with respect to the model prediction, the values of $a_r$ and $b_r$ must be identified anew and thereafter the behavior of $\sigma_r$ and
\( \sigma_r' \) cannot be predicted \textit{a priori}. In other words, the dependence of reaction model uncertainty on the model size is subject to the extent of coupling within model parameters. For the case of strong coupling, the sensitivity of a particular combustion response to the rate parameters may be substantially affected by pathway truncation. Such a condition is indicative of the truncation of critical reaction pathways during model reduction. Hence, the uncertainty of a reduced model, when compared to that of a full model, is indicative of the truncation of the necessary physics in model reduction, as expected.

To verify the above argument in real combustion system, we conducted a prototype study on the auto-ignition of stoichiometric \( n \)-butane-air mixture under atmospheric pressure, with an initial temperature of 1000 K, where the model uncertainty non-monotonically changes, first decreasing with the model size and increases afterwards. The \( n \)-1 model (without optimization) contains all species and reactions contained within the \( n \)-2 model, which in turn contains the species and reactions within the \( n \)-3 model. The set of extra reactions contained in \( n \)-1 but not in \( n \)-2 and those contained in \( n \)-2 but not in \( n \)-3 are termed as \( R_{1-2} \) and \( R_{2-3} \), respectively. The coupling extent of the \( i^{th} \) reaction with other reactions is investigated by comparing the magnitude of the \( a_i \) and \( b_j \) terms. A strong coupling reaction will be represented by a large \( b_j \) term. For reactions within sets \( R_{2-3} \) and \( R_{1-2} \), the magnitudes of the corresponding \( a_i \) and \( b_j \) are illustrated in Fig. 6-9.
The first order coefficients are presented as \(|a_i|\) and the second order coefficients by the average value, \(|\hat{b}_{ij}| = 1/\sqrt{N} \sum_{j=1}^{N} |b_{ij}|\). In the reaction set R_{2-3}, the \(a_i\) and \(b_{ij}\) values are comparable, indicating strong coupling between the reactions. This explains the large change in the prediction uncertainty between the models \(n-2\) and \(n-3\). In the reaction set R_{1-2}, the \(a_i\) values are much larger than the \(b_{ij}\) values, and there is correspondingly a small increase in the prediction uncertainties from models \(n-2\) to \(n-1\). That is, the model uncertainty increases, but only slightly, as the model size is increased.

The above observation leads to a question not previously addressed, but it requires some consideration. Here, that is, whether the model prediction uncertainty is convergent with respect to model size. We note that a fully complete reaction model must consider all binary interactions. For USC Mech II with 108 reactive species, a full, combinatorial description must consider > 10,000 reactions if all of them have only one channel. Of course, each reaction can have and is often associated with a very large number of pathways (and those considered in a conventional reaction models are only the lower-lying potential energy paths). In that regard, all detailed reaction models have already been truncated or reduced to an extent at the onset of model building. Theoretically, additional terms added to Eq. (6-9) due to an increasing number of reactions \(N\) should lead to a convergent sum. This can be proved mathematically by comparing the decay rate of the series of Eq. (6-9) with that of a convergent series. Figure 6-10 compares the
decay rates of \( a_r \) and \( b_r \) with the reciprocals of positive integer numbers \((i^{-1}, i=1,2,\ldots,\infty)\).

Note that the series sum of the reciprocals of square numbers \( \sum_{i=1}^{\infty} i^{-2} \) is convergent. The fact that \( a_r \) and \( b_r \) decay faster than \( i^{-1} \) indicates that Eq. (6-9) is convergent for the \( n \)-butane oxidation problem considered. Of course, we expect the comparison to hold also for other combustion problems.

### 6.4 Conclusions

Reduced chemistry models for \( n \)-butane and \( i \)-butane combustion are derived from USC Mech II by skeletal reduction and model optimization. The yielded models reproduce the prediction of the detailed model. The rate coefficients of the skeletal model are adjusted systematically within their uncertainty bounds using MUM-PCE. The relationship between the model size and the uncertainty of its predictions is explored using three sample skeletal models of different sizes. The completeness, and therefore the reliability, of a reduced model can be assessed by the behavior of the uncertainty of its predictions with respect to the model size. This behavior can also be assessed by the second derivatives of the model predictions with respect to the rate parameters, or in other words the inter-parameter coupling. As long as reactions being removed from the reduced model do not exhibit this second-order coupling with reactions that remain, the model prediction uncertainty increases with an increase in the model size in principle, and this
uncertainty should always be convergent as the model approaches completeness. For a model which has reactions removed that exhibit second-order coupling with the remaining reactions of the model, the behavior of the prediction uncertainty with respect to model size cannot be predicted.
References


## Table and Figures

**Table 6-1.** Summary of skeletal models.

<table>
<thead>
<tr>
<th>Model</th>
<th>$N_s$</th>
<th>$N_R$</th>
<th>$err_{\text{max}}$ (%)</th>
<th>$\tau$</th>
<th>$s_u$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$-butane</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$n$-1</td>
<td>49</td>
<td>384</td>
<td>27.6/6.3$^c$</td>
<td>2.3$^b$/1.1$^c$</td>
<td></td>
</tr>
<tr>
<td>$n$-2</td>
<td>43</td>
<td>309</td>
<td>60.4</td>
<td>3.8</td>
<td></td>
</tr>
<tr>
<td>$n$-3</td>
<td>31</td>
<td>152</td>
<td>100.0</td>
<td>11.1</td>
<td></td>
</tr>
<tr>
<td>$i$-butane</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$i$-1</td>
<td>54</td>
<td>402</td>
<td>24.7$^b$/6.4$^c$</td>
<td>2.4$^b$/1.2$^c$</td>
<td></td>
</tr>
<tr>
<td>$i$-2</td>
<td>47</td>
<td>343</td>
<td>61.3</td>
<td>5.0</td>
<td></td>
</tr>
<tr>
<td>$i$-3</td>
<td>38</td>
<td>233</td>
<td>100.0</td>
<td>12.6</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ The relative error reported is selected as the worst case.

$^b$ Before optimization.

$^c$ After optimization.
Figure 6-1. Dependence of number of species in a skeletal model on the threshold value as determined by DRG based on auto-ignition delay and laminar flame speed of \( n \)-butane-air and \( i \)-butane-air mixtures over the range of thermodynamic and mixture conditions considered (see text).
Figure 6-2. Dependence of maximum percentage deviation from the full model on the model size, calculated for auto-ignition delay and laminar flame speed of n-butane-air and i-butane-air mixtures over the range of thermodynamic and mixture conditions considered (see text).
Figure 6-3. Number of common species versus the total number of species in the skeletal models, developed for auto-ignition delay and laminar flame speed of \( n \)-butane-air mixtures over the entire range of thermodynamic and mixture conditions considered. Symbols are computational data; the line represents a linear fit to the data.
Figure 6-4. Number of common species versus the total number of species in the skeletal models developed for auto-ignition delay of \( n \)-butane-air and \( i \)-butane-air mixtures over the entire range of thermodynamic and mixture conditions considered. Symbols are computational data; the line represents a linear fit to the data.

\[ N_{s,c} = 0.77 N_s \]
Figure 6-5. 45° degree diagonal plot of ignition delays predicted by the skeletal models versus the detailed model (left panel) and laminar flame speeds as a function of the equivalence ratio (right panel) for \(n\)-butane-air and \(i\)-butane-air mixtures using models \(n\)-1 and \(i\)-1, respectively. Star and circle represent the predictions made by the skeletal models with and without optimization; the line represents the prediction made by the detailed model.
Figure 6-6. Changes in the $A$ factors in the constrained skeletal models $n$-1 (top) and $i$-1 (bottom). $i$ represents the reaction index.
Figure 6-7. Uncertainties of three skeletal models for $n$-butane-air (a) and $i$-butane-air (b) mixtures in predicting ignition delays. Symbols represent the standard deviation of model prediction, $\sigma$, calculated for auto-ignitions at pressures of 1, 10 and 20 atm, initial temperature from 1000 to 1400 K and equivalence ratio from 0.6 to 1.5; lines are drawn to guide the eye.
Figure 6-8. Uncertainties of various skeletal models for $n$-butane-air (left panel) and $i$-butane-air (right panel) mixtures in predicting flame speeds. Symbols represent the standard deviation of model prediction, $\sigma$, calculated for premixed flames at pressures 1, 10 and 20 atm, inlet temperature of 300 K and equivalence ratio from 0.6 to 1.5; lines are drawn to guide the eye.
Figure 6-9. Magnitude of derivative of reaction sets $R_{2,3}$ and $R_{1,2}$ computed for the auto-ignition of $n$-butane-air mixture under pressure 1 atm, initial temperature of 1000 K and unity equivalence ratio. $i$ is the reaction index and symbols represent the absolute values of the first and second-order derivatives. Lines are drawn to guide the eye.
Figure 6-10. Decay rate of $a_i$ and $b_i$ of Eq. (6-9) (solid lines) calculated for the auto-ignition of $n$-butane at the pressure 1 atm, initial temperature 1000 K and unity equivalence ratio. The $b_i$ values are presented as the average $\overline{b_i} = \frac{1}{N_r} \sum_{j=1}^{N_r} b_{ij}$, $i$ is the reaction index. Dashed-dotted-dashed lines represent the series of reciprocals of positive integer numbers.
Chapter 7 A Reduced Multicomponent Diffusion Model

