Numerical and experimental evaluation of preheated premixed flames at lean and rich conditions

Joseph Edward Gibson

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NUMERICAL AND EXPERIMENTAL EVALUATION OF PREHEATED PREMIXED FLAMES AT LEAN AND RICH CONDITIONS

A Thesis

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Master of Science in Mechanical Engineering

in

The Department of Mechanical Engineering

by

Joseph Edward Gibson
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Abstract

Preheating a combustible mixture enhances the laminar burning flux characteristic $m_{ad}$ with high reaction firing rates. As a result, the flammable zone as defined by inlet conditions of equivalence ratio and temperature is expanded beyond that available at standard ambient conditions; however, fundamental questions in these combustion regimes have not been addressed. In this thesis, preheated lean and rich combustion of methane/air mixtures is studied numerically and experimentally to catalog and confirm expected trends in these regimes. Numerical simulations were completed using both GRI-Mech 3.0 and San Diego mechanisms in the combustion code Cantera. An adiabatic simulation data set is obtained over a vast range of equivalence ratios ($\phi = 0.15 - 3.5$) and inlet temperatures ($T_{in} = 200 - 1000$K), while further study is completed at lean ($\phi < 0.89$) and rich conditions ($\phi > 1.3$). Detailed analyses of flame structure and reaction pathway analysis, sensitivity, and heat release are completed at a total of ten reference cases, five lean and five rich, selected along contours of constant equivalence ratio $\phi = 0.7, 1.6$ and mass flux $m_{ad} = 0.2190 \frac{kg}{m^2 \cdot s}$. A regression analysis of each regime links adiabatic flame propagation to a characteristic temperature $T^*$, shown to be primarily a function of $\dot{m}$, while $\phi$ and $T_{in}$ are shown to play a subordinate role. Analyses together reveal causal kinetic phenomena contributing to differences in lean and rich combustion. Experiments connect the adiabatic findings to the simplest non-adiabatic application, where stand-off distances of a flat flame burner are used as a metric for flame behavior. Viable flames are established at ultra-lean and rich conditions, but results show mechanism uncertainty at preheated conditions in addition to unmodeled heat transfer phenomena. Further study of flat flame behavior is performed in the computational fluid dynamics code Fluent 12.0, where a two dimensional axisymmetric flame is stabilized for three mass fluxes at a reference case of $\phi = 0.7, T_{in} = 300$K. The model does not attempt to replicate the exact conditions seen experimentally, rather it seeks to evaluate boundary effects and other two dimensional flame structures resulting from exceeding the laminar burning flux.
Chapter 1
Introduction

1.1 Background

Preheated premixed combustion defines a combustion process in which the inlet fuel and oxidizer mixture is heated above standard ambient temperature of 298K. Preheating allows for the expansion of combustion zones into extremely fuel lean (ultra-lean) and fuel rich (ultra-rich) conditions unavailable at standard temperatures, i.e. outside of flammability limits defined at ambient temperature. Early studies noted this phenomena [32] in addition to an increase in the adiabatic flame speed (or laminar burning flux when eliminating the effect of varying gas density) [32, 46, 50]. Figure 1.1 illustrates this effect on the laminar burning flux of a methane/air mixture, while regions of ultra-lean/rich are also labeled. From a slightly rich peak, the laminar burning flux suffers a severe decline as equivalence ratio departs near-stoichiometric conditions. Lean flames continue to exhibit this steep gradient as the lean limit is approached, while rich flames flatten just before the limit is reached due to the asymmetrical definition of equivalence ratio [42]. Preheating is shown to substantially increase the overall burning flux curve, and thus burning zones are reached beyond those attainable from standard temperatures.

Further research into preheating was sparked by the work of Weinberg [70] and Hardesty [25] detailing heat recirculation to attain “excess-enthalpy” or “superadiabatic” combustion, delivering reactor temperatures in excess of the adiabatic limit achievable from standard temperature. Since then, realizations of preheated combustion have utilized various methods of heat recirculation: heat transfer across a wall [45, 54, 56], regenerative heating of a combustion wave in a packed bed [26, 37, 18], or flame stabilization in a porous solid matrix [72, 29]. Preheating alone in these reactors allows for the burning of low calorific fuels [45] while relevant applications of extended burning zones includes the reduction of fuel consumption and pollutant emissions (ultra-lean) [72, 38] and the production of hydrogen rich synthetic gas through fuel-reforming (ultra-rich) [59]. Ultra-lean combustion may be achieved through combustion within porous media, where upstream conductive and radiative heat transfer to the incoming mixture allow for steady state stabilization of a flame [30]. Models for the fluid flow and heat transfer within the media have been well-established [72], including one-dimensional models with detailed
Figure 1.1: Ultra-lean/rich domains reached by preheating. Flammability limits at standard temperature are marked as $\phi = 0.50$ (lean) and $\phi = 1.67$ (rich) [42].

chemistry [5]. Ultra-rich combustion produces synthesis gas, a viable fuel with varying composition of major constituents $\text{H}_2$, CO, and CO$_2$. The relative high hydrogen content of such a fuel lends itself to fuel cell and portable power applications [57]. Specifically, ultra-rich reactors utilizing counter-flow heat exchangers have been researched both experimentally and numerically [56, 58]. Here, it is necessary to distinguish preheating phenomena that occur regularly in common power applications from the works above. As an example, compression and heat transfer to the charge in internal combustion engines [27] lead to preheated combustion; however, the regime under study generally occurs at atmospheric pressure. Thus, temperature effects alone on the combustion process are considered as pressure effects are not applicable.

The combustion processes within heat recirculating reactors are inherently unresolved due to the high rates of heat transfer around and within the reaction zone. In addition, fundamental combustion characteristics for preheated mixtures are not well understood. Thus, the present study seeks to investigate these characteristics in preheated methane/air flames by isolating combustion at ultra-lean/rich conditions. Specifically, preheating will not be implemented around the reaction zone, nor will it be accomplished through heat recirculation. Descriptions of a combustion process within these restrictions may be deemed equivalent to that within heat recirculating reactors through classification of the various length scales present. Within a heat recirculating reactor, the length scale of interfacial heat transfer is larger than that of gas diffusive processes, and both are larger than the reaction scale [51]. Thus, while
the overall temperature is regulated by interfacial heat transfer, local combustion processes will proceed according to conventional combustion theory and may be isolated for further study.

1.2 Reaction Mechanisms

Complex reaction mechanisms, when incorporated into flame simulation codes, provide a high level of detail in flame structure. A chemical mechanism, the building block of numerical codes, describes the elementary reaction steps, or pathways, between reactant and product [42]. Complex mechanisms may include hundreds of species and reactions, although many may be subdivided into a hierarchy based on fuel complexity [71]. Detailed flame simulations solve one-dimensional conservation equations, i.e. mass, species, and energy conservation equations, numerically. These equations, first laid out in modern multicomponent form by Hirschfelder and Curtiss [28], are discussed in detail within Section 2.1, where kinetic mechanisms provide the necessary species and reaction rates. The standard for flame simulation was originally set by the PREMIX code [35] in the CHEMKIN kinetics package [36], now a commercial software. Academic research groups have provided alternatives to CHEMKIN and PREMIX. Of the reaction mechanisms available for methane, GRI-Mech 3.0, a 53 species, 325 reaction mechanism, is considered mature [64]. Forman Williams’ San Diego mechanism seeks to reduce uncertainty by including only essential species and reactions necessary to describe flame properties. The result is highly simplified mechanism of 46 species and 235 reactions [1]. For one dimensional flame simulations, the development of CANTERA has provided a standard platform for incorporating the aforementioned mechanisms. CANTERA is an object-oriented software which provides for the calculation of various kinetic, thermodynamic, and transport processes [19]. For the combustion processes of the present study, CANTERA provides solvers for both adiabatic and burner-stabilized flame problems, in addition to equilibrium calculations. Additionally, the computational fluid dynamics code Fluent 12.0 provides an interface for importing chemical kinetics and implementation of necessary equations. The code allows for two and three dimensional simulations, whereas CANTERA is limited to one dimension.

1.3 Asymptotics

Simplified analyses for flames are of interest in studying the underlying physics of the combustion process. Of these, rate-ratio asymptotics combines a reduced mechanism with asymptotic analysis of flame propagation equations to provide flame properties and basic structure. In asymptotic analysis of adiabatic
flames, two zones are generally established: a preheat zone and reaction zone. The reaction zone is often further subdivided into sublayers, an inner layer, defined by a balance between chain-branching and chain-breaking reactions, and an oxidation layer, which actually includes the inner layer. The inner layer is stabilized about a characteristic temperature, $T^\circ$, that marks the kinetic balance within the structure, and may be subdivided by even smaller length scales [63]. The characteristic temperature then resolves asymptotic equations for the adiabatic flame speed, the desired flame characteristic of the analysis. The locations of these layers relative to the flame structures are shown in Figure 1.2. Here, $T^\circ$ occurs in an intermediate region, between fuel destruction and CO and H$_2$ peaks. The oxidation layer then incorporates both the fuel destruction pathways and oxidation of CO-H$_2$. Asymptotic analyses have been completed on a number of problems, including lean to stoichiometric flames [63, 52, 60], moderately rich flames [62], and rich flames [61] respectively. Lean flames are characterized by a distinct inner layer based on the length scale assumptions employed, and may be resolved in varying detail. However, rich flames are described in the limit $T^\circ \rightarrow T_b$, or the burnt gas temperature. Thus, in rich flames, no inner layer is defined and only an oxidation layer is resolved.

1.4 Literature Review

The present study focuses heavily on two main topics within the literature: adiabatic flames and flat flame burners. The survey focuses on experimental literature for laminar burning fluxes largely to show
the disparities in the known data set (Fig. 1.3a). The literature on flat flame burners covers various experimental studies on the burner in addition to analytical and numerical solutions relevant to the current study.

1.4.1 Laminar Burning Flux

The laminar burning flux, describing the propagation speed of a laminar flame front, is fundamental to other premixed combustion phenomena [42]. It is determined empirically, and methods abound to this end. All require corrections and/or post-processing techniques due to any number of imperfections, including, but not limited to, flame stretch or curvature, heat losses, and non-uniform flow [42]. Thus, the subject has become quite controversial [42]; however, a general consensus on a range useful for validating numerical techniques may be reached by comparing a number of studies. In the following, a selected subset of experimental studies for methane/air mixtures and their respective techniques are documented. Other literature on the subject is catalogued in Andrews and Bradley’s review [3] of methane/air flame speeds, while Law [41] contains a study based on an opposed jet technique, a method predating the zero strain rate method of Vagelopoulos and Egolfopoulos [67] (see below). Experimental literature as a whole, represented by the authors presented, covers flame speeds for standard temperature and pressure well but lacks sufficient data at preheated conditions, particularly outside of conventional burning zones (Fig. 1.3a).

Early research dates back to the 1930s, when Passauer [50] used a bunsen-type flame with the total-area method to determine adiabatic methane-air flame speeds at various mixture temperatures. The total area method utilizes measurements of flame shape to find the flame speed from the volumetric flow rate of the unburned mixture. In a similar study, Dugger and Heimel [12] used a nozzle-type burner and shadow graphs of flames in tandem with the total-area method. More recently, Vagelopoulos and Egolfopoulos [67] used a single jet-plate configuration to create a zero strain rate flame through flow rate reduction of a Bunsen-style burner. Their direct measurement of an adiabatic freely propagating flame has been used previously for validation of numerical results [64]. Boschaart and de Goey [6, 7] have matured flame speed measurement on a flat flame burner by balancing heat fluxes into the burner surface. At a net heat flux of zero, the unburnt gas velocity is shown to be the adiabatic flame speed. Liao, et al. [44] found the flame speed for methane-air mixtures in a constant volume combustion bomb in order to verify their
methods while pursuing similar results for natural gas. Wang [68] used a spherical combustion bomb in microgravity to negate increased buoyancy effects near the lean limit. Figure 1.3a illustrates the available data set from the literature and provides experimental confirmation of the effect of equivalence ratio on burning flux. A high number of consistent data points is available at standard temperature, while only relatively sparse and inconsistent data exists at preheated conditions.

In addition, the effect of temperature on the adiabatic flame speed has also been catalogued. As shown by data above standard ambient temperature in Figure 1.3a, researchers Passauer as well as Dugger and Heimel pursued this result. Gu, et al. [23] used a spherical apparatus to capture an adiabatic flame. They, in addition to Liao, et al. and Wang, used schlieren photography to find the stretched flame speed, which may then be corrected and extrapolated to find the laminar flame speed. Han, et al. [24] ignited methane/air mixtures in an adiabatic cylinder, using pressure transducers to extrapolate the burning

Figure 1.3: Effect of equivalence ratio $\phi$ (a) and inlet temperature $T_{in}$ (b) on the laminar burning flux $\dot{m}$. 

![Graph (a)](image1)

![Graph (b)](image2)
1.4.2 Flat Flame Burners

Porous plug burners, specifically flat flame burners, have been studied for both adiabatic and non-adiabatic purposes. Figure 1.4 illustrates a typical flat flame burner, where a premixed flame stabilizes at a “stand-off distance” [17] from the porous plug. The plug is shown without a cooling mechanism; however, cooling coils may be included to control inlet temperature. While the studies here center on the progression and characteristics of the burner itself, it has become a common laboratory burner for combustion diagnostics, e.g. the “McKenna” burner [2] may be used for developing laser diagnostic techniques [48].

Early research on flat flame burners began in the late 1940’s when Sir Egerton and coworkers [14] developed an uncooled “Egerton-Powling” burner for determining burning fluxes where flat, disc-like flames stabilized between a perforated disc and a downstream iron gauze screen. Shortly thereafter, Botha and Spalding [8] used a cooled flat flame burner to determine flame speeds of propane/air mixtures; however, the flame speed had to be extrapolated due to heat losses to the burner. Kaskan [33] quickly used the burner to show the dependence of flame speed on temperature, confirming the results of earlier researchers. Edmondson and Heap looked at boundary effects on the measured flame speeds by changing the ambient atmosphere [13] and burner diameter [53], concluding that boundary mixing
has a significant impact on the measured flame speeds and questioning the linear extrapolation used by previous investigators. More recently, the problem with extrapolation shown by Edmondson was solved by Bosschaart and de Goey [6] (Fig. 1.3a), who stabilized flames both above and below the adiabatic limit, interpolating the flame speed rather than extrapolating.

The burner itself has been studied and modeled extensively in departure from its original experimental purpose. Ferguson and Keck [17] catalogued aforementioned “stand-off” distances as a function of both flame temperature and equivalence ratio in a numerical and experimental study. These results were later confirmed by Yuuki and Matsui [73] in a numerical study of flame perturbations. Their studies showed that the stand-off distance exhibits a distinct behavior as a function of mass flux. Figure 1.5 illustrates the stand-off curve for a specific reference case, where, beginning at a low non-adiabatic mass flux $\dot{m}$, such that $\frac{\dot{m}}{\dot{m}_{ad}} \ll 1$, the stand-off distance approaches the surface of the burner with increasing $\dot{m}$. The flame reaches a minimum distance before moving away from the burner as $\frac{\dot{m}}{\dot{m}_{ad}} \to 1$. After the laminar burning flux $\dot{m}_{ad}$ is reached, the flame loses its “flatness,” or “wrinkles” to resolve the excess mass flux, eventually blowing off.

In parallel with experimental studies, many analytical and numerical studies have sought to model various aspects of the burner. Specifically, one dimensional analytical models of the burner can provide insight into the underlying physics of the problem. McIntosh and Prothero [47] used large activation energy asymptotic theory to describe both submerged and surface combustion in a porous plug burner.
made of sintered metallic fibers. They found the effects of heat transfer on the stand-off distance due to the changes in the surface temperature of the burner. Chao [11] followed a similar analysis to model flame instabilities due to volumetric heat loss. Kurdyumov and Matalon [39] further refined stability analysis to show the effects of various burner parameters on flame stabilization, including porosity and plug material. Schoegl [55] investigated the effects of radiative heat transfer on the inlet temperatures of the burner. Specifically, he noted the effects of a hot downstream boundary on the inlet temperature of the porous plug, finding significant preheating due to upstream diffusion and radiation. Furthermore, numerical models of the burner have been created, originally as part of the PREMIX package [35]. Eng, et al. [16] utilized this code and experiments to confirm the earlier asymptotic analyses and experimental work. Bouma and de Goey [9] utilized porous media models to compare experimental emission data with predictions from a one dimensional simulation. Computational results showed a flame occurring right at the surface of the burner, with significant preheating within the plug. Lammers and de Goey [40], following the earlier analysis, used similar equations to describe flash-back on porous plug burners due to preheated environments. More recently, Kedia and Ghoniem [34] modeled a two dimensional flame to further investigate flame stabilization and blow-off due to the two dimensional structure at these limits.