7.1 Introduction
Accurate modeling of diffusion is essential in the simulation of the structure and response of flames, which consist of a multitude of chemical species strongly interacting with each other in narrow spatial domains of steep concentration gradients. The task is monumental as the diffusion of a single species would depend on the properties and concentrations of all the species in the mixture. For a mixture of $N$ perfect gas components, the Maxwell-Stefan multicomponent diffusion model, which is derived from Boltzmann’s equation of kinetic theory [1-8] and recently revisited by Lam [9], offers the most rigorous, state-of-the-art description for combustion simulations. Its implementation, however, incurs significant computational cost due to the required matrix inversion, particularly when large reaction mechanisms are involved. As such, it is difficult to employ the multicomponent model in large-scale flame simulations. A simplified description is that of Curtiss and Hirschfelder [1], who obtained the solution to the first-order perturbations of the Boltzmann equation following the Chapman-Cowling procedure [3], and developed a mixture-averaged diffusion model to describe the diffusion of species in low concentrations. For many combustion systems, the mixture-averaged model offers rather good accuracy with substantially lower computational cost, and thus has long been the de facto standard in combustion simulations as reviewed by Smooke [10]. The multicomponent model is typically needed in such special situations when the Soret effect is of interest, for non-dilute mixtures or when high accuracy is required [11-20].
The effects of using the mixture-averaged versus the multicomponent model on flame simulations have been extensively studied. For example, Bongers et al. [15] examined laminar planar premixed flames of H₂–air, H₂–O₂ and CH₄–air, showing that the differences between the two models are discernable in predicting the flame speed. Gopalakrishnan et al. [16] investigated the ignition of n-heptane–air diffusion flames, and reported a 10% difference in the transient temperature and major species profiles. Dworkin et al. [21] studied soot formation in C₂H₄–air counterflow and coflow flames, and found that, although the different diffusion models induce only small differences in the temperature profiles, they could lead to 10%-15% deviation in the peak soot volume fraction. For premixed turbulent flames, Charentenay et al. [22] simulated the interaction of H₂–O₂ flames with turbulence and found that the two models result in rather different instantaneous profiles of temperature and species concentrations, especially for highly curved flames. However, turbulence fluctuations appear to diminish these effects when considering the mean quantities, leading to a rather small change of 7% in the thickness of the flame brush. Kumar et al. [23] studied the heterogeneous combustion of H₂–air and CH₄–air mixtures in a monolithic channel coated by platinum, and found a 2% difference in the fuel concentrations at the exit of the channel. It is also noteworthy that Giovangigli and Ern [11-12] reduced the cost of the Maxwell-Stefan model by expanding the multicomponent diffusion coefficients to a convergent series, whose computational cost becomes typically a quadratic function of the number of species [24], as implemented in the EGLIB software package [25].
The objective of the present study is to develop a systematic approach to reduce the cost of the multicomponent model, hereafter referred to as the reduced multicomponent (RM) model. Its efficiency and fidelity is demonstrated for mixtures of $n$-heptane–air. Results show that the RM model retains the high accuracy of the multicomponent model and features a computational cost linearly proportional to the number of species.

7.2 Comparison of the Diffusion Models in Combustion Simulations

7.2.1 Simulation configuration

To compare the mixture-averaged and multicomponent models in different flames, three combustion systems of heptane–air mixture, namely the planar premixed flame, the counterflow diffusion flame and ignition of the droplet flame, are simulated, covering premixed and non-premixed, stretched and unstretched, and steady and unsteady conditions. The planar premixed flame and counterflow diffusion flame are simulated by using the algorithms of Kee et al. [26] and Nishioka et al. [27], respectively, while ignition of the droplet flame is simulated with the Adaptive Simulation of Unsteady Reacting Flows (A-SURF) code [28-32]. The chemistry of heptane oxidation is described by a skeletal mechanism of 88 species [33] derived from a detailed mechanism [34], which is available online [35].

The planar premixed flame is simulated over the range of parameters with equivalence ratios of 0.6 to 1.5, pressure of 1 to 40 atm, and freestream temperature of 300K. Simulation of the counterflow diffusion flame is conducted for pure heptane against air with temperature of 300K at both inlets and pressure of 1 to 3 atm. Such
parameters are selected to match the operating conditions of the flame speed measurement in [36] and the counterflow flame experiment in [37]. Each simulation starts with coarse grids and the mixture-averaged model. The grid is then refined iteratively until the solution converges. The diffusion model is then switched to the multicomponent model while the mesh is fixed, such that comparison of the models will not be biased due to changes in the mesh. For the unsteady droplet ignition, the droplet has initial radius of 1 mm and uniform temperature of 300 K. The ambient air is quiescent at temperature of 1400 K and pressure of 40 atm, being relevant to the working condition of IC engines [38]. The initial boundary layer at the surface of the droplet spans approximately 100 grid points, with temperature and species concentrations linearly interpolated from the droplet surface condition to the ambient condition. The evolution of the system is simulated by solving the 1-D, unsteady, compressible N-S equations, species equations and energy equation for multicomponent reacting flow in spherical coordinates. Thermal diffusion is not considered in all the simulations.

### 7.2.2 Simulation results with different diffusion models

Figure 7-1 presents the relative error of the mixture-averaged model in predicting the burning flux of the laminar premixed flame, $f^0$, as a function of equivalence ratio, $\phi$, under different pressures. The relative error is 0.5%-1% at atmospheric pressure, and increases to 2% at 40 atm. Compared with the typical uncertainty of 5% in experimental measurements of the flame speed [36], the mixture-averaged model results in only a minor deviation for the planar premixed flame.
Figure 7-2 illustrates the maximum temperature, $T_{\text{max}}$, in counterflow flames of pure heptane against air as a function of strain rate, $\kappa$, at pressures of 1-3 atm. It is seen that the extinction strain rates at the turning points predicted by the mixture-averaged and multicomponent models differ by 4% at atmospheric pressure and 6% at elevated pressures. Consequently, the counterflow diffusion flame is more sensitive to the selection of the diffusion model as compared to the premixed flame, in Fig. 7-1. Furthermore, based on the results in Figs. 7-1 and 7-2, deviation of the mixture-averaged model tends to increase at higher pressures.

In the simulation of unsteady droplet ignition, the fuel and air are mixed within a thin layer near the droplet surface through diffusion. Radicals build up during the induction period until approximately $t = 20$ ms, when thermal runaway is triggered. From 20 to 28 ms, the maximum system temperature rapidly increases from 1500 to 2900 K before a steady diffusion flame is established. The overall progress of the ignition is indicated by the evolution of the maximum temperature as shown in Fig. 7-3 (upper panel), together with the relative errors of the mixture-averaged model (lower panel) in the maximum H mole fraction. Although the mixture-averaged model under-predicts the ignition delay by merely 20 $\mu$s, the intensive unsteadiness amplifies its deviation in the maximum mole fraction of H radical to approximately 10% at 24 ms near the inflection point on the temperature profile, which is widely accepted as the ignition point. Based on the above observations, the mixture-averaged model may result in discernable deviations, say about 10%, in flame simulations and the multicomponent model is needed if higher accuracy is required.
7.3 Methodology for Multicomponent Diffusion Reduction

7.3.1 Review of the multicomponent diffusion model

For a mixture of \( N \) ideal gas components, the diffusion velocity of the \( i \)th species, \( \mathbf{v}_i \), is formulated by the multicomponent model [9] as

\[
\mathbf{v}_i = -\sum_{j=1}^{N} D_{ij}^{M} \mathbf{d}_j + D_{iT} \nabla \ln T
\]

\[
\mathbf{d}_j = \nabla X_j + (X_j - Y_j) \nabla p + \mathbf{g}_j
\]

\[
\mathbf{g}_j = \frac{\rho Y_j}{p} \sum_{k=1}^{N} Y_k (\mathbf{f}_k - \mathbf{f}_j)
\]  \( (7-1) \)

where \( D_{ij}^{M} \) is the multicomponent diffusion coefficient of species \( i \) with respect to \( j \),

\( D_{iT} \) the thermal diffusion coefficient of species \( i \), \( X_i \) and \( Y_i \) the mole and mass fractions of species \( i \), respectively, \( p \) the pressure, \( \rho \) the density, and \( \mathbf{f}_k \) the specific body force acted on the \( k \)th species. The thermal diffusion of the species is neglected in the present study, i.e. \( D_{iT} = 0 \) \( \forall i \).