Overall, the literature demonstrates catalogs various phenomena that may occur on flat flame burners. Of interest are the effects of the porous plug on the combustion process and flame stabilization. The plug is shown to preheat the inlet mixture unless manually cooled, while radiative heat transfer from the outlet boundaries is shown to affect the temperatures within the porous media. Furthermore, preheating is shown to cause flashback into porous plug burners, where the flame reaches a steady state submerged within the plug. However, experimental results are sparse at best, and do not attempt to extend the experimental range of the burner into highly preheated, ultra-lean/rich regimes.

1.5 Overview

The present thesis seeks to study fundamental combustion properties of preheated methane/air flames at lean and rich conditions. Numerical simulations of one dimensional adiabatic flames provide a data set unmatched by experimental literature, in both the scale of conditions surveyed and the depth provided in flame structure. A complete data set is compiled for two kinetic mechanisms: a) GRI-Mech 3.0 and b) the San Diego mechanism. In order to characterize the combustion within this data set, reference cases
of constant equivalence ratio, $\phi = 0.7$ (lean) or $\phi = 1.6$ (rich) and constant mass flux, $\dot{m}_{ad} = .219$ (as defined by the GRI mechanism) were selected for detailed analysis. In all cases, results from the San Diego mechanism are used comparatively against GRI 3.0 as a measure of mechanism independence. Specifically, centered flame structure plots show various species concentrations (mole fractions) relative to the main reaction zone. That, in tandem with a reaction pathway analysis, detail the chemical kinetics driving the flame. Sensitivity analysis highlights key chain-branching and breaking reactions, while a study of the heat release reveals reactions that shape temperature profiles. The underlying goal of these analyses is to link the combustion process to the characteristic temperature of rate-ratio asymptotics. In a departure from this theory, a characteristic temperature $T^*$ is sought at the onset of the combustion process, i.e. at the transition between preheating and reaction zones, rather than at the balance of chain-branching and chain-breaking reactions. A regression analysis of markers set within the numerical data catalogues promising indicators of $T^*$ for each combustion regime, uniting the broad inlet condition spectrum under a single variable. To adequately capture flame properties unique to a given flame, all derivations and analysis were completed for an adiabatic flames. To conclude that these results hold for non-adiabatic conditions, the simplest type of non-adiabatic configuration, the burner-stabilized flat flame, is studied. The regression analysis is completed for non-adiabatic flames at inlet references cases, where the large range of non-adiabatic fluxes provides adequate number of data points. Experimental work completed on a flat flame burner proves the viability of flat flames at both ultra lean and rich conditions. Furthermore, a comparison of the stand-off distances of burner-stabilized lean flat flames to one dimensional simulations illustrate trends and phenomena associated with experimental flames. Additionally, a two dimensional flame model analogous to the one dimensional code is utilized in Fluent to confirm the results. Particular attention is paid to the predicted profiles and the effect of boundary diffusion of air and fuel into the ambient atmosphere. Additionally, a case of mass flux greater than adiabatic allows for a study of two dimensional structures, resulting in the numerical calculation of the laminar burning flux.
Chapter 2
Methodology

2.1 One Dimensional Analysis

2.1.1 Computations

The analysis undertaken for the main body of this study is based on a large set of numerical data covering a broad range of inlet temperatures \( T_{\text{in}} = 200 - 1000\text{K} \) and equivalence ratios \( \phi = 0.15 - 3.5 \). Simulations for standard adiabatic laminar flame propagation were obtained from the chemical kinetics software CANTERA [20], which solves one dimensional conservation of mass, species, and energy at specified inlet conditions for both adiabatic and burner-stabilized flames.

Conservation Equations  In order to describe the physics of the flat flames, conservation equations are presented using the nomenclature of [66]; however, they are consistent with those utilized in CANTERA [21], assuming that \( x \) is normal to the (flat) flame. Resulting overall mass conservation is

\[
\frac{d(\rho u)}{dx} = 0
\]

(2.1)

where \( \rho \) is the density of the mixture and \( u \) is its velocity. Thus, mass flux will remain constant through the domain. Species conservation for the \( i \)th species of the mixture is

\[
\rho u \frac{dY_i}{dx} - \frac{d}{dx}(\rho \mathcal{D}_{\text{im}} \frac{dY_i}{dx}) = \dot{\omega}_i MW_i
\]

(2.2)

where \( Y_i \) is the mass fraction, \( \mathcal{D}_{\text{im}} \) the diffusion coefficient, \( \dot{\omega}_i \) the reaction rate, and \( MW_i \) the molecular weight. Often, the term \(-\rho \mathcal{D}_{\text{im}} \frac{dY_i}{dx}\) is denoted as \( J_i \), the diffusion flux [31] or written in terms of diffusion velocity \( \rho Y_i v_{i,\text{diff}} \) [66]. For speed of computation, mixture-averaged diffusion was specified rather than full multicomponent. In short, the diffusion coefficient \( \mathcal{D}_{\text{im}} \) for each species \( i \) is calculated against the mixture average, while full multicomponent would require it calculation against each species in the mixture. Consequently, thermal diffusion, i.e. Soret diffusion [66], is also ignored. SI units of species conservation are equivalent to those of mass conservation: \( \frac{k\text{g}}{m^3 \cdot s} \). Energy conservation takes into account heat transfer by convection, conduction within the mixture, and diffusion of individual
species in addition to heat generation via chemical reaction. The resulting equation is as follows:

$$\rho c_p u \frac{dT}{dx} - \sum_{i=1}^{N} \rho c_{p,i} \frac{dY_i}{dx} \frac{dT}{dx} = \frac{d}{dx} \left( k \frac{dT}{dx} \right) - \sum_{i=1}^{N} h_i \omega_i MW_i \quad (2.3)$$

where $k$ is the thermal conductivity of the mixture (and a function of $x$), $c_p$ is the specific heat, and $h_i$ is the enthalpy of species $i$. SI units of the energy equation are found per unit volume to be $[\text{W/m}^3]$. In addition to the conservation equations, the ideal gas equation of state is of particular importance as pressure remains constant. Density thus may be calculated such that

$$\rho = \frac{P_0 MW_{\text{mix}}}{RT} \quad (2.4)$$

where $P_0$ is atmospheric pressure and $R$ is the universal gas constant. Within the species and energy equations, the reaction terms are resolved using a chemical kinetic mechanism.

**Mechanism Resolution** Simulation codes utilize compact index notation to resolve the mechanisms in matrix form. In the following, the compact notation detailed in [66] is reproduced for further understanding of the calculations involved in sensitivity and heat release calculations. The species reaction rate $\dot{\omega}_i$ is computed from the mechanism by summing the product of the reaction rates $q_j$ and the stoichiometric coefficient matrix $v_{ij}$ over the number of reactions $L$

$$\dot{\omega}_i = \sum_{j=1}^{L} v_{ij} q_j \quad (2.5)$$

The stoichiometric coefficient matrix is the difference between the matrices for products $v_{ij}''$ and reactants $v_{ij}'$ respectively. The reaction rates $q_j$ are found from the product of the forward and reverse reaction rate coefficients $k_{f,j}$ and $k_{r,j}$ and respective stoichiometrically weighted concentrations such that

$$q_j = k_{f,j} \prod_{i=1}^{N} [\chi_i]^{v_{ij}'} - k_{r,j} \prod_{i=1}^{N} [\chi_i]^{v_{ij}''} \quad (2.6)$$

Here, forward and reverse reaction coefficients are multiplied by the term by term species concentrations ($[\chi_i]$) raised to their respective stoichiometric coefficient. Additionally, $q_j$ is often referred to as the rate of progress variable [19, 66]; however, for the present study, it will be referred to as the reaction rate.
This variable will be used extensively in the detailed analysis of flame structure. Generally, forward reaction rate coefficients are written as a function of temperature in the Arrhenius form

$$k(T) = AT^b e^{-\frac{E_A}{RT}}$$ (2.7)

Here, $A$ is a constant often referred to as the frequency factor and $E_A$ is the activation energy. Constants are catalogued empirically for each reaction such that a mechanism is often presented as a database of these, in addition to respective thermodynamic and transport properties per species. For the calculations of this study, the GRI-Mech 3.0 [64] and the short San Diego mechanisms [1] are utilized. Additionally, $k(T)$ is often presented as the forward reaction rate coefficient $k_f$. To compute the reverse reaction rate coefficient, equilibrium is employed such that the reverse coefficient may be found from the equilibrium constant and the forward coefficient.

**Boundary Conditions** Boundary conditions can be divided into the two main categories: adiabatic and burner stabilized. For adiabatic cases, CANtera allows user specification of the inlet composition and temperature

$$Y_i(x = -\infty) = Y_{i,u} \quad (2.8a)$$

$$T(x = 0) = T_{in} \quad (2.8b)$$

while outlet gradients $\frac{dY_i}{dx}$ and $\frac{dT}{dx}$ are assumed zero [31]

$$\frac{dY_i}{dx}(x = x_{outlet}) = 0 \quad (2.8c)$$

$$\frac{dT}{dx}(x = x_{outlet}) = 0 \quad (2.8d)$$

In addition, a trivial temperature $T_{fix}$ is specified at which the flame will be stabilized in order to determine the inlet mass flux [65]

$$T_{fix}(x_{fix}) - T(x = 0) = 300K \quad (2.8e)$$
This numerical method allows for a freely propagating steady state flame to be established in a finite domain. For the adiabatic simulations of this paper, $T_{fix}$ is specified at 300 K greater than that of the inlet. Changing the fixed temperature has been found to induce error into numerical solutions and will be accounted for in error calculations. For burner stabilized flames, the user sets the inlet temperature and composition while outlet conditions remain unchanged (eqs. 2.8a - 2.8d); however, a non-adiabatic inlet mass flux $\dot{m}$ is set as an additional user-defined boundary condition, rather than a part of the solution set.

\[ \dot{m}(x = 0) = \dot{m}_u \]  

Thus, equation 2.9 replaces 2.8e to create a non-adiabatic burner-stabilized flame. In all cases, inlet diffusion is allowed such that the user-specified inlet composition $Y_{i,u}$ is met in an the upstream domain ($-\infty$) beyond the current computation domain. Thus, the appropriate boundary condition is CANTERA-specified [31] as

\[ \dot{m}_{in}Y_{i,in} = \dot{m}Y_i - \rho \frac{D_{im}}{Dx} \frac{dY_i}{dx} \]  

In adiabatic flame cases, this result is trivial since gradients will be approximately flat until the flame sheet is approached, i.e. $Y_{i,u} \approx Y_{i,in}$. The effect is quite pronounced in burner-stabilized flames; however, flashback will not occur in any simulation since temperature remains user-defined.

**Solution Procedure**  CANTERA simulations were run using a systematic approach. The procedure may be categorized by two main subjects: a description of the numerical capabilities of CANTERA and user-specified tolerances (outside of the boundary conditions and fixed temperature of stabilization).

CANTERA employs a hybrid Newtonian, psuedo-time-stepping algorithm [21]. In such a system, a steady state solution is attempted via the classical Newtonian method of equation 2.11, where $\vec{x}$ is the solution set, $f(\vec{x})$ are the discretized equations, and $J_{ig}$ is the Jacobian matrix $\frac{\partial f_i}{\partial \vec{x}_j}$.

\[ \vec{x}_n = \vec{x}_{n-1} - J_{ij}f(\vec{x}_{n-1}) \]  

If a steady state solution is not found, then unsteady terms are introduced into the conservation equa-
tions, and the solution is stepped for several pseudo-time-steps. Steady state and transient methods are alternated until steady state convergence is reached.

Tolerances are user-specified per solution and convergence categories. Solution tolerances are defined via the ratio, slope, and curve between each respective values within the solution set. The ratio defines the maximum spacing between any two grid points, while the slope and curve define the maximum allowable gradients and curvatures (second derivative) within the solution. An initial solution is Cantera-generated as a constant temperature rise from inlet to equilibrium predictions on the first 20% of a user-specified initial grid, then flat to the end of the domain [19]. This initial solution is adaptively solved via the above algorithm until user-specified values for ratio, slope, and curve are attained. To this end, grid points are adaptively added between any points that do not meet the criteria. Consequently, the final solution grid will be non-uniform, with a high number of grid-points specified within the reaction zone, and will vary based on inlet conditions. Convergence tolerances of interest are the steady-state/time-stepping error tolerances (both relative and absolute) and the max Jacobian age for Newtonian/unsteady solutions.

The tolerances set for the present study are similar to those provided in Cantera demos [19]. Tolerance values per each solution within the present study are shown in Table 2.1. A first solution is found with low solution tolerances and without an energy equation. Resetting the tolerances and enabling energy, the solution is then reiterated to the final tolerance values. The effect of solution tolerances on the burning flux is noted in discussion of the resulting data set (Section 3.1). Convergence tolerances are also presented in Table 2.1, where ranges of values were used to foster convergence for early solutions but final solution tolerances of $10^{-9}$ and $10^{-12}$ were specified for relative and absolute tolerances respectively. The max Jacobian age was also varied to foster convergence, anywhere from 40 – 80. Cantera documentation [21] notes that the Jacobian is the most computationally consuming calculation of the algorithm and need not be updated every solution, thus only affecting the convergence, and not the final solution attained. Burner-stabilized simulations are completed in similar fashion.

**Data Collection** Data points were collected along a rectangular grid in a two dimensional space of equivalence ratios $\phi_i$ and inlet temperatures $T_{in,j}$ (in index notation). The overall grid spanned a range of $\phi = 0.15 – 5$ and $T_{in} = 200 – 1000$K. If boundary grid points did not converge, they were no longer
Table 2.1: Successive user-specified solution tolerances in **CANTERA**: adaptive gridding completed from ratio, slope and curve; individual solutions governed by relative and absolute tolerances.

<table>
<thead>
<tr>
<th>Sol. #</th>
<th>Ratio</th>
<th>Slope</th>
<th>Curve</th>
<th>Rel. Tolerance</th>
<th>Abs. Tolerance</th>
<th>Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6</td>
<td>1</td>
<td>1</td>
<td>$10^{-5} - 10^{-9}$</td>
<td>$10^{-9} - 10^{-12}$</td>
<td>N</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>0.1</td>
<td>0.3</td>
<td>$10^{-5} - 10^{-9}$</td>
<td>$10^{-9} - 10^{-12}$</td>
<td>Y</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>0.05</td>
<td>0.1</td>
<td>$10^{-9}$</td>
<td>$10^{-12}$</td>
<td>Y</td>
</tr>
</tbody>
</table>

considered part of the domain. Additionally, equivalence ratio spacing was manually set within lean, stoichiometric, and rich flame regimes to resolve high rates of change of the laminar burning flux curve. The result is grid spacing in $\phi$ of 0.05 from 0.15 – 1.30 and 0.1 from 1.30 – 3.5, while $T_{in}$ is found at 50K intervals. Thus the solution set of laminar burning fluxes has the form $\dot{m}_{ad,ij} = F(\phi_i, T_{in,j})$. To find contours of constant mass flux within the data set, two interpolations (a) and (b) were performed in $\phi$, holding the temperature intervals constant. The second interpolation (b) produces a higher accuracy interpolation from the inclusion of a third data point. The resulting data set in both GRI and San Diego mechanisms are shown graphically in Section 3.1.

2.1.2 Detailed Analysis

Flame structure and reaction pathways, reaction sensitivity, and heat release are analyzed in detail for selected reference cases, where either equivalence ratio or laminar burning flux are held constant. The analysis is completed for lean and rich regimes, both GRI and San Diego mechanisms.

**Flame Structure**  While flame structure is created as part of the solution set, phenomena at specific locations therein are investigated through reaction pathways. A reaction pathway is computed simply through the net contribution of reaction $j$, i.e. $v_{ij}q_j$, to the net rate of change of species $\omega_i$ at any given point in the flame [69]. The analysis is easily completed using the **CANTERA** simulation tool Mix-Master [20].