The major cost of the multicomponent model is the calculation of the \( D_{ij}^{M} \) term, given by the inverse of the diffusion matrix \( L \) [39] as

\[
D_{ij}^{M} = X_i \frac{16 T m}{25 p m_j} (L_{ij}^{-1} - L_{ii}^{-1})
\]

\[
L_{ij} = \frac{16 T}{25 p} \sum_{k=1}^{N} \frac{X_k}{m_k D_{ik}} \left\{ m_i X_i (1 - \delta_{ik}) - m_k X_k (\delta_{ik} - \delta_{kj}) \right\}
\]  \( (7-2) \)
where $m_j$ is the molecular weight of species $j$, $\bar{m}$ the average molecular weight of the mixture, $D_{ik}^*$ the binary diffusion coefficient of species $i$ with respect to $k$, and $\delta_{ij}$ the Kronecker delta. In the CHEMKIN transport library [39], $L^{-1}$ is solved by the LAPACK package [40] with LU factorization, the cost of which scales as a cubic function of the matrix size.

### 7.3.2 A reduced multicomponent diffusion model

To reduce the cost of the multicomponent model, a reduced model is proposed based on the observation that global responses of combustion systems are sensitive only to the diffusivities of a subset of the species, referred to as the critical-diffusivity-species (CDS) hereafter. Correspondingly, other species are referred to as the non-critical diffusive species (NCDS). In the reduced model, the diffusion velocities of CDS are computed with the multicomponent model, while those of NCDS are computed with the less expensive mixture-averaged model:

\[
\text{If } i \in \text{CDS} \quad v_i = -\sum_{j=1}^{N} D_{ij}^{\text{mul}} d_j \\
\text{If } i \in \text{NCDS} \quad v_i = -\frac{1}{X_i} D_{i}^{\text{mix}} d_i \\
\forall \ j \in \text{NCDS} \\
D_{ij}^{\text{mul}} = X_j \frac{16Tm}{25pm_j} (LR_{ij}^{-1} - LR_{ik}^{-1}) \\
LR_{ij} = \frac{16T}{25p} \sum_{k=1}^{M+1} \frac{X_k}{m_k} D_{sk}^* \{m_r X_r (1 - \delta_{rk}) - m_s X_s (\delta_{ij} - \delta_{ik})\} \quad (7-3)
\]
where \( D_{ij}^{\text{reduced}} \) is the reduced multicomponent diffusion coefficient of species \( i \) with respect to \( j \), \( D_i^{\text{mix}} \) is diffusion coefficient of species \( i \) calculated with the mixture-averaged model, and \( M \) is the total number of CDS. For each NCDS \( j \), a sub-system is formed by including all CDS and \( j \), referred to as the reduced multicomponent system. The multicomponent model is applied to the reduced multicomponent system characterized by the reduced diffusion matrix, \( LR \), and the reduced multicomponent diffusion coefficients, \( D_{ij}^{\text{reduced}} \), computed from the inverse of \( LR \). The cost for each NCDS scales as a cubic function of the dimension of the matrix \( LR \) associated with it, i.e. \( O((M+1)^3) \). Since the similar routine is repeated for every NCDS, for a total of \( N-M \) times, the total cost for evaluation of the reduced multicomponent model is proportional to \( (N-M)(M+1)^3 \). Note that the cost for the inversions of the diffusion matrices in the detailed models is \( O(N^3) \), significant savings can be achieved by breaking the inversion of a large matrix into a set of smaller ones, particularly when \( M \ll N \).

While the time saving of the reduced model only depends on \( M \), the accuracy also depends on specific selections of the \( M \) CDS. A good CDS candidate is expected to be in sufficiently large concentration to have significant effects on the diffusion coefficients, since the diffusion of a species is dominated by its collisions with species in high concentrations. In addition, a radical may also be CDS if it participates in crucial reactions, e.g., H and OH. The mass diffusion of these radicals can modify the profiles of their concentration, subsequently changing the reaction rates.
7.3.3 Species bundling for further reduction

In a multicomponent system, species such as isomers may have similar molecular properties and thus similar diffusivities and can be bundled for diffusivity evaluation. Such species are referred to as similar-diffusivity-species (SDS). Species bundling has been implemented for the binary diffusion coefficients and applied in the reduction of the mixture-averaged model [41], and it is extended to the multicomponent diffusion model in the present work. Based on Eq. (2), the \( j \)th column vector of the diffusion matrix, \( \mathbf{L}_j \), describes the diffusion of other species with respect to the \( j \)th species. If the \( j \)th and \( j' \)th species are SDS, all the other species have similar diffusivities with respect to them. In other words, the difference in their corresponding column vectors must be small compared with a threshold value \( \varepsilon_G \).

\[
\max \left( \frac{L_{ij} - L_{ij'}}{L_{ij} + L_{ij'}} \right) < \varepsilon_G \quad \forall i \in \text{CDS} \quad i \neq j, j'
\]

(7-4)

7.3.4 Correction of the diffusive velocity

Since the RM model is a hybrid of the multicomponent model and the mixture-averaged model, it does not guarantee that the net species diffusion flux is zero. As such, the net diffusive velocity computed with Eq. (3) needs to be corrected to ensure mass conservation, following the approach in the mixture-averaged model in the CHEMKIN transport library [39]. In the present work, a constant correction velocity \( \mathbf{V}_c \) recommended by Coffee and Heimerl [42] is adopted:

\[
\mathbf{V}_c = \sum_{i=1}^{N} v_i Y_i
\]

(7-5)
Note that, although mass conservation can be theoretically guaranteed in the multicomponent model, corrections are still performed in practical simulation due to numerical errors.

7.4 Implementation of RM Model in Heptane-Air Flames
Following the strategy in Section 3.2, construction of the RM model starts with identifying CDS and SDS by using the procedure in Section 4.1. The analysis is based on the simulation results of the planar premixed flame and the counterflow diffusion flame for heptane–air mixtures, covering the parameter space studied in Section 2. The RM model is then validated and discussed in Section 4.2.

7.4.1 Identification of the Reduced Multicomponent Model
The first step in the reduction of the multicomponent model is to identify the CDS through sensitivity analysis, with the sensitivity coefficient defined as

$$s_i = \left| \frac{\partial \ln \psi}{\partial \ln(D_{i}^{Mec})} \right|$$

(7-6)

where $\psi$ is a global flame parameter, such as the flame speed and the extinction strain rate of the counterflow diffusion flame. The sensitivity coefficient $s_i$ can be calculated through numerical perturbations. Figure 7-4 illustrates the sensitive coefficients computed from the planar premixed flame of stoichiometric heptane–air at 40 atm. It is
seen that the sensitivity of the species rapidly decays with the species index. Note that the sensitivity coefficients are shown in logarithmic scale. The top 10 species are O$_2$, H, n-C$_7$H$_{16}$, C$_2$H$_4$, N$_2$, H$_2$O, H$_2$, CO$_2$, CO, and OH. The same species ranking is also identified in other simulations. Figure 7-4 also shows the maximum mole fraction of species, $x_{\text{max}}$, across the domain in the same sequence as that in the upper panel. The top 10 CDS other than H and OH completely overlap with species of the largest $x_{\text{max}}$, suggesting that CDS tend to be in high concentrations. To identify species featuring overall large concentrations across a flame, the species concentrations are sorted on each grid point, and the minimum set of species from the top of the list, which account for at least 97% of the mole fraction in total, are retained for this local grid. The union of all the retained species at each grid then constitutes the set of high-concentration species in the present study. The identified set includes 8 species: N$_2$, n-C$_7$H$_{16}$, O$_2$, H$_2$O, CO, CO$_2$, H$_2$, and C$_2$H$_4$, as indicated by their $x_{\text{max}}$. The same result is also obtained in other simulations. Figure 7-4 therefore verifies the hypothesis in Section 7.2: the combustion system is only sensitive to the diffusivity of a subset of species, which are typically either in high concentrations or are highly reactive radicals such as H and OH.

Based on the above analysis, an alternative approach to construct the set of CDS is proposed to simplify the procedure described above. Procedurally, the CDS in the RM model can be created by merging the high-concentration species with a few important radicals, e.g., H and OH. Moreover, the set of CDS, identified in this work, shows weak dependence on the type of hydrocarbon fuels, and it primarily consists of small molecules. This observation highly suggests that the dimension of RM model is primarily
determined by the number of high-concentration species, and roughly remains a constant regardless of the complexity of fuel molecules. To support this statement, planar premixed flames are simulated for stoichiometric mixtures of different hydrocarbons and air at 40 atm, using the detailed mechanism JetSurF 2.0 [43]. The fuels include $n$-alkanes from heptane to dodecane, 1-alkene, from heptene to dodecene and methyl-cyclohexane. The same set of eight high-concentration species have been identified in all the cases. Therefore, when the RM model is applied for the complex fuel molecules with large mechanisms of an increasing size $N$, its size, $M$, is expected to be invariant while its computational cost, $O \left((N-M)(M+1)^3\right)$, should linearly scale with the size of the mechanism. As such it can be advantageous to use the RM model compared to using the EBLIG [25], which features a cost of $O(N^3)$, when $N$ is large. Furthermore, the RM model can be integrated with EBLIG to solve its diffusion matrix $LR$ to further reduce the cost.