**Sensitivity**  Reaction sensitivity is investigated by perturbing the pre-exponential rate coefficient $A$ of the Arrhenius reaction kinetic coefficient $k$ (eq. 2.7), thus revealing the sensitivity of a desired flame characteristic to individual reactions [42]. The perturbation used was a 10% increase in $A$ for each reaction $j$, and sensitivity $S$ was found as a log-normal value based on laminar burning flux such that

$$S = \frac{\partial \ln \dot{m}}{\partial \ln A}$$  \hspace{1cm} (2.12)
Figure 2.1: Example indicator locations and corresponding temperatures $T^\star$. Indicators are considered the maximum of the profile, as well as at the maximum gradient and curvature.

In all cases, the sensitivity of reaction $j$ is found with respect to the non-perturbed burning flux $\dot{n}_0$ and frequency factor $A_0$. Sensitivity analyses show which reactions most effect the desired flame characteristic in the final solution. Thus, the most sensitive reactions should be carefully studied to understand the underlying kinetics in flame structure.

**Heat Release**  Heat release analysis focuses on the heat release rate per reaction rather than per species in equation 2.3. Thus, for each reaction $j$, the heat release may be found as

$$Q_j \left[ \frac{W}{m^3} \right] = q_j \sum_{i=1}^{N} v_{ij} h_i$$

The overall heat release for the domain is found through trapezoidal integration over the numerical domain. Results are normalized by the total heat released to quantify the net contribution of each reaction, where both exothermic and endothermic reactions are readily observed. Furthermore, partial heat releases may be found by integrating over only a portion of the domain. Heat release analysis reveals reactions driving and detracting from the temperature increase. Since reaction rate coefficients are a function of temperature, it is intuitive that the heat release likewise affects flame structures and should be considered in the present study.

**Numerical Regression**  The comprehensive data set includes detailed information on flame structure: (a) specific species concentrations, (b) their respective creation or destruction rates, and (c) forward or reverse reaction rates, defined by the law of mass action as the product of reactant concentrations and specific reaction rate constants at a given temperature [42]. In each case, the location of physical peaks, peak gradient and peak curvature are determined and catalogued as a function of the local temperature.
Figure 2.1 illustrates these maxima and their corresponding temperatures for a forward reaction rate. Based on these criteria, numerical regressions are used to determine whether characteristic temperatures $T^*$ are universally valid indicators, i.e. they are independent of $\phi$ and $T_{in}$. Detailed analyses are utilized to find the $T^*$ that indicates the transition from preheat to inner layer. In order to preserve the behavior of Arrhenius-type reaction kinetics, reaction rates are related to the laminar burning flux using the expression $\dot{m} = a \cdot T^{*b} \exp\left(\frac{c}{T^*}\right)$, where $\dot{m}$ and $T^*$ are obtained from the comprehensive data set and $a$, $b$, and $c$ are results of a multivariate regression. The quality of the regression is assessed using the standard error of the regression $s$ [49], identified as

$$s = \sqrt{\frac{1}{N-\beta} \sum_{i=1}^{N} (T^* - T^*_{i,\text{regression}})^2} \quad (2.14)$$

where $N$ is the number of data points, $\beta$ is the number of coefficients resolved (3: $a$, $b$, and $c$), and $T^*_i$ are characteristic temperatures. Here, rather than quantifying the error in mass flux $\dot{m}$, it is more intuitive to find the error in the characteristic temperature. Thus, the regression is inverted to compare $T^*$ as predicted by the regression ($T^*_{i,\text{regression}}$) to actual data ($T^*_i$). The standard error of the regression is used interchangeably as regression uncertainty throughout the work.

2.2 Experiments

2.2.1 Apparatus

The experimental apparatus consists of a burner, preheater, and flow control systems. Temperature control is dedicated per system, i.e. burner and preheater are separate systems. The entire system was monitored through a LabVIEW Virtual Interface (VI), which is included in Appendix 5 for further reference. The VI communicated with the system through a National Instruments USB-6218 Data Acquisition (DAQ) and may also be viewed in the Appendices. A photograph of the setup is shown in Figure 2.2 for further reference, minus the flow control system, which is shown in Figure 2.8.

**Burner** The porous plug burner used for this study was designed for high temperature operation and is shown in Figure 2.3. A flat flame is stabilized above a silicon-carbide (SiC) porous plug, where inlet temperatures are monitored by a type K thermocouple located upstream of the porous plug. If necessary, a disc of porous SiC is placed at an appropriate distance downstream of the burner exit to shield the
Figure 2.2: Experimental apparatus, including preheater, burner, radiation shield, camera, and DAQ (Data Acquisition system).
surface of the burner plug from radiative heat losses. In order to reduce heat losses from the burner at elevated temperatures, several measures are taken. The plenum chamber, filled with alumina beads, is contained within an insulating ceramic micro-porous shell, where an outer steel casing provides a rigid containment structure. Then a temperature-controlled 1200 W guard heater, shown in Figure 2.4a, is wrapped around the casing and further insulated. Temperature of the heater is controlled on a dedicated circuit with an ON/OFF controller, shown in Figure 2.4b. The thermocouple wire is also run to the LabVIEW VI for monitoring in combination with gas flow control (Fig. 2.7).

**Preheater**  The preheater is likewise designed specifically for high temperature gas operation, upwards of 950K for the fluid. Heating was achieved through an internal cartridge heater (Fig. 2.5b) and five band heaters (Fig. 2.5a) for a total of 3625 W of heating power. Efficient heat transfer was attained by forcing the premixed fuel and air through a porous media, which contacted the inner heated shell via a stainless steel foil to reduced contact resistance. Figure 2.6 contains a drawing of the preheater detailing the components. Beginning at the center, the cartridge heater is contained in a cylindrical steel shell. The gas mixture flows through the media, which also contacts the outer steel shell. The band heaters are wrapped around this outermost shell, where six thermocouple ports allow for temperature measurement and control. The entire preheater is wrapped in high-temperature insulation to reduce heat loss to the
(a) TEMPCO (Grainger® # 2VYU6) 1200 W heater.

(b) Omega® CN7500 temperature controller.

Figure 2.4: Burner heating equipment: guard heater (a) and temperature controller (b).

(a) TEMPCO (Grainger® # 2VYF7) 450 W band heater

(b) OMEGA® (#CIR-5121/240) 1375 W cartridge heater

Figure 2.5: Preheater equipment: band heater (a) and cartridge heater (b).
Figure 2.6: Preheater sectioned drawing: fuel/air mixture flows through a porous matrix where heat is added via a cartridge heater (Fig. 2.5b) and five band heaters (Fig. 2.5a). Thermocouple ports allow for monitoring along the entire length of the preheater.
Figure 2.7: Gas and temperature control diagram: fuel and air are regulated, mixed, and heated before reaching the burner. Both flow and temperature are monitored and controlled.

Environment. The preheater has dedicated temperature control via an additional controller to that shown in Figure 2.4b. A single controller reads the outlet temperature of the preheater and alternately turns all heaters on and off as needed. Additional thermocouples are used to monitor temperature.

**Gas Flow Control and Mixing**  Figure 2.7 provides a flow diagram of the system, including flow controls. Upstream of the burner assembly, research grade methane and high-purity compressed industrial air are limited to a pressure less than 150 psig, regulated by individual mass flow controllers, mixed, and passed into the preheater. Mass flow controllers are Cole-Parmer 10 LPM and 100 LPM models depicted in Figure 2.8. These controllers are high precision, factory calibrated controllers that measure volumetric flow rate from the pressure drop over a laminar flow element. The controllers are gas specific, and thus, the mass flow may be calculated, corrected for both temperature and pressure via ideal gas and compressibility properties. The controllers are operated through a LabVIEW VI and DAQ system. The VI converts user-specified equivalence ratios and ambient temperature flow velocities to control signals for the mass flow controllers. During heat-up of the burner assembly, an alternate low pressure laboratory air supply is used, which accommodates higher flow rates and thus decreases the time required to reach
Figure 2.8: Flow controllers, Cole-Parmer 10 LPM (#32907-71) and 100 LPM (#32907-75). Air and fuel (CH$_4$) are regulated separately and mixed before entering the preheater. Laboratory air may be used during transient heating.

steady state conditions.

**Camera** Figure 2.9 shows the camera, lens, and filter used to capture flame images. The camera takes digital images of 1280 x 1024 pixels through a 16 mm fixed focal length lens. To capture CH* luminescence, a using a narrow-bandwidth optical filter with a central wavelength of 430 nm is attached to the lens. The camera is connected into the computer via USB, and images are taken per manufacturer software.

### 2.2.2 Method

**General Procedure** Experiments achieve specific objectives for lean and rich regimes; however, a general procedure may be detailed in the following. In order to observe combustion characteristics at elevated inlet temperatures, numerical simulations are used to predict inlet conditions of $\phi$ and $T_{in}$ for constant $m_{ad}$. The system is heated using laboratory air to $T_{in}$, determined by the thermocouple located directly beneath the porous plug. Flame images of CH* chemiluminescence are taken at desired
Figure 2.9: Camera, lens, and filter, all from THORLABS. The camera is calibrated to the level of the burner surface and provides filtered flame images corresponding to CH* luminescence.

non-adiabatic mass fluxes, allowing the system to reach steady state at each mass flux. To achieve this end, the user specifies an ambient temperature velocity and equivalence ratio in the VI, which converts it into mass fluxes for both fuel and air mass flow controllers. For lean cases, stand-off distances along the entire range of non-adiabatic fluxes were desired. To achieve this end, the ambient temperature velocity (specified in the VI) was increased in increments of 1 cm/s from the low to adiabatic mass flux limits, i.e. where the flame lost its flatness at low and high velocities. In this case, three images per increment were taken, one as the velocities were increased, then decreased, and increased again. Thus, any hysteresis or other error could be adequately captured and identified.

Flame Position Determination  The stand-off distances are found from digital flame images for lean reference cases. The process includes the calibration of the camera, i.e. creating a scale from pixels to millimeters and finding the burner surface, and reading of flame images. All image processing was done using MATLAB’s image processing toolbox.

Calibration is achieved through comparative scaling in calibration images. First, the camera is visually leveled with the burner surface. A photograph is taken with a flame placed behind the burner to pinpoint the burner surface. Then, an object of known height, a simple hex nut in the present study, is placed on the burner to find a pixel/millimeter scale. Pixel locations are found by reading the contrasted intensities of y-pixel coordinates corresponding to the calibration flame. Here, the contrasted images provide sharp gradients and flat-topped flame profiles to allow for accurate object readings. Figure 2.10
Figure 2.10: Example calibration images where a) is the raw filtered image, b) is a gray-scaled false color image used for actual flame readings, and c) is a contrasted false color image used for calibration. Illustrates a set of example calibration images. From the images, the small flame is visible just above the object, where the contrasted image (Fig. 2.10c) is read to pinpoint the exact pixel location of its height. Figure 2.11 shows the intensity plot along a vertical line of pixels corresponding to the calibration flame location. Contrasted noise must be filtered out by reading only a specific range of pixels. Similar photographs are taken with the hex nut placed on the front and rear of the burner surface relative to the camera position to indicate uncertainty in the camera position. If the camera was inadvertently moved at any point in the experiments, the camera was re-calibrated accordingly. Additionally, a similar range of x-pixels is read in all measurements to eliminate any systematic error due to a non-horizontal burner surface. Flat flame positions are determined by simply finding the pixel of maximum brightness in a
gray-scaled non-contrasted image, where contrasted noise is no longer an issue. The difference between it and the burner surface is scaled into millimeters to find the stand-off distance. These measurements are comparable to burner-stabilized simulations at matching conditions, using the peak value of CH as the metric for flame position.

2.3 Fluent

A two dimensional, axisymmetric model of burner-stabilized flames, supplemental to the one dimensional flat flames simulated in CANtera, was created at a lean reference case of $\phi = 0.7$, $T_{in} = 300K$ in the computational fluid dynamics code Fluent 12.0 [4]. Methodology follows a known solution approach for models involving reaction chemistry [58]. In the following, two-dimensional conservation equations, model parameters, and the repeatable solution procedure are all presented and discussed.

2.3.1 Conservation Equations

Conservation equations are similar to those presented for Cantera in the previous section; although an transient axisymmetric model was used. For completeness, the equations are represented here, following that in Fluent documentation [4]. Mass conservation, similar to before, is

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x}(\rho u) + \frac{\partial}{\partial r}(\rho u_r) + \frac{\rho u_r}{r} = 0 \quad (2.15)$$
where \( u \) is the velocity in the axial direction and \( u_r \) is in the radial direction. Species conservation includes both diffusion of species in the axial and radial directions,

\[
\frac{\partial (\rho u_Y)}{\partial x} + \frac{1}{r} \frac{\partial (\rho u_r Y)}{\partial r} - \frac{\partial}{\partial x} (\rho \frac{dY}{dx}) - \frac{\partial}{\partial r} \left( r \rho \frac{dY}{dr} \right) = \dot{\omega}_i MW_i \tag{2.16}
\]

The Fluent model also uses the full momentum formulation,

\[
\frac{\partial}{\partial t} (\rho u) + \frac{1}{r} \frac{\partial}{\partial x} (r \rho uu) + \frac{1}{r} \frac{\partial}{\partial r} (r \rho u_r u) = -\frac{\partial P}{\partial x} + \frac{1}{r} \frac{\partial}{\partial x} [r \mu (\frac{\partial u}{\partial x} - \frac{2}{3} (\nabla \cdot \vec{u}))]
+ \frac{1}{r} \frac{\partial}{\partial r} [r \mu (\frac{\partial u}{\partial r} + \frac{\partial u_r}{\partial x})] + F_x \tag{2.17}
\]

\[
\frac{\partial}{\partial t} (\rho u_r) + \frac{1}{r} \frac{\partial}{\partial x} (r \rho u_r u) + \frac{1}{r} \frac{\partial}{\partial r} (r \rho u_r u_r) = -\frac{\partial P}{\partial r} + \frac{1}{r} \frac{\partial}{\partial x} [r \mu (\frac{\partial u_r}{\partial x} + \frac{\partial u_x}{\partial r})]
+ \frac{1}{r} \frac{\partial}{\partial r} [r \mu (\frac{\partial u_r}{\partial r} - \frac{2}{3} (\nabla \cdot \vec{u}))]
- 2 \mu \frac{u}{r^2} + \frac{2}{3} \mu \frac{u_r}{r} (\nabla \cdot \vec{u}) + \rho \frac{u^2}{r} + F_r \tag{2.18}
\]

where \( P \) is the pressure, \( \mu \) is the viscosity, and \( F \) is a body force. Additionally, \( \nabla \cdot \vec{u} \) may be found by

\[
\nabla \cdot \vec{u} = \frac{\partial u}{\partial x} + \frac{\partial u_r}{\partial r} + \frac{u_r}{r} \tag{2.19}
\]

Finally, the energy equation takes heat transport by advection, diffusion, and convection in both radial and axial directions,

\[
\rho c_p \left( \frac{\partial T}{\partial t} + u \frac{\partial T}{\partial x} + u_r \frac{\partial T}{\partial r} \right) + \sum_{i=1}^{N} \vec{J}_i \nabla T = \frac{\partial}{\partial x} (k \frac{\partial T}{\partial x}) + \frac{1}{r} \frac{\partial}{\partial r} \left( kr \frac{\partial T}{\partial r} \right) - \sum_{i=1}^{N} h_i \dot{\omega}_i MW_i \tag{2.20}
\]

in which \( \vec{J}_i \) has been used in place of the diffusion terms for simplicity.

### 2.3.2 Model Parameters

The computational model utilizes the geometry of the experimental apparatus of this work; however, the model is analogous to Cantera burner-stabilized flat flame code. Thus, the model is useful in evaluating flame properties affected by specific conditions and does not attempt to replicate experimental observations. Additionally, the chemistry in the model was limited to GRI-Mech 2.11, a 49 species 277
reaction mechanism [10], by the number of species importable under the current Fluent version.

Figure 2.12a presents model geometry, a 5 cm long axial length with a 3.81 cm radial width. The computational domain has been reduced to half the actual burner geometry through an axis-symmetric assumption; thus, the inlet is 2.54 cm wide, corresponding to the porous plug radius. To allow for the inward diffusion of air into the flame region, a 1.27 cm buffer between it and the radial outlet boundary is provided. The outlet boundary here is set as a pressure outlet, which allows for reverse flow, specified as ambient temperature and pressure air. In keeping with the model application, the buffer surface co-linear to the inlet is modeled as a boundary only, where thermophysical properties of ceramic insulation, thermal conductivity \( k = 0.028 \frac{W}{m\cdot K} \), and a no slip condition are applied. The inlet itself is a velocity inlet, where additional parameters of temperature and inlet composition are specified, but inlet diffusion is allowed. Finally, the axial outlet boundary is also set as a pressure outlet with ambient air as a reversed flow parameter.