The second step of the RM model is to identify the SDS by comparing the column vectors of the diffusion matrix $L$ from Eq. (4). Figure 7-5 correlates the number of SDS, $N_{\text{SDS}}$, with the species grouping threshold, $\epsilon_g$. Thirty-two species are identified as SDS for $\epsilon_g < 1\text{E-4}$, and they correspond to the isomers in the system. When $\epsilon_g$ is larger than 7E-4, the number of SDS increases rapidly by including non-isomeric species, leading to significant deviation in the simulation results. It is found that simulations of the counterflow diffusion flame can fail to converge when $\epsilon_g > 8\text{E-4}$, and at most 37 SDS are bundled into 10 groups as displayed in Table 1. No CDS is identified as SDS in such
cases, and 78 NCDS are bundled into 51 groups, reducing the cost of the reduced multicomponent model from $O((N-M)(M+1)^3)$ to $O(N_g(M+1)^3)$, where $N_g$ is the number of bundled species groups.

**7.4.2 Validation of the Reduced Multicomponent Model**

For heptane-air mixtures, the RM model is validated in simulating the burning flux of planar premixed flames, the extinction strain rate of counterflow diffusion flames and the evolution of the maximum H radical mole fraction during droplet ignition. Figures 7-6-7-8 compare the accuracy of the different diffusion models. In all cases, the RM model agrees well with the multicomponent model. The error in the reduced multicomponent model is smaller than that of the mixture-averaged model by about an order of magnitude, while the SDS bundling step also does not induce any significant error in addition.

The computational cost of the different diffusion models is illustrated in Fig. 7-9. While the assessment is based on the planar premixed flame of the stoichiometric heptane-air at 40 atm, the cost is not sensitive to the flame configuration for fixed $M$ and $N$ values. It is seen that the multicomponent model takes about 2 s for each evaluation of the diffusion coefficients. It is about five times that of the reduced multicomponent model, and is mostly consistent with the estimation based on the cost to invert the matrices, 

$$(N - M)(M + 1)^3 / N^3 \approx 15\%,$$

for the current model with 10 CDS species. The extra 5% of the cost is attributed to the overhead of reduced multicomponent model such as assembling the diffusion matrices of the multiple reduced multicomponent systems. The strategy of bundling SDS introduces additional 35% saving, proportional to
The reduced multicomponent model with bundled SDS requires a computational time of 0.26 s, which is 2.5 times that of the mixture-averaged model of 0.11 s.

To further investigate the dependence of accuracy and efficiency of the RM model on the model size, planar premixed flames for stoichiometric heptane-air at 40 atm are simulated with different numbers of CDS, with SDS bundling disabled. The results are shown in Fig. 7-10. It is noted that the CDS are sequentially added to the reduce models based on the species ranking in the upper panel of Fig. 7-4. The minimal RM model in the simulations contains three CDS, namely n-C\textsubscript{7}H\textsubscript{16}, O\textsubscript{2}, N\textsubscript{2}, and it shows similar accuracy and computational cost compared to the mixture-averaged model, with the relative error being about 1% and the computational time being 0.13 s per iteration. It is seen that the model accuracy increases with the model size and reaches a plateau for more than 10 species, which justifies the truncation at 10 CDS species in the present study. Furthermore, the cost of the RM model peaks around 65 species, corresponding to the maximum value of function \((N-M)(M+1)^3\), achieved at \(M = 0.75N\). The maximum cost is about ten times that of the multicomponent model. As such, computational savings can only be achieved by using the reduced model when \(M\) is significantly smaller than \(N\).
7.5 Conclusions
The mixture-averaged and the Maxwell-Stefan multicomponent diffusion models are compared in flame simulations for the heptane-air mixtures. It is shown that the mixture-averaged model leads to limited errors in predicting the flame speed of planar premixed flame, but its deviation is amplified at elevated pressure, large strain rates and the intensive unsteadiness in the counterflow diffusion flame and during droplet ignition. A new strategy is proposed to obtain the RM model by emphasizing only on critical-diffusivity-species and bundling species with similar diffusivities. The critical-diffusivity-species are verified to be species in high concentrations and some critical radicals by the sensitivity analysis, while the species with similar diffusivities are identified by comparing the column vectors of the diffusion matrix. The RM model is validated in different heptane-air flame configurations with an 88-species chemical mechanism, showing good agreement with the multicomponent model at only 15-20% computational time, and the cost of the RM model linearly scales with the size of chemical mechanisms.
References

Computer Code Package for the Evaluation of Gas-Phase Multicomponent Transport


Table and Figures

Table 1. Species with similar diffusivities identified with $\varepsilon_g = 8E - 4$.

<table>
<thead>
<tr>
<th>Group</th>
<th>Member species</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\text{C}_7\text{H}_15\text{O}_2$-1</td>
</tr>
<tr>
<td></td>
<td>$\text{C}_7\text{H}_14\text{OOH}$-1</td>
</tr>
<tr>
<td></td>
<td>$\text{C}_7\text{H}_14\text{OOH}$-4</td>
</tr>
<tr>
<td>2</td>
<td>$\text{C}_7\text{H}_14\text{OOH}$-1$\text{O}_2$</td>
</tr>
<tr>
<td>3</td>
<td>$\text{NC}_7\text{KET}$13</td>
</tr>
<tr>
<td>4</td>
<td>$\text{C}_7\text{H}_15$-1</td>
</tr>
<tr>
<td>5</td>
<td>$\text{CH}_3\text{COCH}_2$</td>
</tr>
<tr>
<td>6</td>
<td>$\text{C}_7\text{H}_14\text{O}$-1</td>
</tr>
<tr>
<td>7</td>
<td>$\text{C}_7\text{H}_14$-2</td>
</tr>
<tr>
<td>8</td>
<td>$\text{C}_4\text{H}_8\text{OOH}$-1</td>
</tr>
<tr>
<td>9</td>
<td>$\text{CH}_3\text{CO}$</td>
</tr>
<tr>
<td>10</td>
<td>$\text{CH}_2\text{CO}$</td>
</tr>
</tbody>
</table>
Figure 7-1. Relative error of the mixture-averaged model in predicting the burning flux of planar premixed heptane-air flame as a function of equivalence ratio, at pressures of 1 to 40 atm and freestream temperature of 300 K.
Figure 7-2. The maximum temperature in the counterflow flame as a function of the strain rate, for pure heptane flowing against air at pressure of 1 to 3 atm and boundary temperature of 300 K at both inlets, calculated with different diffusion models. Dash dot line: mixture-averaged model; solid line: multicomponent model.
Figure 7-3. Time evolution of the maximum temperature during the ignition of heptane droplet flame (upper panel). The relative error of the mixture-averaged model in predicting the evolution of the maximum H radical mole fraction during the ignition of heptane droplet flame (lower panel). The inset shows a closer observation from 24 to 24.5 ms. The simulation is conducted for a heptane droplet of initial radius of 1 mm and uniform temperature of 300 K, with quiescent air at temperature of 1400 K and pressure of 40 atm, calculated with different diffusion models. Dash dot line: mixture-averaged model; solid line: multicomponent model.
Figure 7-4. The sensitivity coefficient of the burning flux for the planar premixed flame of stoichiometric heptane-air at 40 atm and freestream temperature of 300 K, with respect to the species diffusivities sorted in descending order (upper panel). And the maximum mole fraction of species presented in the order the same as the upper panel (lower panel). The simulation employs the mixture-averaged model.
Figure 7-5. The number of similar-diffusivity-species, with respect to the criteria on the species grouping. The analysis is conducted for the planar premixed flame and the counterflow diffusion flame. The planar premixed flame is simulated for the heptane-air mixture of the equivalence ratio 0.6 to 1.5 under 1 to 40 atm, with the freestream temperature of 300 K. The counterflow diffusion flame is simulated for the pure heptane following against the air under 1 to 3 atm, with the boundary temperature of 300 K at both inlets. The simulation employs the mixture-averaged model.
Figure 7-6. Relative error of various diffusion models in predicting the burning flux of the planar premixed flames for heptane-air, at equivalence ratio of 0.6 to 1.5, pressure of 1 to 40 atm, and freestream temperature of 300 K. Dash-dot line: mixture-averaged model; dash line: RM model without SDS bundling; circle: RM model with bundled SDS. The RM model is composed of 10 CDS. 37 SDS are bundled into 10 groups by $\varepsilon_G = 8E - 4$. 
Figure 7-7. Maximum temperature as a function of strain rate for counterflow diffusion flames of pure heptane flowing against air, at pressure of 1 to 3 atm and temperature of 300 K at both inlets, calculated with different diffusion models. Dash dot line: mixture-averaged model; solid line: multicomponent model; dash line: RM model without SDS bundling; circle: RM model with bundled SDS. The RM model is composed of 10 CDS. 37 SDS are bundled into 10 groups by $\varepsilon_g = 8E - 4$. 
Figure 7-8. Relative error of different diffusion models in predicting the evolution of the maximum H radical mole fraction during the ignition of a heptane droplet in quiescent air, with the initial droplet radius of 1 mm, droplet temperature of 300 K, ambient temperature of 1400 K, and pressure of 40 atm. Dash-dot line: mixture-averaged model; dash line: RM model without SDS bundling; circle: RM model with bundled SDS. The RM model is composed of 10 CDS. 37 SDS are bundled into 10 groups by $\varepsilon_G = 8E - 4$. 

$\varepsilon_G$
Figure 7-9. Computational time for each evaluation of the diffusion coefficients using the different diffusion models. From left to right: multicomponent model, RM model without SDS bundling, RM model with bundled SDS, mixture-averaged model. The reduced multicomponent model is composed of 10 CDS. 37 SDS are bundled into 10 groups by $\varepsilon_\gamma = 8E - 4$. 
Figure 7-10. Performance of the RM model as a function of the model size. The simulation is conducted for the planar premixed flame of stoichiometric heptane-air at pressure of 40 atm and freestream temperature of 300 K. For reference, the relative error is 2% and the computational time is 0.11 s per iteration for the mixture-averaged model.
Chapter 8 A Mechanistic Evaluation of Soret Diffusion in Heptane/Air Flames

8.1 Introduction
In most subsonic combustion processes, mass diffusion is dominated by Fickian diffusion caused by concentration gradients. However, mass diffusion can also occur in the presence of temperature gradients by Soret diffusion [1, 2], through which the lighter and heavier species respectively migrate up and down the temperature gradient. Although the magnitude of Soret diffusion is usually much smaller than that of Fickian diffusion, it could become significant for sufficiently heavy and light molecules in the presence of steep temperature gradients, typically associated with flames. For the influence of Soret diffusion on particulates, Sung et al. [3] found that the motion of the seeding particles in LDV measurements can be substantially affected by Soret diffusion, while Leusden et al. [4], Arias-Zugasti and Rosner [5], and Dworkin et al. [6] studied the influence of Soret diffusion on soot formation. For light gaseous fuels species, Ern and Giovangigli [7, 8] and Bongers and de Goey [9] numerically studied Soret diffusion in H₂/air flames and found that, when Soret diffusion was included, the flame speeds of planar premixed flames and the extinction limits of counterflow premixed flames were substantially modified. Grcar et al. [10] computationally showed that inclusion of Soret diffusion in lean hydrogen-air flames increases the burning rate and aggravates the propensity of cellular instability. For heavy fuel species, Dakhlia et al. [11] found that the flame temperature of heptane spray diffusion flames can be substantially reduced when
allowing for Soret diffusion, while Gopalakrishnan and Abraham [12] demonstrated that Soret diffusion lengthened the ignition delay of a one-dimensional heptane-air diffusion layer in conditions simulating those of internal combustion engines. Finally, Palle and Miller [13] studied the effects of cross-diffusion on diffusion flames of hydrogen, methane and heptane, with realistic chemistry and over extensive range of pressure variations. Results show substantial influence of cross-diffusion for the relatively light hydrogen and relatively heavy heptane, and the deficiency in existing thermal diffusion coefficient models is observed.

Yang et al. [14] recently extended the worthwhile studies discussed above by systematically investigating the effects of Soret diffusion on the response of hydrogen flames for the three major classes of laminar flames, namely the unstretched planar premixed flame as well as the corresponding stretched counterflow premixed and diffusion flames. The study focused on the mechanistic interpretation of the roles of H₂ and the kinetically dominant radical H in modifying the diffusive and reactive structures of these flames and through them the global response of these flames such as the burning rate and the state of extinction.

The objective of the present study is to extend the work of [14] to flames of large hydrocarbons, with the objective of identifying the separate and coupled effects of Soret diffusion and the dominant reaction kinetics, as will be discussed in due course. We shall adopt mixtures of n-heptane (hereafter referred to as heptane) and air for illustration, not only because of the practical significance of heptane as a reference fuel, but perhaps more importantly because it is almost four times as heavy as the average molecular weight of
the heptane/air system, whose diffusive efficiency is expected to be dominated by the abundant species, \( \text{N}_2 \). Consequently it is reasonable to expect that discernable effects of Soret diffusion should be exhibited by heptane, as was already demonstrated by some of the earlier studies [11-13]. These effects are non-trivial because they directly modify the diffusive flux of the primary fuel, heptane, which in turn impacts the properties and structure of the flame, especially the flame temperature. On the other hand, since heptane decomposes to species of smaller molecular weights as it enters the flame structure, it is not clear to what extent its role in Soret diffusion is obviated. Furthermore, the decomposition yields the secondary fuel, \( \text{H}_2 \), which is a strong Soret-diffusing species, except its Soret diffusive flux is in the opposite direction as that of the heptane. The net effect is therefore not clear (\textit{a priori}). As such, we expect that heptane/air flames would have features that are different from those previously identified for \( \text{H}_2/\text{air} \) flames [14]. Specifically, in the \( \text{H}_2/\text{air} \) system, the Soret effect is primarily represented by the two light species, \( \text{H}_2 \) and the \( \text{H} \) radical, which respond to temperature gradients similarly. In the heptane/air system, however, at least three species must be taken into consideration, namely the heavy fuel species, heptane, and the light species \( \text{H} \) and \( \text{H}_2 \). Since heptane responds to temperature gradients oppositely to \( \text{H} \) and \( \text{H}_2 \), as just mentioned, and since these three species assume different roles in the reaction process, with heptane and \( \text{H}_2 \) being the primary and secondary fuels respectively and with \( \text{H} \) being a key chain radical, the Soret-chemistry coupling renders a new dimension to the study of Soret diffusion. In this regard we also recognize that, while Soret diffusion assumes only a secondary, and hence at most quantitative, role in some of the problems studied herein, there exist
situations such as supercritical combustion [15] in which it is of leading-order importance because of the vanishing of Fickian diffusion.

We note in passing a recent study [16] on the Soret diffusion of n-butane/air flames. This study was only for the unstretched premixed flame and, since the molecular weight of butane deviates minimally from that of air, as compared to heptane, prominent effects of Soret diffusion were not observed, as expected.

This chapter is organized as follows. In the next section, the problem of interest is introduced. This is followed by Sections 3 to 5, in which we study effects of Soret diffusion in the three major classes of laminar flames, namely the unstretched planar premixed flame, the counterflow premixed flame, and the counterflow diffusion flame. The study is mechanistic in nature, aiming to identify the various roles of Soret diffusion on the structure and response of these flames.

8.2 Specification of Flames
We first specify the three flame configurations studied in the present work: unstretched planar premixed flames, counterflow premixed flames, and counterflow diffusion flames. The first is an idealized one-dimensional flame, for which a planar flame is situated in a uniform flow field of doubly infinite extent. The counterflow is created by impinging two uniform flows onto one another. For premixed flames, these two flows are identical in terms of composition, resulting in two symmetrical flat flames situated on each side of the stagnation surface. For diffusion flames, these two flows are composed of mixtures of
fuel and of oxidizer respectively, with a single flame appearing on the side of the stoichiometrically-deficient reactant.

These three flames therefore cover most typical combustion systems, namely premixed and diffusional, and stretched and unstretched. For the unstretched premixed flames, the impact of Soret diffusion is studied for its effect on flame propagation, while in the counterflow flames, the global response parameters are the flame temperature and the state of extinction. It is noted that extinction is an important limit phenomenon of flames, and that the nominally small influence of Soret diffusion could possibly become pronounced around the extinction state, at which these flames become sensitive to small perturbations in the reactant concentrations and thereby the flame temperature and overall reactivity.

The planar premixed flames and counterflow flames were simulated by using the algorithms of Kee et al. [17] and Nishioka et al. [18], respectively. The chemistry of heptane oxidation is described by a skeletal mechanism [19] derived from the detailed mechanism of Ref. [20], with multicomponent transport. Since the skeletal mechanism has been extensively validated against the performance of the detailed mechanism, its use greatly facilitates the computation without compromising its chemical fidelity. It is also noted that because the goal of the present study is to identify the mechanistic effects of Soret diffusion within a reactive environment, the conclusions and insights drawn herein do not sensitively depend on the specific reaction mechanism and transport description used, as long as it is at the state of the art.
The burning intensities of the simulated flames are represented by the burning fluxes of the unstretched premixed flames and the maximum temperature of the counterflow flames. Simulations were performed with and without the inclusion of Soret diffusion for heptane, H₂, H as well as other species as needed.