A quadrilateral mesh is created in the domain, specifically designed to ensure flame stabilization. A biased grid of 0.5 mm average element size is established in the axial direction. A bias factor, or the ratio of largest to smallest edges, of 10 is set towards the inlet in the expectation of flame stabilization one millimeter or less from the inlet. Grid sizing in the radial direction is a non-biased 1 mm, yielding
Three mass fluxes are selected for the current study at a reference case of $\phi = 0.7$, $T_{in} = 300K$. The adiabatic mass flux, corresponding to an inlet velocity of 19.3 cm/s, serves a base case, and two other fluxes are selected at $\pm 15\%$ of the adiabatic flux at inlet velocities of 16 (low) and 22 cm/s (high) respectively. The low mass flux will serve as a comparison to one dimensional flat flame simulations, where boundary effects may be studied. The high mass flux is used to demonstrate the two dimensional structure that results after the burning flux has been exceeded. In order to quantify the accuracy of the simulation in resolving the two dimensional structures, a calculation of the laminar burning flux is utilized. In this calculation, the surface area of a wrinkled flame is found from radial and axial coordinates of flame position. When divided by the inlet mass flow rate, the resulting mass flux should approximate the adiabatic mass flux, ignoring the effects of flame stretch. To find the surface area of this flame, radial, or flat, portions are found simply by subtracting the areas of two concentric circles; however, another method must be utilized for those lengths that contain a vertical component. Here, the surface area of a cone is used to approximate the straight-line surface area between two points. A representation of this methodology is shown in Figure 2.13. An angle $\theta$ is backed off the triangle formed by the points, and then two conical surface areas may be found. The surface area of a cone, not including the base is given by $\pi rs$, where $s$ is the length of the conical surface. By subtracting the surface areas of each cone formed, the surface area is approximation. A summation of all the areas gives an overall surface area.
Figure 2.14: Nodes added in successive refinements, (1) green (2) red, to the original mesh (blue). Shown is the alternate second refinement, adding a third level of refinement shown by the high concentration of points near the inlet.

Table 2.2: Successive gradient refinement criteria. An alternate second refinement was utilized to further refine the reaction zone to a total of three levels of refinement.

<table>
<thead>
<tr>
<th>Refinement #</th>
<th>Parameter</th>
<th>Normalized Refinement Threshold</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>temperature</td>
<td>.5</td>
</tr>
<tr>
<td>2</td>
<td>reaction rate of $H + O_2 \rightarrow O + OH$</td>
<td>.5</td>
</tr>
<tr>
<td></td>
<td>temperature</td>
<td>.5</td>
</tr>
<tr>
<td></td>
<td>mole fraction $H_2$</td>
<td>.5</td>
</tr>
<tr>
<td></td>
<td>mole fraction $H$</td>
<td>.2</td>
</tr>
<tr>
<td>2, alternate</td>
<td>mole fraction $H_2$ (third level)</td>
<td>.5</td>
</tr>
</tbody>
</table>

2.3.3 Solution Procedure

Parameters The model used is transient rather than steady state due to solver limitations in the Fluent code. The domain is initially filled with quiescent hot nitrogen at 2000K to ensure combustion initialization. Time-steps are implemented in $t = .01$ ms using the first order implicit scheme [55]. Per each time-step, chemistry is resolved using a second-order up-wind [4]. Energy conservation is resolved using second order up-wind as well. Momentum, shown to be trivial in the one-dimensional model, is resolved using only using first order up-wind [4].

Refinement The solution is stepped in time until steady state is approximated, at 250 ms after 25,000 time-steps. The grid is then refined in two steps to resolve the large gradients contained in the reaction zone, where an alternative second refinement provides the highest level of refinement. Refinements divide quadrilateral elements into four sub-elements based on a refinement threshold [4]. Table 2.2 shows the refinement thresholds and criteria of the current work, where normalized gradients of temperature and a reaction rate respectively. Figure 2.14 illustrates the effect of successive refinements on the flame zone of the low mass flux case, where added nodes are shown on the original mesh grid. The first refinement seeks to add more points in the high temperature gradient found at the beginning of the reaction zone.
Table 2.3: Grid dependence of the solution temperature. Error is calculated with respect to the finest grid, provided by the alternate second refinement.

<table>
<thead>
<tr>
<th>Mass Flux $\frac{kg}{m^2 \cdot s}$</th>
<th>Original Mesh</th>
<th>Refinement 1</th>
<th>Refinement 2</th>
<th>Alternate Refinement 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>.186</td>
<td>18</td>
<td>8</td>
<td>8</td>
<td>-</td>
</tr>
<tr>
<td>.219</td>
<td>126</td>
<td>52</td>
<td>14</td>
<td>-</td>
</tr>
<tr>
<td>.252</td>
<td>112</td>
<td>133</td>
<td>114</td>
<td>-</td>
</tr>
</tbody>
</table>

$||\Delta T||_{2}$

(green), while the alternate second (red) resolves several flame layers: the high temperature gradient, reaction zone, and post-flame zone. This refinement applies a third level of refinement to the high temperature gradient, as shown by the intense cluster of nodes in that area. Alternatively, the original second refinement only added points to the flame zone; thus, the alternate refinement gives a better solution. The refinements are separated by 3000 time-steps, and the final solution is reached at 31,000 time-steps, or $t = 310$ ms.

**Error** The error may be quantified using the $L_2$ error norm of temperature $||\Delta T||_{L_2}$ [58] at the final solution time of 310 ms,

$$||\Delta T||_{L_2} = \sqrt{\frac{1}{N} \sum_{i=1}^{N} [T_k(t = .31, r_i, x_i) - T_{best \ sol.}(t = .31, r_i, x_i)]^2} \quad (2.21)$$

where $N$ is the number of points on the coarsest grid, $T_k$ is the temperature solution vector of the $k$th refinement, and $T_{best \ sol.}$ is the temperature solution of the most refined case. The error norms are presented in Table 2.3 for each inlet mass flux. As expected, the error is shown to drop per each refinement, with the exception of the two dimensional mass flux. The error increases with mass flux due to increasing two dimensional behavior and formation of complex structures.
Chapter 3
Adiabatic Flames

3.1 Adiabatic Solution Set

The principal adiabatic solution characteristic under study is the laminar burning flux $\dot{m}_{ad}$, a function of equivalence ratio $\phi$, inlet temperature $T_{in}$. The effect of each is considered separately, and experimental data is included for comparison of numerical solutions to the literature at selected inlet conditions, from which conclusions may be drawn on the data set. The complete multivariate solution set is presented for the GRI 3.0 mechanism to demonstrate the combined effects of the two parameters.

3.1.1 Effect of Equivalence Ratio $\phi$

GRI 3.0 and San Diego solutions, with experimental data from the literature (Section 1.4), are shown as a function of $\phi$ in Figure 3.1 at comparative inlet temperatures. Both mechanisms predict burning fluxes comparable to experiments at standard ambient conditions, although the San Diego mechanism is notably lower than the experimental cluster at moderately rich conditions. Regardless, the mechanisms also converge for standard temperature solutions well beyond corresponding flammability limits, particularly on the rich side. This result has been noted previously, and kinetic criterion have been defined to resolve the physically applicable domain [43, 15]. For the purposes of this study, a lower mass flux limit eliminates these data points in the analysis. The overall effect of equivalence ratio is shown to be decreased burning fluxes in both lean and rich regimes. High gradients in the flux remain as the lean limit is approached, but the curve levels off at rich conditions due to the asymmetrical definition of $\phi$. As temperature is increased, the experiments and numerical predictions diverge considerably. Whether this is a result of uncertainties in the mechanisms or in the experimental techniques is unknown; however, two observations of the data should be considered. First, the experimental data points were collected in early combustion studies in the 1950’s and before, so the experimental and measurement techniques cannot be confirmed [3]. Secondly, the large discrepancy between the two mechanisms at preheated conditions suggests mechanism uncertainty at higher temperatures where experimental validation data is sparse. Indeed, Figure 3.1 overall illustrates the large domain reached with numerical solutions that remain unresolved experimentally.
3.1.2 Effect of Inlet Temperature $T_{in}$

The laminar burning fluxes predicted by respective mechanisms are compared with experiments at elevated inlet temperatures in Figure 3.2. Again, the numerical solutions show a consistent discrepancy between one another with correctly indicated trends. In fact, the two mechanisms effectively bracket experimental results with GRI predicting a higher burning flux than the data and San Diego lower. Also of note is the non-linear nature of the curve as well as its similarity at all inlet conditions, shown by the additional solution set of $\phi = 0.5$. 

Figure 3.1: Comparison of experimental and numerical burning flux data as a function of equivalence ratio $\phi$.

Figure 3.2: Comparison of experimental ($\phi = 1$) and numerical burning flux data as a function of inlet temperature $T_{in}$ at selected equivalence ratios $\phi$. 

Figure 3.3: Contours of constant laminar burning flux as a function of $T_{in}$ and $\phi$ for the GRI mechanism, and the underlying comprehensive data set of 1299 simulated conditions are indicated by dots (·). Reference inlet conditions are chosen along lines of constant $\phi = 0.7$, $\phi = 1.6$, and constant $\dot{m} = 0.219$ kg/m$^2$s are marked by squares (■) for lean and triangles (▲) for rich respectively.

3.1.3 Multivariate Solution

The dependence of the laminar burning flux $\dot{m}$ on both unburned temperature $T_{in}$ and equivalence ratio $\phi$ is illustrated by constant mass flux contours in Figure 3.3 for the GRI mechanism. The San Diego mechanism, with 1270 similar simulated conditions, is presented comparatively in future sections for the data sets under current study only. Regardless, several effects are readily visible in the data set. Aforementioned effects of equivalence ratio squeeze the contours of mass fluxes together near the lean limit, indicating the sharp gradient visualized in Figure 3.2, while rich conditions show a broader curve. The ranges of possible equivalence ratios are likewise extended with increasing inlet temperature. Within this data set, present study focuses on the specific regimes of $\phi = 0.15 - 0.9$ (lean) and $\phi = 1.3 - 2.7$ (rich). Of note are the data points beyond the lower mass flux limit of $0.05\frac{kg}{m^3s}$, particularly at rich conditions. These data points will be dropped in the numerical analysis.

3.1.4 Error

Estimates for uncertainties in the numerical data are assessed for the 10 marked reference cases (■, ▲ in Fig. 3.3), and results are shown in Table 3.1. Specifically, numerical error may be introduced by the user-specified solution tolerances ($\Delta \dot{m}_{alg}$) detailed in Section 2.1.1, through the computation grid or fixed temperature of flame stabilization. Second, all simulations are run using the mixture averaged diffusion model rather than full multicomponent diffusion ($\Delta \dot{m}_{trans}$). Finally, the impact of reaction mech-
Table 3.1: Relative uncertainty of numerical simulations introduced by numerical solver ($\Delta \dot{m}_{\text{alg}}$), transport mechanism ($\Delta \dot{m}_{\text{tran}}$) and reaction mechanism ($\Delta \dot{m}_{\text{kin}}$).

<table>
<thead>
<tr>
<th>$\phi$</th>
<th>$T_{\text{in}}$</th>
<th>$\dot{m}$</th>
<th>$\Delta \dot{m}_{\text{alg}}$</th>
<th>$\Delta \dot{m}_{\text{tran}}$</th>
<th>$\Delta \dot{m}_{\text{kin}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.365</td>
<td>800</td>
<td>0.219</td>
<td>1.93</td>
<td>-</td>
<td>28.8</td>
</tr>
<tr>
<td>0.53</td>
<td>550</td>
<td>0.219</td>
<td>1.54</td>
<td>-</td>
<td>16.0</td>
</tr>
<tr>
<td>0.7</td>
<td>800</td>
<td>0.778</td>
<td>1.95</td>
<td>-</td>
<td>11.4</td>
</tr>
<tr>
<td>0.7</td>
<td>550</td>
<td>0.435</td>
<td>1.47</td>
<td>-</td>
<td>11.5</td>
</tr>
<tr>
<td>0.7</td>
<td>300</td>
<td>0.219</td>
<td>1.03</td>
<td>-</td>
<td>11.36</td>
</tr>
<tr>
<td>1.34</td>
<td>300</td>
<td>0.219</td>
<td>0.14</td>
<td>1.04</td>
<td>41.7</td>
</tr>
<tr>
<td>1.60</td>
<td>300</td>
<td>0.088</td>
<td>2.11</td>
<td>0.73</td>
<td>23.1</td>
</tr>
<tr>
<td>1.60</td>
<td>600</td>
<td>0.219</td>
<td>1.28</td>
<td>0.71</td>
<td>27.2</td>
</tr>
<tr>
<td>1.60</td>
<td>900</td>
<td>0.507</td>
<td>1.85</td>
<td>0.23</td>
<td>27.1</td>
</tr>
<tr>
<td>2.16</td>
<td>900</td>
<td>0.219</td>
<td>2.05</td>
<td>3.30</td>
<td>10.6</td>
</tr>
</tbody>
</table>

*Lean multicomponent cases did not converge; however, error may be assumed similar.

anism selection is illustrated by a comparison to results from the San Diego mechanism, which predicts consistently lower laminar burning fluxes ($\Delta \dot{m}_{\text{kin}}$). Table 3.1 shows that the kinetics model introduces significantly larger uncertainties than solver parameters and diffusion model, which is explained by a lack of validation data available for substantially preheated combustion. As expected from Figure 3.1, the error is generally lower in the lean regime, but, coincidentally, error decreases at the ultra-rich case where GRI and San Diego solutions intersect.

### 3.2 Lean Analysis

The lean regime ($\phi = 0.15 – 0.9$) is analyzed in detail for five reference inlet conditions, while a regression analysis encapsulates its entirety. Figure 3.4 provides a multivariate visualization of the data set under consideration, which includes over 400 points per mechanism. Reference cases are shown based on inlet conditions of a constant equivalence ratio ($\phi = 0.7$) and those derived from $\dot{m}_{\text{ref}} = .2190$ in the GRI mechanism. Differences in the predicted mass fluxes are visible through comparison of the reference inlet conditions for each. Constant $\dot{m}$ cases should be along the contour of $\dot{m} = .2190$; however, San Diego predicts significantly lower fluxes. As expected, constant equivalence ratio cases are also shown to be lower than their GRI counterparts. In the following, flame structures and reaction paths are presented from the GRI mechanism, while San Diego results show the similarity of major species profiles within the structure. Significant differences in the reaction pathways are discussed. Similarly, sensitivity and heat release results are presented using GRI, while San Diego results are used comparatively. Here,
the San Diego mechanism is a so-called “short” mechanism, in that it seeks to minimize the number of species and reactions necessary. For this reason, in addition to providing a more accurate burning flux curve (Fig. 3.2), the GRI mechanism is taken to be the most complete solution of the two and the best representation of structure. Findings are applied as such to the regression analysis to explain both the quality of indicators and discrepancies in characteristic temperatures between the mechanisms.

3.2.1 Flame Structure and Reaction Paths

Figure 3.5 shows axially scaled flame structures for reference cases at constant $\dot{m}$ and constant $\phi$. The structures are normalized by the flame thickness, defined as the maximum temperature difference divided by the maximum slope of the temperature profile: $\ell = \Delta T / \max (dT/dx)$ [66]). Table 3.2 shows that both mechanisms predict similar trends and magnitudes in flame thickness. The thickness is shown to grow slightly wider as ultra-lean conditions are reached, whereas preheating alone causes a significant decrease. In the flame structure, at constant $\dot{m}$, temperature profiles cross at the origin (Fig. 3.5a), whereas they show a similar progression at constant $\phi$ (Fig. 3.5b). Varying $\phi$ affects magnitudes while trends are similar. Concentrations of reactant and major product species – CH$_4$/O$_2$ and CO$_2$/H$_2$O – show nearly identical progressions, as does the heat release while their magnitudes differ. As expected, CO$_2$ product concentration decreases in the ultra-lean domain; however, heat release is likewise affected. CO approaches negligible concentrations in all cases (Fig. 3.5a). The impact of increased $\dot{m}$ is limited to a slight decrease of CO$_2$ in favor of H$_2$/CO while heat release shows a significant gain (Fig. 3.5b). In addition, the relative position of species is generally unaffected by the variation of inlet conditions. As the fuel is consumed, the intermediate species CH$_2$O and HO$_2$ show significant rises in concentration,
Figure 3.5: Normalized flame structures showing profiles of temperature and molar species concentrations at constant laminar burning rate $\dot{m}$ (a) and constant equivalence ratio $\phi$ (b). Profiles are centered at the largest curvature of the reaction $\text{H} + \text{O}_2 \rightarrow \text{O} + \text{OH}$ and non-dimensionalized by the flame thickness $\ell = \Delta T / \max (dT/dx)$, where $\Delta T$ is the adiabatic temperature increase.

where peak $\text{HO}_2$ is approximately at the axis. Afterwards, peak concentrations of $\text{CH}_3$ and $\text{HCO}$ are observed, while $\text{H}_2$ and $\text{CO}$ have broader profiles. These species are accompanied by a rise in product species and radical concentrations. The lack of radicals until this point is easily explained by their rate-limiting nature in the the reaction zone. Overall, Figure 3.5 illustrates that flame characteristics may be normalized and compared despite vastly different $T_{in}$, $\phi$ and $\dot{m}$.