8.3 Unstretched Planar Premixed Flames
Planar premixed flames of equivalence ratios from 0.6 to 1.5 were simulated with a freestream temperature of 300K and system pressure of 1 atm. The burning fluxes of the mixture as a function of equivalence ratio (from 1.00 to 1.25 for clarity) are shown in Figure 8-1, obtained with the presence of Soret diffusion for various species. The reference case is labeled “No Soret”, obtained by suppressing Soret diffusion for all species. If we then activate Soret diffusion for heptane (curve labeled hep-Soret), Figure 8-1 shows no noticeable effect on the burning flux. Next, if only H₂ Soret diffusion is activated (H₂-Soret), a small reduction in the burning flux is observed. The reduction becomes more substantial if only H Soret diffusion is activated (H-Soret). Finally, an even larger reduction results if Soret diffusion is activated for both H and H₂, labeled as (H+H₂)-Soret. This curve is nearly identical to that obtained by activating Soret diffusion for all the species (Total Soret), suggesting that H and H₂ are the primary species that contribute to noticeable Soret effects on the burning flux. It is however also of interest to note that the sum of the individual H and H₂ effects, labeled as (H-Soret + H₂-Soret), does not add up to the combined (H+H₂)-Soret, thereby suggesting possible interaction between the H and H₂ fluxes arising from Soret diffusion, causing further reduction in the
burning flux. In the following we shall provide a comprehensive, mechanistic explanation
of these results, recognizing that although they are quantitatively small, they reveal the
“symptoms” of Soret diffusion which could become more prominent in other situations or
can be judiciously exploited to either facilitate or inhibit the burning response.

To interpret the above results, we first recognize that the burning characteristics of a
flame can be affected by the diffusive fluxes of various species through two major factors,
namely modification of the total energy entering the flame and the distribution of the
species concentrations within it. The first effect is represented by the modification of the
flame temperature which affects the overall reaction rate, while the second affects the
reaction rates of the relevant reactions. The first effect is expected to have a stronger
impact on the flame response because flame temperature is of leading-order importance
in a combustion system. However, since the present 1D premixed flame in the doubly-
infinite domain is unstretched, the system is an adiabatic one in that the total energy
entering the flame is not influenced even though the diffusional flux of the individual
species can be locally affected by Soret diffusion. Since the flame temperature remains at
the adiabatic value, the energetics of the overall flame propagation is not affected, while
those of the individual reactions are expected to be also minimally affected. This
therefore explains the small influence of Soret diffusion for this flame.

Small as it is, the influence of Soret diffusion is nevertheless still noticeable and
mechanistically it is of interest to identify the causes, particularly modification of the
concentration distributions and through them the reaction rates of the Soret-affected
species. To assess the relative importance of these species through their chemistry
coupling, we have performed a sensitivity analysis of the burning flux with respect to the representative reactions involving H, H\textsubscript{2} and heptane, with the sensitivity coefficient defined as:

$$s_i = \frac{\partial \ln(f^0)}{\partial \ln(A_{i,j;i})} \quad i = \text{H, H}_2, \text{heptane}$$ (8-1)

where \(f^0\) is the laminar burning flux, \(s_i\) the sensitivity coefficient of species \(i\), and \(A_{i,j}\) the pre-exponential factor of reaction \(j\) for species \(i\). In this evaluation, the burning flux was computed by perturbing the pre-exponential factors of all reactions involving the \(i^{th}\) species.

The sensitivity coefficients for \(i = \text{H, H}_2, \text{heptane}\) for \(\phi = 1.13\) are shown in Figure 8-2 for the reference case without considering Soret effect of all species, noting that the burning fluxes are close to their maximum values around this mixture concentration. It is seen that reactions involving the H radicals are substantially more important than those involving H\textsubscript{2}, while those involving heptane are very small. Similar results were also obtained for other equivalence ratios.

To interpret the above Soret-affected results from the viewpoint of chemistry interaction, we consider the kinetics of the high-temperature oxidation of heptane. First we note that recent studies [21] have shown that the laminar burning rates of \(n\)-alkanes are largely the same for the C\textsubscript{5} and larger molecules. This has three implications. First, the diffusivities of the large fuel molecules have very small influence on the flame propagation rate, which in turn would imply that modifications of its diffusion rate
through Soret diffusion would be small as well. Second, it substantiates the understanding that the initial fuel decomposition within the flame structure is sufficiently fast that it is not rate limiting. Third, it also agrees with the understanding that the high-temperature oxidation of hydrocarbons, at least for pressures that are not too high, is controlled by the H-O₂ chain cycle, given by:

\[
\begin{align*}
H + O₂ & \rightarrow OH + O \quad (R1) \\
H₂ + O & \rightarrow OH + H \quad (R2) \\
H₂ + OH & \rightarrow H + H₂O \quad (R3)
\end{align*}
\]

which does not depend on the specific hydrocarbon. In the above reaction (R1) is singularly important in chain propagation and consequently flame propagation. (R2) and (R3) could also be contributing not only because they are integral to the H-O₂ chain cycle, but they also generate the H radicals needed by (R1).

To quantify the relative importance of these reactions on the effects of Soret diffusion, we have evaluated the sensitivity coefficients of the burning flux for each of them, also shown in Figure 8-2. The results then clearly show the dominance of (R1) on the burning flux, with its sensitivity being almost the same as that for the H radicals, and as such should be affected by Soret diffusion through the mobility of H. Furthermore, the small, albeit finite, influence of H₂ Soret diffusion on the burning flux is reflected in the correspondingly small and finite influence of (R2) and (R3). This influence is through the direct concentration effect of H₂ on the reactivities of (R2) and (R3), as well as through their production of H which in turn affects (R1). This coupling then leads to the interaction effect observed in the difference in the (H+H₂)-Soret and (H-Soret)+(H₂-Soret)
curves shown in Figure 8-1.

To gain further understanding on the Soret-chemistry coupling in general, and the fact that such a coupling leads to weakening of the flame propagation, we plot in Figure 8-3 for $\phi = 1.13$ the diffusion flux as well as the concentration profiles of the H radicals and the rates of (R1) for the reference case of no Soret diffusion for all the species and for the case allowing for Soret diffusion of H, with the temperature profiles superimposed. These results demonstrate that the monotonically increasing temperature profile Soret-diffusively draws the H radicals away from where it is needed for reaction (R1) towards the downstream. This reduction in the concentration, even small, reduces the burning rate.

Figure 8-4 is a similar plot for the profiles of H$_2$ and the rates of H$_2$-affected reactions (R2) and (R3). Here H$_2$ is also Soret-diffused towards the downstream direction, and hence the concentration of H$_2$ is again reduced in the reaction zones of (R2) and (R3). Moreover, this effect suppresses the production of H radicals and therefore further reduces their concentration in the reaction zone of (R1). On the other hand, since the peak of Soret diffusion for H$_2$ is spatially decoupled from the reaction zones of (R2) and (R3), the reduction of the H$_2$ concentration in these reaction zones is minor. Consequently the Soret effect for H$_2$ is less pronounced than that of the H radicals.

8.4 Counterflow Premixed Flames
Counterflow premixed flames were simulated with 300K freestream temperature and 1 atm pressure. Heptane/air mixtures of $\phi = 0.6$ and 1.5 were selected for the lean and rich cases, with their response curves of the maximum temperature as a function of strain rate.
Different from unstretched planar premixed flames, for which the flame temperature is independent of the diffusivities of the fuel/oxidizer species entering the flame, the flame temperature of a counterflow premixed flame is highly sensitive to the nonequidiffusive nature of the mixture because it directly modifies the flame temperature and hence the state of extinction through flow straining. For example, Figure 8-5 shows that the net Soret effect weakens the burning intensity of the lean flame and reduces the extinction strain rate from 54 to 43 s\(^{-1}\), while the opposite holds for the rich flame, increasing the extinction strain rate from 1590 to 1680 s\(^{-1}\), shown in Figure 8-6.

We now consider the roles of Soret diffusion for the individual species (heptane, H\(_2\), H) on the burning intensity of the lean and rich flames. Clearly heptane exhibits the strongest Soret effect, weakening it for the lean flame and strengthening it for the rich flame. This is readily apparent because heptane Soret-diffuses away from the flame zone and thereby reduces its concentration as it enters the flame zone. This then leads to the further departure from stoichiometry for the lean flame but approaching stoichiometry for the rich flame. The effect is particularly strong because it effectively modifies the stoichiometry and thereby the flame temperature, reducing it from the adiabatic flame temperature for the lean flame and elevating it for the rich flame. We have therefore clarified the role of Soret diffusion of heptane raised in the introduction.