A reaction pathway analysis further confirms that main pathways are similar for all five reference cases. Specifically, two standard pathways [42, 71], methane oxidation (reactions (Ia)-(VII)) and the $\text{H}_2$-$\text{O}_2$ sub-mechanism (reactions (VIIa)-(VIIe)), are identified as central to the flame structure and characteristics. The pathways are reproduced here as confirmed by the reaction pathway analysis tool Mix-Master.
Table 3.2: Flame thicknesses used for normalization of lean regime flame structures. Respective thicknesses are shown for GRI ($l_{GRI}$) and San Diego ($l_{SD}$).

<table>
<thead>
<tr>
<th>$\phi$</th>
<th>$T_{in}$ K</th>
<th>$l_{GRI}$ mm</th>
<th>$l_{SD}$ mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.365</td>
<td>800</td>
<td>0.75</td>
<td>0.89</td>
</tr>
<tr>
<td>0.53</td>
<td>550</td>
<td>0.68</td>
<td>0.74</td>
</tr>
<tr>
<td>0.7</td>
<td>800</td>
<td>0.33</td>
<td>0.33</td>
</tr>
<tr>
<td>0.7</td>
<td>550</td>
<td>0.43</td>
<td>0.45</td>
</tr>
<tr>
<td>0.7</td>
<td>300</td>
<td>0.66</td>
<td>0.70</td>
</tr>
</tbody>
</table>

Fuel breakdown is initiated by H-abstraction, i.e.

$$\begin{align*}
\text{OH} + \text{CH}_4 & \to \text{CH}_3 + \text{H}_2\text{O} \quad \text{(Ia)} \\
\text{H} + \text{CH}_4 & \to \text{CH}_3 + \text{H}_2 \quad \text{(Ib)}
\end{align*}$$

where (Ia) is shown to be a low temperature pathway and (Ib) dominates at higher temperatures. CH$_3$ is found to be an active intermediate radical within the combustion process. It is consumed in low temperature pathways to form either C$_2$ hydrocarbons through (IIa) or oxygenated hydrocarbons through (IIb).

$$\begin{align*}
2\text{CH}_3 (+\text{M}) & \to \text{C}_2\text{H}_6 (+\text{M}) \quad \text{(IIa)} \\
\text{HO}_2 + \text{CH}_3 & \to \text{OH} + \text{CH}_3\text{O} \quad \text{(IIb)}
\end{align*}$$

C$_2$ chain hydrocarbons are quickly recycled back into CH$_3$, while CH$_3$O breaks down further into formaldehyde. Two important observations stem from these reactions: i) the dependence of pathway (IIb) on the low temperature radical HO$_2$ rather than H, O, or OH and ii) the formation of the C$_2$ chain in lean flames. Both of these features will be shown to have impacts on overall flame behavior. As temperature increases, CH$_3$ bypasses these along two pathways initiated by the O radical

$$\begin{align*}
\text{O} + \text{CH}_3 & \to \text{H} + \text{CH}_2\text{O} \quad \text{(IIIa)} \\
\text{O} + \text{CH}_3 & \to \text{H} + \text{H}_2 + \text{CO} \quad \text{(IIIb)}
\end{align*}$$

where the latter reaction actually bypasses CH$_2$O oxidation altogether. Also of note as temperature
increases is the recombination reaction

\[ H + CH_3 (+M) \rightarrow CH_4 (+M) \] (IV)

which significantly slows the combustion progression (Section 3.2.2) but contributes greatly the heat release (Section 3.2.3). This reaction is responsible for the late rise of CH$_3$ observed in the flame structure, rather than chronologically oriented with fuel breakdown in the preheat layer [71]. Further radical attack on the formaldehyde intermediate leads to the formation of carbon monoxide through the intermediate HCO.

\begin{align*}
H + CH_2O & \rightarrow HCO + H_2 \quad (Va) \\
OH + CH_2O & \rightarrow HCO + H_2O \quad (Vb) \\
HCO + O_2 & \rightarrow HO_2 + CO \quad (Vc) \\
H + HCO & \rightarrow H_2 + CO \quad (Vd)
\end{align*}

CO$_2$ is then almost exclusively formed through the oxidation of CO through the reaction

\[ OH + CO \rightarrow H + CO_2 \] (VI)

The majority of radicals are created through reactions of the H$_2$-O$_2$ sub-mechanism,

\begin{align*}
H + O_2 + (N_2, H_2O) & \rightarrow HO_2 + (N_2, H_2O) \quad (VIIa) \\
H + HO_2 & \rightarrow 2OH \quad (VIIb) \\
H + O_2 & \rightarrow O + OH \quad (VIIc) \\
O + H_2 & \rightarrow H + OH \quad (VIIId) \\
OH + H_2 & \rightarrow H + H_2O \quad (VIIe)
\end{align*}

making it essential to the upstream fuel breakdown. Reaction (VIIc), generally considered one of the most important reactions in a combustion process [42], breaks down O$_2$ in a chain-branching reaction to
form both O and OH. The oxygen radical O further contributes to the radical population through (VII\textit{d}).

The majority of H is produced by (VII\textit{e}) in a chain carrying reaction between OH and H\textsubscript{2} and is involved in the attack on both fuel and oxidizer (VII\textit{c/lb}). Reactions (VII\textit{a}) and (VII\textit{b}), relevant mainly in low temperature regimes, create and destroy the HO\textsubscript{2} radical in competition with reaction (VII\textit{c}). Negligible concentrations of H, O, and OH in the preheating zone are attributed to their rate-limiting nature; in contrast, HO\textsubscript{2} accumulates relatively early and participates in other reactions to form H\textsubscript{2}O\textsubscript{2} and CH\textsubscript{3}O, among others.

Figure 3.6 shows axially scaled and normalized (Tab. 3.2) flame structures of comparable reference cases utilizing the San Diego mechanism. Here, constant $\dot{m}$ will remain as nomenclature only, as San Diego predicts different $\dot{m}$ for the corresponding reference inlet conditions. The behavior of each respective set of reference cases, relative to reaction (VII\textit{c}) is similar to that of GRI. Species concentrations and
heat release show only subtle differences as well. However, differences in the reaction paths are noted in the preheat layer. Rather than reacting with HO$_2$ in reaction (IIb), CH$_3$ forms C$_2$H$_6$ more readily in the preheat zone. The result is a slightly higher HO$_2$ concentration and a shift in CH$_2$O concentrations as its early formation through CH$_3$O is subsequently delayed. Additionally, the formaldehyde bypass of reaction (IIIb) is not included in the mechanism, and many third body reactions, such as (VIIa), specified in GRI are lumped into a single reaction utilizing (+M). Third body HCO destruction reaction (VIII) shows increased activity in the San Diego mechanism; however, GRI does not provide additional third body reactions in this case.

\[ \text{HCO} (+M) \rightarrow \text{H} + \text{CO} (+M) \]  
(VIII)

### 3.2.2 Sensitivity Analysis

Figure 3.7a illustrates results of a sensitivity analysis at the five reference conditions, where the laminar burning flux is used as the benchmark. Results show that chain-branching reactions increase the burning flux, while chain-breaking reactions slow the burning. Specifically, reaction (VIIc) significantly enhances the laminar burning flux, whereas reaction (IV) has an adverse effect through radical scavenging. Similarly, the formation of HO$_2$ is detrimental to the burning flux both because it competes with reaction (VIIc) and because HO$_2$ itself is less reactive than O and OH. However, HO$_2$ is shown to be key in reaction (IIb), which enhances the burning flux and is shown to be an important low temperature pathway. Reaction (VI) produces H radicals slightly later than reaction (VIIc) in a chain-carrying reaction, which enhances the burning flux due to its heat release (Section 3.2.3). Other reactions are shown to affect the laminar burning flux to a lesser degree; however, most show increased sensitivity at ultra-lean conditions ($\phi = 0.365$).

San Diego results at the same reference inlet conditions are shown in Figure 3.7b. Not surprisingly, reaction (VIIc) remains the most sensitive reaction, followed by reaction (VI) as before, and reactions (VIIa) and (IV) continue to exhibit chain-breaking behavior. As expected from analyses of reaction pathways, reaction (IIb) plays a diminished role, but reaction (VIII), not even included in GRI results, is shown to be the third most sensitive. San Diego results as a whole confirm the majority of sensitive
Figure 3.7: Log-normal sensitivity of a) GRI and b) San Diego reactions with largest impact on the lean laminar burning flux $\dot{m}_{\text{ad}}$. 

\[ \text{H + O}_2 \Leftrightarrow \text{HO}_2 + \text{H}_2 \text{O (VIIa)} \]
\[ \text{H + CH}_3 (+ \text{M}) \Leftrightarrow \text{CH}_4 (+ \text{M}) (\text{IV}) \]
\[ \text{HCO + O}_2 \Leftrightarrow \text{HO}_2 + \text{CO (Vc)} \]
\[ \text{H + O}_2 + \text{N}_2 \Leftrightarrow \text{HO}_2 + \text{N}_2 (\text{VIIa}) \]
\[ \text{O + CH}_3 \Leftrightarrow \text{H} + \text{CH}_2\text{O (IIa)} \]
\[ \phi \ T_n \]
\[ \begin{array}{c}
\text{0.36} & 800 \\
\text{0.53} & 550 \\
\text{0.70} & 800 \\
\text{0.70} & 550 \\
\text{0.70} & 300 \\
\end{array} \]
\[ \text{(VIIc) H + O}_2 \Leftrightarrow \text{O} + \text{OH} \]
\[ \text{(IIb) CH}_3 + \text{O}_2 \Leftrightarrow \text{CH}_3\text{O} + \text{OH} \]
\[ \text{CH}_3 + \text{OH} \Leftrightarrow \text{S-CH}_2 + \text{H}_2\text{O} \]
\[ \text{(VIII) HCO + M} \Leftrightarrow \text{CO} + \text{H} + \text{M} \]
\[ \text{(VI) CO + OH} \Leftrightarrow \text{CO}_2 + \text{H} \]
\[ \text{(VIIc) H + O}_2 \Leftrightarrow \text{OH} + \text{O} \]
Figure 3.8: GRI heat release rates for $\phi = 0.7$, $T_{in} = 300K$, normalized and centered as before. The overall heat release rate (---) is provided as a reference.

reactions as well as increased sensitivity at ultra-lean conditions.

3.2.3 Heat Release

Figure 3.8 shows axially centered heat release rates of the highest contributing reactions (Fig. 3.9a) for the base reference case ($\phi = 0.7$). HO$_2$ reaction(s) provide early heat release, accelerating before the onset of the main chain-branching reaction. Within the main heat release zone, exothermic reactions overcome the endothermic nature of (VIIc) as indicated by the total heat release rate. The main heat releasing reaction, (IIIa), occurs at a similar rate to the reaction (VIIc). Reaction (VI) provides late heat release as the adiabatic temperature is approached. While Figure 3.8 is illustrative in the relative positions of heat releasing reactions, a more comprehensive analysis finds contributions to the overall heat release.

Figure 3.9a shows respective reaction heat release contributions, both overall and within the pre-heat layer for the five reference conditions. Reaction (VIIc) has been shown to be the principal chain-branching reaction with lean methane-air flames but is now shown to be the most endothermic, requiring significant amounts of heat to produce rate-limiting radicals necessary for fuel breakdown. Main heat releasing reactions within the flame are shown to be reactions involving CH$_3$ (IIIa/IIIb), carbon monoxide (Vc/VI) and HO$_2$ (VIIa/IX). Surprisingly, reaction (IV), although shown to have a significant detrimental effect on the burning flux, is shown to release heat. Also of note is the reaction

$$\text{HO}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}_2$$

(IX)
Figure 3.9: Largest contributors per reaction to the lean heat release for a) GRI and b) San Diego mechanisms.
Figure 3.10: Heat release rates of GRI and San Diego, centered at the maximum curvature of reaction (VIIc) in the GRI mechanism and normalized per respective flame thickness.

which appears as a minor pathway; however, heat release results show it has a major impact. Other contributing reactions may be found within the main pathway between fuel and product (Section 3.2.1). It is also intuitive to look separately at early reactions and their effect in preheating, or priming, the flame. The preheat domain is defined up to the maximum curvature of reaction (VIIc) in keeping with previous results. Reactions supplying the early heat release necessary for the acceleration of this reaction are found to be initial fuel breakdown (Ia), the recombination reaction (IV), as well as the formation of \( \text{C}_2 \) hydrocarbons through (IIa).

As before, San Diego results are presented for comparison in Figure 3.9b. The main exothermic and endothermic reactions retain similar positions. As noted previously, San Diego omits reaction (IIIb), and the effect is shown in the increased role of reaction (IIIa). Similarly, the higher reaction rates of (VIII) cause for its inclusion as an endothermic reaction, although its effect is still small in comparison to (VIIc). More importantly, the positions and magnitudes of the heat release rates may also be compared to GRI. Figure 3.10 shows an axially centered heat releases rates for both mechanisms. Both sets of data are centered about a common local temperature for consistency; thus, any differences in flame profile may be eliminated. Here, the San Diego mechanism shows a similar progression, albeit later than GRI. As expected from overall heat releases, reaction (IIIa) shows a much higher peak than in GRI, matching the overall heat release peak.
3.2.4 Regression

The regression analysis determines whether the laminar burning rate follows Arrhenius-type expressions for characteristic temperatures $T^*$, that are defined by local maxima of values, gradients, or curvatures within the flame structure (Section 3.2.1). The performance of an indicator $T^*$ for the comprehensive data set is assessed using the standard error $s$ of the respective regression. Thus, indicators with a low uncertainty value identify $T^*$ that are a function of $\dot{m}$ only, i.e. they are a function of reaction temperatures and thus are driven by chemical kinetics. Likewise, those with high uncertainty, or lack thereof\(^1\), indicate a significant impact of $\phi$ and/or $T_{in}$, i.e. $T^*$ is affected by the inlet conditions. Figure 3.11, an Arrhenius type plot, illustrates the data points and regressions for peak curvature of the selected indicators. These indicators show the temperature-based progression, or zones, at which $T^*$ may be found. Characteristic temperatures of reaction (Ib), a fuel-breakdown reaction, occur prior to that of reaction (VIIc). In addition, the figure illustrates that the impact of inlet conditions is increased at lower mass flux, shown by the increased data scatter.

In the following, $T^*$ tied to maximum curvature are used to identify accelerations of species and reaction rates within the flame structure. Table 3.3 presents selected indicators from both mechanisms ranging from low to high $T_{avg}^*$, i.e. reactions and species involved in the fuel breakdown to those linked to product formation. Regressions tied to preheat zone reactions are observed with extremely poor performance, many of which do not converge. After a temperature threshold is reached, $T_{avg}^* \approx 1200K$

\(^1\)In some cases, the regression could not be found due to extremely scattered data, resulting in a lack of uncertainty.
Table 3.3: Regression performance for characteristic temperatures $T^*$ within the flame structure for GRI (left) and San Diego (right). $T_{avg}^*$ is based on constant mass flux reference cases, and $R^2$ values are calculated for the comprehensive data set.