Figure 8-5 shows that next to heptane, H\(_2\) also has discernable influence on the flame temperature and hence the extinction state for the lean flame, albeit in the opposite
direction. This is because H₂ is rapidly produced as heptane enters the flame zone, and as such is far upstream of the active reaction zone for all the key branching reactions, (R1) to (R3), as shown in Figure 8-4. Consequently H₂ can be considered as a secondary fuel species in the same manner as that of heptane, except that being lighter, it Soret diffuses downstream towards the active reaction zone. This has two effects: increasing the net fuel flux as experienced by the flame and hence its final temperature and the reactivities of the chain reactions - indirectly through the change in the flame temperature and directly through the increase of its concentration in the reaction zone. The first effect increases the burning intensity of the flame while the second effect leads to an increase in the reactivity for the present lean flame because both the flame temperature and H₂ concentration are increased.

A straightforward interpretation for the rich flame, based on the reasoning for the lean flame, would indicate that inclusion of Soret diffusion for H₂ would lead to a reduction of the flame temperature, weakening of the burning intensity, and consequently facilitated extinction, at a smaller strain rate as compare to the case where it is suppressed. Figure 6, however, shows the opposite: Soret diffusion of H₂ allows the burning to persist to larger strain rates before extinction.

This apparent “inconsistency” can be readily resolved by recognizing the qualitatively different extinction mechanisms for lean and rich heptane/air mixtures [1], whose effective Lewis numbers (Le) are respectively greater and smaller than unity. Specifically, since the counterflow flame is positively stretched, its flame temperature is reduced with increasing strain rate for the lean flame (Le > 1) when started out from a
weakly stretched state, and eventually extinguishes before it reaches the stagnation surface. The response of the rich flame, with $Le < 1$, is however completely opposite as its flame temperature increases with increasing straining and as such does not extinguish until the flame reaches the stagnation surface. Extinction eventually occurs with further increase in the stretch rate due to the finite residence time that limits the attainment of complete reaction and hence reduces the flame temperature. Therefore the availability of more fuel in the form of $H_2$, as the flame reaches the stagnation surface, delays the onset of extinction.

To substantiate the above interpretation, and recognizing that the plot in Figure 8-6 is for the large-strain-rate, near-extinction, situations, we have plotted in Figure 8-7 situations of moderate strain rates when the flame is situated far from the stagnation surface and as such can attain complete reaction. It is then seen that Soret diffusion of $H_2$ indeed leads to lower flame temperatures due to the increased effective fuel concentration for the rich mixtures.

We have so far focused our discussion on stretched flames only on the Soret diffusion of the primary and secondary fuels, heptane and $H_2$, and the key radical $H$. Our studies have in addition shown that the other major species: $O_2$, $N_2$, $CO_2$ and $H_2O$, also exert finite Soret effects on the flame response. We shall defer the discussion of their effects to the next section, on counterflow diffusion flames, so as not to clutter the discussion of the specific Soret-affected mechanisms identified in this section.
8.5 Counterflow Diffusion Flames
Simulation of counterflow diffusion flames was conducted for air against 20% heptane by volume diluted with 80% N₂. The boundary temperatures at both freestreams are 300 K and the system pressure is 1 atm. Response curves of the maximum temperature as a function of strain rate are shown in Figure 8-8. To interpret the results, we first note that since the temperature profile is bell shaped, the temperature gradient is positively directed towards the flame on both the fuel and oxidizer sides. Furthermore, reaction between fuel and oxidizer is close to stoichiometric such that an increase in the fuel or the O₂ concentration will always increase the flame temperature. Finally, reaction is always limited by residence time, leading to incomplete reaction even for states removed from near extinction.

Recognizing the above, it is then apparent that Soret diffusion of heptane will lead to a reduction of the heptane concentration entering the flame and hence a corresponding reduction of the flame temperature, while the opposite holds for the secondary fuel, H₂, as it Soret diffuses toward the flame and therefore increases the flame temperature. Soret diffusion of H increases its concentration in the high-temperature reaction region, hence promoting more complete reaction. The last effect was also identified in Ref. [8] for the hydrogen/air flames.

We finally consider the separate and combined effects of Soret diffusion of O₂, N₂, CO₂ and H₂O, as shown in Figure 8-9. To appreciate these results, let us first consider Soret diffusion on the air side of the flame. Thus if N₂ is taken as the abundant species referenced to which the effects of Soret diffusion of other species are to be assessed, then
it is seen that since CO₂ and H₂O are respectively heavier and lighter than N₂, they will in
turn Soret diffuse away and towards the flame, hence increasing and reducing the reactant
concentrations at the flame and subsequently rendering it burning stronger and weaker
respectively. Similarly, since O₂ is heavier than N₂, it will Soret diffuse away from the
flame and as such weaken its burning. As far as N₂ itself is concerned, since it is lighter
than the bulk air mixture, it Soret diffuses towards and weakens the flame, as is shown by
the calculated results. Similar interpretation can be extended to the fuel side of the flame
and largely arrive at the same response. When the Soret diffusion of all these major
species, together with the radical H, is considered, Figure 8-9 shows that the result
basically reproduces that obtained by considering Soret diffusion of all the species.

8.6 Conclusions
The present investigation has systematically studied the influence of Soret diffusion on
heptane/air flames. The impact of Soret diffusion is attributed to two factors: modifying
the flame temperature through the reactant concentration, and affecting the reactivity
through the concentrations of the key radicals within the relevant reaction zones. The first
effect is more important since the flame temperature governs the flame intensity.
Consequently, the effect of Soret diffusion is small for the unstretched planar premixed
flames because the flame temperature is unaffected. In stretched counterflow flames,
however, Soret diffusion of the primary fuel, heptane, has a dominant influence on the
flame response, while that of the oppositely directed secondary fuel H₂ can also have
moderate effects. Localization of the flame by the stagnation surface for the near-
extinction rich premixed flame and by the counter-diffusion of the fuel and oxidizer species also plays an essential role in enhancing the rates of reaction through enrichment of the H and H$_2$ concentrations. Enrichment and dilution of the reactant concentration in the flame through the Soret diffusion of O$_2$, N$_2$, CO$_2$ and H$_2$O further exert finite effects on the burning intensity.
References


**Figure 8-1.** Burning fluxes of heptane/air planar premixed flames at 1 atm, allowing Soret diffusion for various species as indicated.
Figure 8-2. Sensitivity coefficients of the burning fluxes with respect to (R1), (R2), (R3), and reactions involving H, H\textsubscript{2} and heptane of an equivalence ratio of 1.13 heptane/air planar premixed flame, suppressing Soret diffusion for all species.
Figure 8-3. Profiles of the diffusion flux, concentration of the H radicals, reaction rate of H+O₂=OH+O, and temperature for a heptane/air planar premixed flame with an equivalence ratio of 1.13.
Figure 8-4. Profiles of the diffusion flux, concentration of H₂ and H radicals, reaction rates of the relevant reactions, and temperature for a heptane/air planar premixed flame with an equivalence ratio of 1.13.
Figure 8-5. Response of the maximum temperature including the state of extinction as a function of strain rate for lean heptane/air counterflow premixed flames, allowing Soret diffusion for various species as indicated.
Figure 8-6. Response of the maximum temperature including the state of extinction as a function of strain rate for rich heptane/air counterflow premixed flames, allowing Soret diffusion for various species as indicated.
Figure 8-7. Response of the maximum temperature for states far away from extinction as a function of strain rate for rich heptane/air counterflow premixed flames, allowing Soret diffusion for various species as indicated.
Figure 8-8. Response of the maximum diffusion flame temperature including the state of extinction as a function of strain rate for nitrogen-diluted heptane counterflowing against air, allowing Soret diffusion for various species as indicated.
Figure 8-9. Response of the maximum diffusion flame temperature around the state of extinction as a function of strain rate for nitrogen-diluted heptane counterflowing against air, allowing Soret diffusion for various species as indicated.
Chapter 9 Summary and Future Work

9.1 Summary
This dissertation research consists of two parts. The first part discusses a kinetic study on the heterogeneous combustion of C_1–C_3 hydrocarbons over unsupported Pd-based catalyst, leading to the development of an elementary kinetic model from apparent kinetic studies surface analysis, and numerical simulations. The second part explores the fundamental knowledge of combustion systems by detailed numerical simulations, including investigations of the flame front instability and the Soret effect in n-heptane-air flames, and the development of an optimized model reduction strategy and a reduced multicomponent diffusion model.