<table>
<thead>
<tr>
<th>Label</th>
<th>Indicator$^d$</th>
<th>$T_{avg}^*$</th>
<th>$s$</th>
<th>Label</th>
<th>Indicator$^d$</th>
<th>$T_{avg}^*$</th>
<th>$s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(VIIa)</td>
<td>$H + O_2 + N_2 \rightarrow HO_2 + N_2$</td>
<td>879K</td>
<td>-</td>
<td>(IIa)</td>
<td>$2CH_3 (+M) \rightarrow C_2H_6 (+M)$</td>
<td>1112K</td>
<td>-</td>
</tr>
<tr>
<td>(IIa)</td>
<td>$2CH_3 (+M) \rightarrow C_2H_6 (+M)$</td>
<td>1039K</td>
<td>-</td>
<td>(IIb)</td>
<td>$HO_2 + CH_3 \rightarrow OH + CH_4O$</td>
<td>1118K</td>
<td>-</td>
</tr>
<tr>
<td>(IIb)</td>
<td>$HO_2 + CH_3 \rightarrow OH + CH_4O$</td>
<td>1054K</td>
<td>-</td>
<td>(IV)</td>
<td>$H + CH_3 (+M) \rightarrow CH_4 (+M)$</td>
<td>1135K</td>
<td>-</td>
</tr>
<tr>
<td>(IV)</td>
<td>$H + CH_3 (+M) \rightarrow CH_4 (+M)$</td>
<td>1155K</td>
<td>-</td>
<td>(VIIa)</td>
<td>$H + O_2 (+M) \rightarrow HO_2 (+M)$</td>
<td>1263K</td>
<td>131K</td>
</tr>
<tr>
<td>(Va)</td>
<td>$HCO + O_2 \rightarrow CO + HO_2$</td>
<td>1138K</td>
<td>36K</td>
<td>(la)</td>
<td>$CH_4 + OH \rightarrow CH_3 + H_2$</td>
<td>1268K</td>
<td>11K</td>
</tr>
<tr>
<td>(b)</td>
<td>$CH_4 + OH \rightarrow CH_3 + H_2$</td>
<td>1182K</td>
<td>17K</td>
<td>(VIIa)</td>
<td>$H + O_2 \rightarrow HO_2$</td>
<td>1274K</td>
<td>-</td>
</tr>
<tr>
<td>(laa)</td>
<td>$CH_4 + OH \rightarrow CH_3 + H_2O$</td>
<td>1188K</td>
<td>21K</td>
<td>(VIIb)</td>
<td>$H + HO_2 \rightarrow 2OH$</td>
<td>1284K</td>
<td>-</td>
</tr>
<tr>
<td>(VIIa)</td>
<td>$H + O_2 + H_2O \rightarrow HO_2 + H_2O$</td>
<td>1189K</td>
<td>-</td>
<td>(DR)</td>
<td>$CH_3$</td>
<td>1275K</td>
<td>51K</td>
</tr>
<tr>
<td>(DR)</td>
<td>$CH_3$</td>
<td>1196K</td>
<td>20K</td>
<td>(Va)</td>
<td>$HCO + O_2 \rightarrow CO + HO_2$</td>
<td>1278K</td>
<td>-</td>
</tr>
<tr>
<td>(Va)</td>
<td>$H + CH_2O \rightarrow HCO + H_2$</td>
<td>1197K</td>
<td>18K</td>
<td>(Va)</td>
<td>$H + CH_4O \rightarrow HCO + H_2$</td>
<td>1314K</td>
<td>16K</td>
</tr>
<tr>
<td>(Vb)</td>
<td>$OH + CH_2O \rightarrow HCO + H_2O$</td>
<td>1235K</td>
<td>23K</td>
<td>(VIb)</td>
<td>$H + HO_2 \rightarrow 2OH$</td>
<td>1274K</td>
<td>-</td>
</tr>
<tr>
<td>(VIIb)</td>
<td>$H + HO_2 \rightarrow 2OH$</td>
<td>1239K</td>
<td>25K</td>
<td>(CR)</td>
<td>$H_2O$</td>
<td>1333K</td>
<td>15K</td>
</tr>
<tr>
<td>(CR)</td>
<td>$H_2O$</td>
<td>1255K</td>
<td>26K</td>
<td>(DR)</td>
<td>$H$</td>
<td>1333K</td>
<td>18K</td>
</tr>
<tr>
<td>(DR)</td>
<td>$H$</td>
<td>1264K</td>
<td>21K</td>
<td>(DR)</td>
<td>$H$</td>
<td>1333K</td>
<td>18K</td>
</tr>
<tr>
<td>(DR)</td>
<td>$H$</td>
<td>1264K</td>
<td>24K</td>
<td>(DR)</td>
<td>$H$</td>
<td>1333K</td>
<td>15K</td>
</tr>
<tr>
<td>(VIII)</td>
<td>$HCO (+M) \rightarrow CO + H (+M)$</td>
<td>1290K</td>
<td>23K</td>
<td>(VIII)</td>
<td>$HCO (+M) \rightarrow CO + H (+M)$</td>
<td>1362K</td>
<td>11K</td>
</tr>
<tr>
<td>(IIIa)</td>
<td>$O + CH_4 \rightarrow H + CH_2O$</td>
<td>1291K</td>
<td>16K</td>
<td>(IIIa)</td>
<td>$O + CH_3 \rightarrow H + CH_2O$</td>
<td>1346K</td>
<td>15K</td>
</tr>
<tr>
<td>(IIb)</td>
<td>$O + CH_3 \rightarrow H + H_2 + CO$</td>
<td>1291K</td>
<td>16K</td>
<td>(IVa)</td>
<td>$O + CH_3 \rightarrow H + H_2 + CO$</td>
<td>1375K</td>
<td>22K</td>
</tr>
<tr>
<td>(CR)</td>
<td>$O$</td>
<td>1299K</td>
<td>34K</td>
<td>(VIIa)</td>
<td>$H + O_2 \rightarrow O + OH$</td>
<td>1376K</td>
<td>7K</td>
</tr>
<tr>
<td>(CR)</td>
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<td>22K</td>
<td>(DR)</td>
<td>$O$</td>
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<td>13K</td>
</tr>
<tr>
<td>(VIIc)</td>
<td>$H + O_2 \rightarrow O + OH$</td>
<td>1323K</td>
<td>14K</td>
<td>(Vd)</td>
<td>$H + HCO \rightarrow H_2 + CO$</td>
<td>1396K</td>
<td>13K</td>
</tr>
<tr>
<td>(DR)</td>
<td>$O$</td>
<td>1325K</td>
<td>17K</td>
<td>(VIIe)</td>
<td>$OH + H_2 \rightarrow H + H_2O$</td>
<td>1403K</td>
<td>27K</td>
</tr>
<tr>
<td>(Vd)</td>
<td>$H + HCO \rightarrow H_2 + CO$</td>
<td>1332K</td>
<td>28K</td>
<td>(CR)</td>
<td>$O$</td>
<td>1406K</td>
<td>11K</td>
</tr>
<tr>
<td>(CR)</td>
<td>$O$</td>
<td>1343K</td>
<td>18K</td>
<td>(VI)</td>
<td>$OH + H_2 \rightarrow H + OH$</td>
<td>1418K</td>
<td>28K</td>
</tr>
<tr>
<td>(VIIe)</td>
<td>$OH + H_2 \rightarrow H + H_2O$</td>
<td>1355K</td>
<td>41K</td>
<td>(VIIId)</td>
<td>$OH + H_2 \rightarrow H + OH$</td>
<td>1452K</td>
<td>36K</td>
</tr>
<tr>
<td>(VI)</td>
<td>$OH + CO \rightarrow H + CO_2$</td>
<td>1370K</td>
<td>39K</td>
<td>(VIIId)</td>
<td>$O + H_2 \rightarrow H + OH$</td>
<td>1419K</td>
<td>48K</td>
</tr>
</tbody>
</table>

$^d$Inflfection point of: reaction rate of elementary reaction, or creation (CR) and destruction rate (DR) of individual species.
Figure 3.12: Comparison of characteristic temperatures $T^*$, as determined from the maximum curvature of reaction (VIIc), and asymptotic $T^\circ$ from reference [60] at various $\phi$ at $T_{in} = 300K$.

(GRI), 1300K (San Diego), reactions show moderate to excellent agreement, with the exception of HO$_2$ oxidation. Major species show moderate performance, while radicals O and H perform well. Both mechanisms predict a similar progression from fuel to products; however, categorical discrepancies in $T^*_{avg}$ are observed. These are a function of the San Diego mechanism, which predicts a slower oxidation, due to its tendency to form C$_2$H$_6$ more readily in the preheat layer, shown via reaction pathways (Section 3.2.1) and sensitivity analysis (Section 3.2.2). Thus, profiles are somewhat skewed with respect to GRI as was shown in Figure 3.10.

Overall, results verify that the chain branching reaction (VIIc), used for centering of the flame structure in Section 3.2.1, is a function of laminar burning flux $\dot{m}$ only, and thus qualifies as a reliable predictor. The reaction has been shown to be both the most important reaction in the combustion process and indicative of the reaction zone. Thus, the maximum curvature of this reaction will predict the location where rate of reaction begins to substantially increase, and is therefore taken to be the characteristic temperature $T^*$.

### 3.2.5 Asymptotics

The previous analysis has found a characteristic temperature $T^*$, marking the transition between preheat and reaction zones. The idea of $T^*$ is derived from the classical analysis of rate-ratio asymptotics, which distinguish three distinct layers of varying length scales: preheat, inner, and oxidation layers. The inner layer, corresponding to the reaction zone, seeks to capture the balance between chain-breaking
Figure 3.13: Solution sets of a) GRI (432 points) and b) San Diego (377 points).

and chain-branching reactions at a local temperature $T^\circ$. As the present work attempts to capture the transition between preheat and inner layer, the expectation is for $T^*$ to occur before $T^\circ$. Figure 3.12 reveals that, in fact, the opposite is true when asymptotic predictions are compared to the current work at ambient temperature. Nonetheless, it should be noted that asymptotics are naturally coarse in nature, utilizing a global mechanism and a host of simplifications. Thus, the current work, correctly capturing a transition before $T^\circ$, reveals significant limitations of asymptotic analyses to describe flame structure. If $T^\circ$ was sought in the current work, it would be certainly be at a higher temperature, at the maximum gradient or peak reaction rate of (VIIc), corresponding with the overall heat release curve, both of which are indicative of high reaction rates.

While the lean regime has been resolved, some additional information may be gained by comparison to rich regime results. After the regime is thoroughly analyzed, a summary of both and their respective similarities and differences will be provided in Section 3.4.

### 3.3 Rich Analysis

The rich regime is now analyzed in detail for five reference inlet conditions, and a second regression analysis focuses on the rich regime ($\phi = 1.30 - 2.70$). Figure 3.4 provides a multivariate visualization of lean regime under consideration, which includes approximately 400 points per mechanism. Reference cases are shown based on inlet conditions of a constant equivalence ratio ($\phi = 1.60$) and those derived from the same lean contour: $\dot{m}_{ref} = 0.2190$. Again, differences in the predicted mass fluxes from the mechanisms are visible through comparison of the reference inlet conditions for each. In keeping with previous analysis, the San Diego mechanism is used comparatively against GRI. Each of the same analy-
Figure 3.14: Normalized flame structures at constant laminar burning rate $\dot{m}$ (a) and constant equivalence ratio $\phi$ (b). Profiles are centered at the largest gradient of reaction (Xa) and non-dimensionalized by the flame thickness as before.

ses is completed here, and, although many pathways are similar, some reactions are reproduced to create a comprehensive view of rich flames.

### 3.3.1 Flame Structure and Reaction Paths

Figure 3.14 shows axially scaled flame structures for reference cases at constant $\dot{m}$ and constant $\phi$. The structures are again normalized by the flame thickness, as shown in Table 3.4. Here, some discrepancies are observed between the mechanisms. Both mechanisms predict similar trends and values for constant $\phi$; however, San Diego predicts that flame thickness shrinks as ultra-rich conditions are reached, whereas GRI shows a slight increase in width. This error is consistent with the results of Sections 3.1.1 (Effect of Equivalence Ratio $\phi$) and 3.1.4 (Error), which show a larger disagreement between the mechanisms than in the lean regime. Moving forward to the flame structures themselves, in a departure from lean flame analysis, the maximum gradient is found to be a better indicator for the
Table 3.4: Flame thicknesses used for normalization of rich regime flame structures. Respective thicknesses are shown for GRI ($l_{\text{GRI}}$) and San Diego ($l_{\text{SD}}$).

<table>
<thead>
<tr>
<th>$\phi$</th>
<th>$T_{\text{in}}$ (K)</th>
<th>$l_{\text{GRI}}$ (mm)</th>
<th>$l_{\text{SD}}$ (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.34</td>
<td>300</td>
<td>0.72</td>
<td>1.15</td>
</tr>
<tr>
<td>1.60</td>
<td>300</td>
<td>1.65</td>
<td>2.06</td>
</tr>
<tr>
<td>1.60</td>
<td>600</td>
<td>0.81</td>
<td>1.06</td>
</tr>
<tr>
<td>1.60</td>
<td>900</td>
<td>0.46</td>
<td>0.57</td>
</tr>
<tr>
<td>2.16</td>
<td>900</td>
<td>0.86</td>
<td>0.89</td>
</tr>
</tbody>
</table>

flame position, and thus flame structures are centered there rather than at the curvature. This location corresponds to a higher temperature, and an explanation will be discussed in later sections. Otherwise, constant $\dot{m}$ and constant $\phi$ behaviors are similar to lean observations. Major reactant and product species are similar to lean, but products also include carbon monoxide and hydrogen, which are shown to increase in the ultra-rich reference cases. Of note is the inclusion of the species $\text{C}_2\text{H}_6$, which peaks upstream of the origin.

A second reaction pathway analysis is performed for rich flames. While some pathways are similar to lean counterparts, they are represented here for a comprehensive view of rich combustion. Again, the well-known $\text{H}_2$-$\text{O}_2$ chain cycle

$$\text{H} + \text{O}_2 \rightarrow \text{O} + \text{OH}$$ (Xa)

$$\text{O} + \text{H}_2 \rightarrow \text{H} + \text{OH}$$ (Xb)

$$\text{OH} + \text{H}_2 \rightarrow \text{H} + \text{H}_2\text{O}$$ (Xc)

(see also reactions (VIIc), (VIIId), (VIIe)) is once again identified as central to the combustion process. Low temperature $\text{HO}_2$ pathways become less relevant in the rich regime as oxygen limits the combustion; consequently, reaction

$$2\text{CH}_3 (+\text{M}) \rightarrow \text{C}_2\text{H}_6 (+\text{M})$$ (XI)

(see also reaction (IIa)) dominates the early flame structure. $\text{C}_2$ chain formation will be shown to delay the combustion process (Section 3.3.2), and so Figure 3.14 was centered at the location where the
reaction rate of (Xc) shows the largest gradient. Going back to fuel breakdown, it remains initiated by H-abstraction. Reaction (XI) is the first step of a C₂ chain characteristic of rich combustion, which generates C₂H₄ and C₂H₂ in successive reactions, eventually terminating back at CH₃ [42]. Once again, CH₃ is also consumed by the recombination reaction

\[ \text{CH}_3 + H (+M) \rightarrow \text{CH}_4 (+M) \] (XII)

(see also reaction (IV)). Methane oxidation then progresses from low to high temperature pathways primarily via the standard reaction pathway, detailed in lean regime results of Section 3.2.1. However, this process is shown to be inhibited due to the formation of C₂ hydrocarbons.

In rich combustion, H₂ and CO are major product species and so reactions involved in their formation are discussed. The majority of H₂ is formed in fuel breakdown and “steam-reforming”

\[ \text{H} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H}_2 \] (XIIIa)
\[ \text{H}_2\text{O} + \text{H} \rightarrow \text{H}_2 + \text{OH} \] (XIIIb)

(see also reaction (Ib)) where reaction (XIIIb) is the reverse of (Xc). CO is predominantly formed via the reactions

\[ \text{HCO} + \text{O}_2 \rightarrow \text{CO} + \text{HO}_2 \] (XIVa)
\[ \text{HCO} (+M) \rightarrow \text{CO} + \text{H} (+M) \] (XIVb)
\[ \text{CH}_2\text{CO} + \text{H} \rightarrow \text{CO} + \text{CH}_3 \] (XIVc)

(see also reactions (Vc) and (VIII)) where HCO is produced via CH₂O (Sect. 3.2.1). CH₂CO is part of the C₂ chain, where it is formed from intermediate species CH₂CHO and C₂H₂. At high temperatures, additional CO originates from

\[ \text{HCCO} + \text{H} \rightarrow \text{CO} + \text{CH}_2(S) \] (XVa)
\[ \text{CO}_2 + \text{H} \rightarrow \text{CO} + \text{OH} \] (XVb)
where HCCO stems from H-abstraction of CH$_2$CO and oxidation of C$_2$H$_2$. It is noted that equation (XVb) is the reverse of the main oxidation path of CO,

$$\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H} \quad \text{(XVI)}$$

Reactions (XIIIa), (XIIIb), and (XVb) all contribute to endothermic “steam-reforming” in the post-flame zone [37].