In Part I, Chapter 2 specifies the experimental facilities, the simulation configuration and the surface analysis for the kinetic study of catalytic hydrocarbon combustion. The chapter begins by introducing wire microcalorimetry and mass spectrometry, and then describes the details of CFD simulation, while the following surface analysis confirms the formation of a stable PdO layer on the wire surface during hydrocarbon oxidation. The SEM image of PdO layer shows a porous structure, with the median pore radius 0.5 µm and average length 10 µm. Chapter 3 investigates the oxidation of methane over PdO. The rates of surface reactions are measured for the lean methane-air mixtures with equivalence ratios of 0.1 to 0.3, over 600 to 800 K, under atmospheric pressure conditions. The examined regime is controlled by surface kinetics, and the apparent kinetic parameters are extracted as the unity reaction order in methane and an activation energy 62.3±1.6 kJ/mol. Form DFT calculations [1-3] and the experimental observations,
a detailed kinetic model is proposed, with the crucial steps of adsorption/desorption of oxygen and dissociative adsorption of methane, identified by a sensitivity analysis. From molecule beam experiments [4] and Monte Carlo simulation, the rate coefficient of oxygen adsorption is described as

\[ k_{2f} (\text{cm/s}) = 6.42 \times 10^2 T^{0.5} \exp\left(-\frac{T}{540} - 8.8\theta\right) \]  \hspace{1cm} (9-1a)

where \( T \) and \( \theta \) are surface temperature and coverage, respectively. The rate coefficient of oxygen desorption is correlated to the adsorption by the equilibrium constant, which is derived from the thermodynamic properties of adsorbed oxygen atom [5-7], leading to the expression

\[ k_{2b} (\text{cm/s}) = 3 \times 10^{26} T^{-0.5} \exp\left(-\frac{28 - 14\theta}{T} \times 10^3\right) \]  \hspace{1cm} (9-1b)

The intrinsic rate coefficient of methane adsorption is fitted from the experimental data as

\[ \text{CH4: } k_{16} (\text{cm/s}) = (5.7 \pm 0.2) \times 10^4 \exp\left(-\frac{7000 \pm 300}{T}\right) \]  \hspace{1cm} (9-2a)

Chapter 4 extends the kinetic study from methane to C\(_2\)-C\(_3\) hydrocarbons, which concentrates on the lean hydrocarbon-air mixtures with equivalence ratios ranging from 0.1 to 0.3 over 600 to 800 K under atmospheric pressure conditions. For the alkanes of
ethane and propane, the adsorption/desorption of oxygen and the dissociative adsorption of fuel molecule are still the crucial steps, which is supported by the DFT calculations [1-3], the apparent kinetic study, and the sensitivity analysis of the detailed model. The intrinsic rate coefficients of the dissociative adsorption of ethane and propane are extracted from the experimental results of wire microcalorimetry,

\[ C_2H_6: k_{19} \text{ (cm/s)} = (4.5 \pm 0.2) \times 10^4 \exp\left(-\frac{6400 \pm 300}{T}\right) \]  
(9-2b)

\[ C_3H_8: k_{21} \text{ (cm/s)} = (1.6 \pm 0.1) \times 10^4 \exp\left(-\frac{5300 \pm 400}{T}\right) \]  
(9-2c)

On the other hand, the oxidation of ethylene presents a temperature-dependent scenario. Below 580 K, the oxidation rate is insensitive to the gas-phase ethylene concentration and surface temperature; above 580 K, the oxidation rate increases drastically, where the reaction order is unity in ethylene concentration and the apparent activation energy is 48.2 kJ/mol. To understand the kinetics of ethylene oxidation at different temperatures, the reaction products are revealed by the mass spectrum. Below 580 K, a significant amount of H\(_2\) production is captured, which suggests the dehydrogenation as an important reaction channel; above 580 K, the dominant generation of H\(_2\)O indicates complete combustion. Based on the kinetic model of alkane oxidation, the dissociative adsorption of ethylene is proposed to be the rate-determining step, with the rate coefficient being fitted from the microcalorimetry data.

\[ C_2H_4: k_{23} \text{ (cm/s)} = (2.5 \pm 0.1) \times 10^4 \exp\left(-\frac{5200 \pm 100}{T}\right) \]  
(9-2d)
In Part II, Chapter 5 studies the hydrodynamic instability in the self-accelerating propagation of hydrogen-air flame. The direct numerical simulation is conducted for a stoichiometric mixture at eight atmospheres of pressure in a cylindrical domain. The full scale compressible Navier–Stokes equations, species equations, and energy equation are solved with a detailed chemistry model, while the time step and grid are selected as 2 ns and 4 microns, respectively. The acceleration of flame propagation is demonstrated to be caused by the increase of flame length, and the local burning intensity is constant. The instantaneous acceleration of the flame front presents a strong intermittent feature, which is attributed to the development of cells. The fractal structure of the flame front is confirmed by a box-counting method with the fractal dimension of 1.07±0.02, and the fractal structure distributes from the length scales of hydrodynamic cut-off to the flame radius.

In Chapter 6, an optimized model reduction strategy is proposed and verified for butane combustion. The detailed model of USC Mech II is reduced to skeletal models of different sizes by Directed Relation Graph (DRG) and DRG-Aided sensitivity analysis (DRGASA). The method of uncertainty analysis using polynomial chaos expansions (MUM-PCE) is employed to optimize the skeletal models, with adjusting kinetic parameters within their uncertainty bounds. Consequently, a significant improvement is achieved on the model accuracy. Moreover, the uncertainties of reduced models are correlated with the model size, showing a conditional dependence subject to the model completeness. If the reduced model includes all important reactions, the model uncertainty should be convergent with increasing model size. Otherwise, the behavior of
the model uncertainty with respect to model size cannot be predicted.

In Chapter 7, a simplified Maxwell-Stefan model is proposed for multicomponent diffusion, based on the concept of model reduction. The reduced multicomponent model identifies the species whose diffusivity is critical to accurately predict combustion processes and calculates their diffusivities by the Maxwell-Stefan model. In contrast, the reduced multicomponent model approximates the diffusivities of other species by the less expensive Mixture-averaged model. In a prototype study of \textit{n}-heptane-air flames with a mechanism of 88 species, the critical-diffusivity species are verified as the species in large concentrations and a few highly reactive radicals by a sensitivity analysis. The reduced multicomponent model yields predictions, which closely agree with the multicomponent model to 15-20\%, in predicting the burning flux of planar premixed flames, the extinction strain rate of counterflow diffusion flames, and the ignition of droplet flames.

In Chapter 8, the impact of the Soret effect is systematically investigated in \textit{n}-heptane/air flames under atmospheric pressure conditions. In the unstretched case of planar premixed flames, the Soret effect slightly changes the burning flux of the flame by adjusting the diffusion flux of the H radical, which perturbs the profiles of the H concentration and consequently the rates of chain-branching reactions. In stretched counterflow flames, Soret diffusion plays a more important role through its coupling with the stretch effect in that Soret diffusion affects the diffusion flux of the primary fuel, \textit{n}-heptane and consequently the flame temperature. As such, the extinction strain rate can be modified up to 20\% in counterflow lean premixed flames and 10\% in counterflow rich
premixed flames and diffusion flames.

9.2 Future Work

9.2.1 Wire Microcalorimetry

In this dissertation, wire microcalorimetry has been shown as a convenient approach for the kinetic study of gas-surface reactions. We suggest interesting topics for wire microcalorimetry in three aspects. First, wire microcalorimetry can be used to study other surface reactions, e.g., the oxidation of graphite and hydrocarbon oxidation assisted by the Pt-based catalyst. Second, the methodology can also be applied to study the surface kinetics at elevated pressures especially those of super-critical conditions. As reviewed in [8], the proper use of supercritical fluids has the advantages of enhanced reaction rate as well as mass transfer. Thirdly, we strongly suggest the adoption of nano-wire in microcalorimetry because of the unique physical and chemical properties of nano-materials. For instance, the heat transfer rate in the nano-scale exceeds the limit set by Planck's blackbody radiation law by 1,000 times [9], while gold nano-particles with the diameter less than 8 nm is an amazingly active and selective catalysts for a variety of important reactions [10], recognizing that bulk gold has been known to be chemically inactive for thousands of years.

9.2.2 DNS Flame Front Instability

Chapter 5 sets up the direct numerical simulation with detailed chemistry to study flame propagation in hydrogen-air mixtures, which can be extended to three exciting topics: turbulence-forced flame acceleration, instability-induced flame acceleration, and the instability-turbulence transition. For the first topic, the computer code S3D is designed
for turbulence simulation, and hence the turbulence can be introduced in the current simulation readily, with a broad range of intensity and length scale. It offers a great opportunity to investigate the propagation of flames in various turbulent flows with the comprehensive information of all details, which is invaluable for turbulent flame modeling. Furthermore, the fractal structure has also been verified in turbulence, and it will be of great interest to explore the coupling between the two fractal objects in a variety of time and length scales. For the second topic, by adjusting the simulation parameters, the current DNS can be applied to investigate other types of instabilities. For instance, the thermal-diffusional and thermal-acoustic instability will be activated by lean hydrogen-air mixtures and closed boundaries. Thirdly, for the potential transition from instability to turbulence, the simulation can be extended to larger domains under elevated pressures because the transition is expected to be enhanced by the longer development time and thinner flame front.
References