Figure 3.15 shows axially scaled flame structures of comparable reference cases utilizing the San Diego mechanism. As in the lean regime, behaviors of major species show only a subtle difference in relation to the origin. The most striking result is the lower heat heat release values at constant $\dot{m}$, which predicts half of the value of GRI for the case of $\phi = 1.34$. However, the results show overall that the GRI flame structures are accurate in their representation of major species. Since reaction pathways are
the underlying cause of flame structure, the pathways should be similar to those of GRI. Including the observations of the lean regime, the only difference in the major pathways was the diminished role of reaction (XVa). Thus, the only routes in the mechanism for the creation of CO at high temperatures are reactions (XIVc) and (XVb). Overall, the results show that the trends in flame structure predicted by GRI are accurate via numerical simulation.

3.3.2 Sensitivity Analysis

Figure 3.16a illustrates results of a sensitivity analysis of the burning flux at the five rich reference conditions. Results show that the chain branching reaction (Xa) again significantly increases the flux, and chain breaking reactions (XI) and (XII) have an adverse effect. This indicates that reactions (XI) and (XII) counteract reaction (Xa), delaying the onset of the combustion process. In confirmation of rich pathway analysis, reaction (Iib) is shown to have a significantly lower sensitivity, particularly as the flame becomes richer. Interestingly, the initial fuel breakdown step (XIIIa) has an adverse effect, which is attributed to the exchange of a highly reactive H radical with a less reactive CH₃ radical in a chain carrying reaction. Three additional reactions identified by the sensitivity analysis affect flame speeds to a lesser extent, and appear to lose importance at the richest reference case of φ = 2.16. Interestingly, reactions show considerably lower sensitivities in all cases than lean counterparts.

Looking into the San Diego results, Figure 3.16b illustrates that the mechanisms predict similar results. Reaction (Xa) drops in sensitivity when compared to GRI but remains the most sensitive by far. Reactions (XII) and (XI) also show similar chain-breaking qualities in confirmation of GRI results. Other minor reactions are similar to GRI results as well, involving CH₃ and CH₂O intermediates. Interestingly, reaction (IIIa) of the lean standard pathway enhances the burning flux at the moderately rich extremum (φ = 1.33), but slows down the flame at all other conditions. This phenomena is closely related to the rate-limiting nature of the oxygen radical.

3.3.3 Heat Release

As a first step in heat release analysis, Figure 3.17 shows the relative positions of main heat releasing reactions of rich flames with respect to the overall release curve. As would be expected from lean analysis, the main heat releasing reaction occurs simultaneously with the main endothermic reaction (Xa). Early preheat release is contributed by C₂ chain formation while later heat release is provided by
Figure 3.16: Log-normal sensitivity of a) GRI and b) San Diego reactions with largest impact on the rich laminar burning flux $\dot{m}_{\text{ad}}$. 
Figure 3.17: Heat release rates in a rich flame, inlet conditions of $\phi = 1.33$, $T_{in} = 300K$. Profiles are normalized and centered as before. 

hydrogen breakdown from (Xc), complementary to (Xa).

Proceeding with the analysis, Figure 3.18a presents the reactions of largest contributions, both positive and negative, to the overall heat release at the reference conditions. The most sensitive reaction (Xa) is shown to be highly endothermic, fueled by exothermic fuel breakdown. The recombination reactions (XI) and (XII), although showing a negative sensitivity, contribute the most heat in rich flames. C$_2$ hydrocarbon recombination interactions, similar to (XII), are also endothermic, particularly at ultra-rich conditions where these compounds are formed more readily. Other fuel breakdown reactions of importance correspond to those seen in lean flames. As would be expected, an analysis of preheat zone reactions reveals that reaction (XI) generates the most heat by far. Reaction (Xa) delayed from onset by this behavior, absorbs a smaller portion of release relative to C$_2$ chain recombination reactions.

Figure 3.18b illustrates that the San Diego mechanism predicts similar reactions, although their relative importances show subtle differences. As previously noted, C$_2$ chain formation occurs more heavily in this mechanism, and is reflected by reaction (XI) as the most exothermic, with (XIIIa) of less importance. Of particular note is the switch of reaction (XIIIa) from exothermic to endothermic in the ultra-rich case. San Diego predicts that the reverse of the reaction, normally substantially smaller than the forward rate, actually becomes the dominant direction towards the end of combustion. The large differences in the heats of formation for the participating species at these temperatures overpowers the earlier exothermic release. Furthermore, a comparison of heat release rates in Figure 3.19 reveals significant differences between the two. As in the lean cases, the heat release in the San Diego mechanism lags behind, and shows substantially lower peak rates. This reduction in volumetric heat release is
Figure 3.18: Largest contributors of heat release per reaction of a) GRI and b) San Diego.
Figure 3.19: Heat release rates of GRI and San Diego, centered at the temperature of maximum gradient of reaction (VIIc) in the GRI mechanism and normalized per respective flame thickness.

Figure 3.20: Regression results for characteristic temperatures $T^*$ at inflection points of: (a) species creation (CR) and destruction rates (DR), and (b) reaction rates of the GRI mechanism.

directly coupled with the lower mass flux predicted by the mechanism.

3.3.4 Regression

The regression analysis is repeated in the rich regime, focusing on the highlighted reactions and species of the regime. Properties of $T^*_{avg}$ and the standard error $s$ retain their original implications of indicator behavior and quality. Figure 3.20 illustrates the regression curves and data points of rich flames for peak gradients of H and O radical creation (Fig. 3.20a), and major reactions responsible for their creation (Fig. 3.20b).

In the following, $T^*$ tied to inflection points (maximum gradients), as opposed to maximum curvature, are used to identify transitions within the flame structure. Table 3.5 a presents selected indicators of the GRI mechanism ranging from low to high $T^*$, i.e. reactions and species involved in the fuel breakdown to those linked to endothermic reactions in the post-flame zone. With low uncertainties ($s < 20$K),
Table 3.5: Regression performance for characteristic temperatures \( T^* \) within the flame structure for GRI (left) and San Diego (right). \( T^\text{avg} \) is based on constant mass flux reference cases, and uncertainty values \( s \) are calculated in \( T^* \) for the comprehensive data set.

<table>
<thead>
<tr>
<th>Label</th>
<th>Indicator(^a)</th>
<th>( T^\text{avg} )</th>
<th>( s )</th>
<th>Label</th>
<th>Indicator(^d)</th>
<th>( T^\text{avg} )</th>
<th>( s )</th>
</tr>
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<td>(XIVa) HCO + O(_2) → CO + HO(_2)</td>
<td>1422K 55K</td>
<td>(XIVa) HCO + O(_2) → CO + HO(_2)</td>
<td>1425K 30K</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>(XI) 2CH(_3) (+M) → C(_2)H(_6) (+M)</td>
<td>1478K -</td>
<td>(XI) 2CH(_3) (+M) → C(_2)H(_6) (+M)</td>
<td>1578K -</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>(Ia) CH(_4) + OH → CH(_3) + H(_2)O</td>
<td>1570K 32K</td>
<td>DR O(_2)</td>
<td>1649K 21K</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>DR O(_2)</td>
<td>1606K 15K</td>
<td>(XIVb) HCO(+M) → CO + H(+M)</td>
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<tr>
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<td></td>
<td></td>
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</tr>
<tr>
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<td>1619K 53K</td>
<td>CR CO</td>
<td>1689K 23K</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CR CO</td>
<td>1635K 13K</td>
<td>DR O</td>
<td>1704K 15K</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(XIIIa) CH(_4) + H → CH(_3) + H(_2)</td>
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<td>CR O</td>
<td>1704K 15K</td>
<td></td>
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<td></td>
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<tr>
<td>(XII) CH(_3) + H(+M) → CH(_4)(+M)</td>
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<tr>
<td>(Xa) H + O(_2) → O + OH</td>
<td>1643K 14K</td>
<td>(XIVc) CH(_2)CO + H → CO + CH(_3)</td>
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</tr>
<tr>
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<td>1644K 8K</td>
<td>DR CH(_4)</td>
<td>1746K -</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CR O</td>
<td>1645K 7K</td>
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<td></td>
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<td></td>
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<tr>
<td>(XIVc) CH(_2)CO + H → CO + CH(_3)</td>
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<td>(XIIIa) CH(_4) + H → CH(_3) + H(_2)</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DR H</td>
<td>1693K 16K</td>
<td>(Xb) O + H(_2) → H + OH</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>1709K 8K</td>
<td>DR H</td>
<td>1794K 27K</td>
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<td>CR H</td>
<td>1802K 17K</td>
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<td>CR CO(_2)</td>
<td>1807K 50K</td>
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<tr>
<td>CR H(_2)O</td>
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<td>CR H(_2)</td>
<td>1814K 25K</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CR CO(_2)</td>
<td>1743K 28K</td>
<td>CR H(_2)</td>
<td>1821K 14K</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>1759K 18K</td>
<td>DR H(_2)O</td>
<td>1825K 38K</td>
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<td>(XVI) CO + OH → CO(_2) + H</td>
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<tr>
<td>(Xc) OH + H(_2) → H + H(_2)O</td>
<td>1808K 26K</td>
<td>(Xc) OH + H(_2) → H + H(_2)O</td>
<td>1872K 34K</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(XVI) CO + OH → CO(_2) + H</td>
<td>1809K 23K</td>
<td>DR H(_2)O</td>
<td>1889K 24K</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DR H(_2)O</td>
<td>1820K 19K</td>
<td>(XVa) HCCO + H → CO + CH(_3)(S)</td>
<td>1900K 28K</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>(XIIIb) H(_2)O + H → H(_2) + OH</td>
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<td>(XIIIb) H(_2)O + H → H(_2) + OH</td>
<td>1914K 26K</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>DR CO(_2)</td>
<td>1868K 18K</td>
<td>DR CO(_2)</td>
<td>1939K 26K</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>(XVb) CO(_2) + H → CO + OH</td>
<td>1887K 21K</td>
<td>(XVb) CO(_2) + H → CO + OH</td>
<td>1941K 25K</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

\(^a\) Inflection point of: reaction rate of elementary reaction, or creation (CR) and destruction rate (DR) of individual species.
Figure 3.21: Asymptotic and numerical results for a) $T_{in} = 300K$ and b) $T_{in} = 900K$, where $T^*$ is the maximum gradient of reaction Xa.

Regressions for $T^*$ connected to the H$_2$-O$_2$ sub-mechanism again show excellent agreement, whereas $T^*$ tied to the initial fuel breakdown fare poorly. Furthermore, relatively low $s$ values for destruction of H$_2$O and CO$_2$ at high $T^*$ show that reactions (XIIIA) and (XVb) are driven by high reaction temperatures only. Results are similar within the San Diego mechanism (Tab. 3.5b) due to a smaller range of uncertainties. $T^*_{avg}$ values differ significantly, with San Diego predicting much higher values, where fuel breakdown reactions are shown to have moved well into the H$_2$-O$_2$ reaction zone. This behavior is a function of differing flame structure predicted by between the two mechanisms. Flame structures (Figs. 3.14/3.15) are scaled and set per the mechanism; however, inspection of actual profiles (Fig. 3.19) reveals a skewed set. Regardless of position, results show that $T^*$ as defined by reaction (Xa) is independent of the mechanism, where the $T^*_{avg}$ values are identical in both cases. Specifically, results verify that the maximum gradient of this reaction is indicative of the transition from preheat to reaction zones and is thus concluded to be $T^*$ in rich flames.

3.3.5 Asymptotics

The asymptotic analysis of rich flames does not distinguish an inner layer, noting that $T^o$ approaches the adiabatic flame temperature $T_{ad}$ [61]. It is noteworthy that the maximum temperature in the flame is above that of $T_{ad}$; however, asymptotics assumes a flat profile once $T_{ad}$ is reached. In departure from lean analysis, where actual asymptotic data was necessary, the adiabatic temperature is easily calculated from equilibrium results of a complex reaction mechanism. These were found to be equivalent for both GRI and San Diego. Figure 3.21 illustrates that $T^*$ occurs at a lower temperature than $T_{ad}$ and, consequently,
earlier in the flame. $T_{\text{ad}}$ drops below $T^*$ in Figure 3.21 at high equivalence ratios, but these occur well beyond the flammability limit for the system and may be ignored. Thus, rich results are consistent with asymptotic results, as the heat release peaks close to the peak temperatures.

3.4 Summary and Comparison

The complex nature of flame structure often clouds conclusive evidence of flame property phenomena. Here, the combination of several flame analysis tools, including a novel regression application of classical asymptotics allows for several overarching observations to be made regarding lean and rich flames. In all cases, the reaction zone is dictated by preheating reactions that are necessary to overcome the endothermic nature of the main chain branching reaction (Xa). In turn, this reaction releases a host of radicals which diffuse upstream to participate in preheat zone reactions. Through this cycle of heating and radical diffusion, a steady state reaction zone is established. Kinetic differences may be summed in part by following the fuel and oxidizer breakdown in the preheat layer. In both types of flames, CH$_4$ breaks into the methyl radical CH$_3$, and paths quickly diverge due to respective rate-limiting aspects. In lean flames, hydrogen radicals also interact with oxygen to form HO$_2$. HO$_2$ reacts readily with CH$_3$ in the preheat layer, thus moving methane oxidation forward while also releasing heat. Negative sensitivities of HO$_2$ formation are due to its later competition with the main chain-branching reaction. Some C$_2$ hydrocarbons are formed from CH$_3$ as is the original fuel molecule; however, their impacts are diminished with respect to rich flames. Due to a lack of oxygen, CH$_3$ is found in more excess and is thus more likely to reform higher order molecules; additionally, oxygen radicals are in shorter supply. While HO$_2$ and other standard pathway reactions occur, their progressions are much slower throughout the length of the reaction layer. Thus, the C$_2$ chain continuously cycles, scavenging H and CH$_3$ radicals until temperatures increase beyond the limit of reaction (XI). Through this explanation, the difference in better regression results for curvature in lean flames and gradient in rich flames becomes clear. Reactions of the standard pathway occur sooner in lean flames; thus, the curvature, particularly of reaction (VIIC) provide better fits for the characteristic temperature $T^*$. Due to C$_2$ hydrocarbon cycling in rich flames, the position of this corresponds better with the maximum gradient, which occurs later in the rate profiles, and thus at a higher temperature. As shown in asymptotics, the net result is the approach of $T^\circ$ to the adiabatic temperature $T_{\text{ad}}$. 
Furthermore, the mechanism discrepancies observed throughout the analysis may be quantified. Slight differences in reaction pathways due to the “shortness” of the San Diego mechanism cause profiles and structures to skew with respect to GRI. Particularly, San Diego’s propensity towards the C₂ hydrocarbon chain causes a delay in the heat release. In rich flames, this, coupled with a larger error in mass flux, causes the volumetric heat release to drop in response. Since the difference is systematic between lean and rich regimes, the results presented for the GRI mechanism may be considered accurate. However, the comparison shows that mechanism choice impacts flame properties within the flame thickness length scale and thus must be considered in studies within this scale. Particular attention should be paid to the completeness of the mechanism to ensure the correct structures are created.
Chapter 4
Burner-Stabilized Flames

To adequately conclude that the results of the adiabatic data set may be used in inherently non-adiabatic applications, the simplest non-adiabatic configuration, a burner-stabilized flat flame, is studied in detail. The regression is applied to one-dimensional flat flame simulations of comparable reference inlet conditions. Experimental work in both lean and rich regimes demonstrate the viability of flat flames at the extreme conditions of the study, while showing similar qualitative behavioral characteristics predicted by the adiabatic simulations. Furthermore, stand-off positions were found in lean flames and compared to positions predicted by $T^\circ$, i.e. the location of the inner layer rather than the transition predicted in $T^*$, in flat flame simulations to provide an assessment of the numerical model and experimental conditions. Finally, a Fluent model provides an additional study in the characteristics of two dimensional flames. In keeping with adiabatic analysis, the work is presented in the same order as before, divided into lean and rich results.

4.1 Lean

4.1.1 Application of Regression

In the following analysis, regressions are compared to burner-stabilized flames to determine the applicability of indicators in non-adiabatic conditions. Figure 4.1 illustrates the effects of heat losses on the regression performance. Data points were obtained for the full range of non-adiabatic mass fluxes $\dot{m}$ for the defined reference cases in Section 3.2. Moderate to high non-adiabatic mass fluxes show good agreement with indicators; however, divergence due to inlet conditions becomes apparent at low mass fluxes. Regardless, the results are intuitive to the nature of non-adiabatic flames. The regression predicts a lower $T^*$ over the length of the domain but approaches the adiabatic curve at a specific point for a given set of inlet conditions. Table 4.1 presents all adiabatic indicators as applied to burner-stabilized simulations to show the similar behavior of all indicators to Figure 4.1. As expected, $T^{*_{\text{avg}}}$ values drop due to heat losses in the flame. The order of indicators also remains similar, despite flame stretching and inlet diffusion seen in these flames. Uncertainty values remain acceptable, particularly of the main chain-branching reaction, and so indicators are deemed applicable to non-adiabatic flames.
Table 4.1: Regression performance for characteristic temperatures $T^*$ in lean burner-stabilized flames. Since $\dot{m}$ is an inlet condition, $T^*_{\text{avg}}$ is based on constant mass flux reference inlet conditions, with $\dot{m}$ corresponding to the minimum stand-off distance. Uncertainty values $s$ are calculated for the comprehensive data set.

<table>
<thead>
<tr>
<th>Label</th>
<th>Indicator</th>
<th>$T^*_{\text{avg}}$</th>
<th>$s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(VIIa)</td>
<td>$H + O_2 + N_2 \rightarrow HO_2 + N_2$</td>
<td>976K</td>
<td>-</td>
</tr>
<tr>
<td>(IIa)</td>
<td>$2CH_4 (+M) \rightarrow C_2H_6 (+M)$</td>
<td>1011K</td>
<td>-</td>
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<tr>
<td>(IIIb)</td>
<td>HO$_2$ + CH$_3$ $\rightarrow$ OH + CH$_3$O</td>
<td>1022K</td>
<td>-</td>
</tr>
<tr>
<td>(Va)</td>
<td>HCO + O$_2$ $\rightarrow$ CO + HO$_2$</td>
<td>1157K</td>
<td>-</td>
</tr>
<tr>
<td>(IV)</td>
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<td>CH$_4$ + OH $\rightarrow$ CH$_3$ + H$_2$O</td>
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<td>71K</td>
</tr>
<tr>
<td>(Va)</td>
<td>H + CH$_2$O $\rightarrow$ HCO + H$_2$</td>
<td>1178K</td>
<td>20K</td>
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<tr>
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<td>CH$_4$</td>
<td>1195K</td>
<td>40K</td>
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<tr>
<td>(VIIa)</td>
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<td>1209K</td>
<td>-</td>
</tr>
<tr>
<td>(VIIb)</td>
<td>H + HO$_2$ $\rightarrow$ 2OH</td>
<td>1216K</td>
<td>-</td>
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<tr>
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<td>33K</td>
</tr>
<tr>
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<td>O$_2$</td>
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<td>18K</td>
</tr>
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<td>OH</td>
<td>1281K</td>
<td>27K</td>
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<tr>
<td>(IIIa)</td>
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<td>19K</td>
</tr>
<tr>
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<td>O + CH$_3$ $\rightarrow$ H + H$_2$ + CO</td>
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<td>19K</td>
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<tr>
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<td>H</td>
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</tr>
<tr>
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<td>O + H$_2$ $\rightarrow$ H + OH</td>
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4.1.2 Experimental Results

The previous numerical analysis of preheated burner-stabilized flames predicts similar flat flame behavior along any given contour $\dot{m} = \text{const}$. Accordingly, combinations of $\phi$ and $T_{in}$ are chosen along a contour where GRI simulations predict $\dot{m} = 0.219 \text{ kg/m}^2\text{s}$, which corresponds to an laminar flame speed of 19 cm/s at standard ambient conditions. Digital images of CH* chemiluminescence of burner-stabilized flames are shown in Figure 4.2, where $\dot{m}$ was reduced by 15% in an attempt to avoid blow-off conditions. Two main observations may be drawn from the images. First and foremost, viable flames are established in the ultra-lean regime, thus validating that adiabatic solution set. Furthermore, flame behavior consistent with adiabatic mass flux, specifically the collapse of flame behavior at constant mass flux, is observed. Secondly, radiative effects are visually evident. Without a shield at $\phi = 0.53$, flame wrinkling indicates the local laminar burning flux is well exceeded, while, with a shield, flame behavior matches that at $\phi = 0.7$. Without a shield, ultra-lean flames at $\phi = 0.365$ could not be established; additionally, the radiation shield had to be moved closer to the burner surface. Figure 4.3 provides a quantitative measurement of these flames through stand-off distances. Here, only flames exhibiting similar behavior were examined, i.e. radiation shields were used as needed, and the stand-off distances from the images of Figure 4.2 are circled. Thus, the collapse of flame behavior is confirmed as each measurement lies within uncertainties for the data. Although this collapse continues for other mass fluxes at no to moderate preheating ($\phi = 0.7 – 0.53$), $\phi = 0.365$ shows increased sensitivity to radiative heat losses, manifested in a lower shield height and accelerated low mass flux blow-off. To further
investigate this and other heat transfer associated with the burner, these stand-off distances, as well as others from lean references conditions are compared to equivalent simulations from CANTERA.

Figure 4.4 compares simulated flame positions determined from the peak concentration of CH against experimental results for each reference equivalence ratio. This indicator is utilized for consistency with the flame images, which are filtered for CH* luminescence. At $\phi = 0.7$ (Fig 4.4a), simulations show that the flame is expected to move closer to the porous plug as inlet temperature is increased. Thus, a flame position closer than expected is indicative of upstream diffusion of heat and/or overheating from a radiative shield. No radiation shield was necessary at this reference case; in fact, flashback of preheated mixtures was observed at elevated inlet temperatures, demonstrated by stand-off distances of zero. Flashback will occur in an uncooled porous plug where surface (or inlet) temperatures well exceed those measured underneath the plug [40], whereas simulations assume a set inlet temperature (or cooled/controlled plug) and cannot predict flashback. Inclusion of the porous plug and subsequent expansion of the numerical domain in the burner model is necessary to predict the flashback conditions [40, 55]; however, simulations and experiments together are qualitatively consistent, i.e. the flame moves
closer when preheated. At leaner conditions, a radiative shield is necessary to stabilize a flame (Figs. 4.4b/c). At $\phi = 0.53$ (Fig. 4.4b), the flame experienced “blow-off” at mass fluxes lower than predicted, while shielded flames were established closer to the burner surface than predicted. Radiative heat transfer losses associated with the experiments are thus documented; without a shield, the flame moves further away, indicative of a lower inlet temperature while the flames move closer to the burner surface when a shield is used. Furthermore, the simulation is bracketed by these two experimental curves, suggesting that the shield actually induces some overheating of the burner. Moving to the next reference case, at $\phi = 0.365$ (Fig. 4.4c), a flame could not be established without a shield, and, as shown previously, the stand-off position shows increased sensitivity to both radiative losses to the environment and overheating from the shield when compared to simulations.

In summary, experimental results fulfill their primary goal in flame establishment in the ultra-lean regime while also correctly showing qualitative trends expected in the stand-off distance. However, experimental uncertainties in the surface temperature of the porous plug cannot provide conclusive evidence on numerical mechanism accuracy without a) complete control of the surface temperature of the porous plug or b) a radiative model that includes the porous media. This result will be confirmed by rich regime experiments; however, the effect of radiation should be further discussed. The adiabatic flame results do not take into account any form of radiation in the equations for flame propagation. While this may be cause for concern, an adiabatic flame should not have any radiative interaction with its environment. Radiative interactions within the flame itself are considered negligible except for highly sensitive
analyses, such as those at the flammability limits [15], or diffusion (non-premixed) flames where sooting is important [66]. Radiation should also be considered when implementing any experimental apparatus for determining preheated laminar burning fluxes, such as in the zero strain rate single-plate method [67], where the flame may be affected from environmental radiation on the plate and/or burner outlet.

Figure 4.4: Flame positions as determined by simulation and experiment at equivalence ratios of a) $\phi = 0.70$, b) $\phi = 0.53$, and c) $\phi = 0.365$. Average uncertainties are computed in a) for visual clarity of the data.
4.2 Rich

4.2.1 Application of Regression

Figure 4.5 illustrates that regression results for the rich regime follow a similar pattern to lean. The non-adiabatic regression curve indicates lower characteristic temperatures along the entire range of mass fluxes obtained from reference inlet conditions. In keeping with the better rich regression performance seen in adiabatic flames, lower mass flux cases diverge at a significantly lower rate than in lean. Furthermore, several selected indicators along the full breadth of the flame are shown in Table 4.2 to conclusively show similar patterns exist among all indicators. As expected, $T^*_{\text{avg}}$ is lower than adiabatic for all indicators and the temperature of progression remains similar. Again, the conclusion is reached that adiabatic indicators may be applied to non-adiabatic flames.

4.2.2 Experimental Results

For rich flames, the burner apparatus was used only to provide images, as in Figure 4.2, that show the viability of flames in the ultra-rich regime. The same laminar burning flux contour of reference inlet conditions was used in the rich; however, a higher number of points along this curve were chosen, rather than detailed analysis of three conditions. Additionally, a radiation shield was used in all cases for consistency of results, rather than applying it only at elevated inlet temperatures where heat losses are expected. Digital images of CH* chemiluminescence of burner-stabilized flames for a range of $T_{\text{in}} = 300$ to 850K are shown in Figure 4.6. At low inlet temperatures, the flame is stabilized close to the surface of
Table 4.2: Selected regression performance for characteristic temperatures $T^*$ in rich burner-stabilized flames. $T_{\text{avg}}^*$ and uncertainty values $s$ are calculated as before.

<table>
<thead>
<tr>
<th>Label</th>
<th>Indicator</th>
<th>$T_{\text{avg}}^*$</th>
<th>$s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(XIVb)</td>
<td>$\text{HCO}(+\text{M}) \rightarrow \text{CO} + \text{H}(+\text{M})$</td>
<td>1551K</td>
<td>3K</td>
</tr>
<tr>
<td>DR</td>
<td>$\text{CH}_4$</td>
<td>1574K</td>
<td>14K</td>
</tr>
<tr>
<td>CR</td>
<td>O</td>
<td>1583K</td>
<td>4K</td>
</tr>
<tr>
<td>(Xa)</td>
<td>$\text{H} + \text{O}_2 \rightarrow \text{O} + \text{OH}$</td>
<td>1585K</td>
<td>4K</td>
</tr>
<tr>
<td>(XII)</td>
<td>$\text{CH}_3 + \text{H}(+\text{M}) \rightarrow \text{CH}_4(+\text{M})$</td>
<td>1602K</td>
<td>13K</td>
</tr>
<tr>
<td>(Xb)</td>
<td>$\text{O} + \text{H}_2 \rightarrow \text{H} + \text{OH}$</td>
<td>1632K</td>
<td>12K</td>
</tr>
<tr>
<td>CR</td>
<td>H</td>
<td>1646K</td>
<td>6K</td>
</tr>
<tr>
<td>CR</td>
<td>H$_2$</td>
<td>1654K</td>
<td>7K</td>
</tr>
<tr>
<td>DR</td>
<td>H$_2$</td>
<td>1685K</td>
<td>13K</td>
</tr>
<tr>
<td>(Xc)</td>
<td>$\text{OH} + \text{H}_2 \rightarrow \text{H} + \text{H}_2\text{O}$</td>
<td>1725K</td>
<td>23K</td>
</tr>
<tr>
<td>(XVI)</td>
<td>$\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$</td>
<td>1723K</td>
<td>19K</td>
</tr>
<tr>
<td>(XIIIb)</td>
<td>$\text{H}_2\text{O} + \text{H} \rightarrow \text{H}_2 + \text{OH}$</td>
<td>1773K</td>
<td>14K</td>
</tr>
<tr>
<td>(XVb)</td>
<td>$\text{CO}_2 + \text{H} \rightarrow \text{CO} + \text{OH}$</td>
<td>1796K</td>
<td>15K</td>
</tr>
</tbody>
</table>

the porous plug. Increasing $T_{\text{in}}$ along the numerically predicted contour $\dot{m} = \text{const}$, the flame is observed to move away from the burner surface. This is most evident at the highest temperature, $T_{\text{in}} = 850K$, where at $\phi = 2.05$ and $\dot{m} = 0.186$ the flame loses its flatness, i.e. $\dot{m}$ exceeds the local laminar burning flux. Reducing $\dot{m}$ to 0.151, 70% of the numerically predicted value, reestablishes flat flame behavior. While this phenomenon may indicate that chemical kinetics over-predict $\dot{m}$ at highly preheated rich conditions, additional uncertainties, as noted previously, are introduced by the experimental setup. Again, radiative heat transfer between burner surface and environment are known to affect flame behavior [55]; thus, unexpected uncertainty in the surface temperature of the burner was introduced. However, experiments again yield not only proof of flame viability in the ultra-rich regime, but also qualitative confirmation of similar flame behavior at constant $\dot{m}$ as predicted by adiabatic results. It should also be noted that rich flame results show a much lower sensitivity to radiative loss, shown in a constant shield height into the ultra-rich regime.

### 4.3 Fluent Results

Due to computational restraints, the Fluent model could only be run for the base reference case ($\phi = 0.7$, $T_{\text{in}} = 300K$) at three mass fluxes. Inlet mass fluxes were chosen below the one-dimensionally predicted flux (low), one at the adiabatic mass flux (medium), and one beyond the mass flux (high). Each is presented here in ascending mass flux. The low mass flux demonstrates effects of boundary mixing
Figure 4.6: CH* chemiluminescence of burner-stabilized flat flames. White lines indicate level of the burner surface.
and the quality of one dimensional assumptions of previous simulations, as well as the quality of the two dimensional mesh. Medium and high mass flux cases together are used to show two dimensional flame structures after flame flatness is lost and may be used to find a numerical equivalent to the laminar burning flux.

### 4.3.1 Low Mass Flux

Figure 4.7 illustrates contours of temperature and flow speed, including streamlines, for the low inlet mass flux, \( v = 16 \text{ cm/s} \). Temperature contours indicate that a flame is stabilized very close to the burner-surface, and cooling from the inward diffusion of air causes a bend in the axial burner temperature boundary as the burned gases flow upwards. Streamlines confirm this behavior, where the air is pulled in parallel to the inlet boundary near the burner surface, and angled towards the end of the axial domain. The majority of the burned gas domain, including the reaction zone, is negligibly affected by the entrainment of air. The reaction zone itself only serves to increase the flow velocity in conservation of the ideal gas equation of state. As expected from experiments and one-dimensional simulations of flat flames, the only two dimensional effects visible are on the boundary, which will be studied in further detail.

**Boundary Effects**  The boundary effects are examined via contours of two different species, \( \text{N}_2 \) and \( \text{O}_2 \), in the flame as well as the reaction rate of the main chain-branching reaction, \( \text{H} + \text{O}_2 \rightarrow \text{O} + \text{OH} \)}
Figure 4.8: Boundary effects on the flat flame in a) % N\textsubscript{2}, b) % O\textsubscript{2}, and c) reaction zone.

(VIIc/Xa), marked previously as indicative of the reaction zone. Figure 4.8 illustrates the dual movement of outside air into the reaction zone and reactants outward, causing a “cupping” behavior [13] seen in lean flames (Fig. 4.2). The high concentrations of oxygen and nitrogen in each of these zones is subsequently diluted by diffusive compounds formed in the combustion process, particularly hydrogen [69]. Thus, the flame is shown to expand outward as the mixing occurs, demonstrated by the reaction zone in Figure 4.8c, although the majority appears unaffected by the boundary. A more quantitative approach is used by applying the stand-off distance. From Fluent data, the peak reaction rate of (VIIc/Xa) is easily obtained and will be used for flame position. Figure 4.9 illustrates that the stand-off distance remains constant for the length of the flame. At the boundary, the reaction rate of (VIIc/Xa) decreases and moves away from the burner surface, a quantitative measurement of “cupping” behavior. Additionally, it may be noted that this behavior occurs beyond the inlet port (in the radial direction), implying the expansion of the flame into the ambient air. The “cupping” behavior may then be explained by a decreased local laminar burning
Figure 4.9: Stand-off distance of the low mass flux flame \( \dot{m} = 1.86 \, \text{kg/m}^2 \text{s} \) as a function of \( r \). Peak reaction rate of \( \text{VIIc/Xa} \) provides the basis for the measurement.

Figure 4.10: Curves of a) temperature and b) reaction rate of \( \text{VIIc} \) for Fluent and Cantera.

flux because of a leaner mixture here.

**One Dimensional Analysis**  The low mass flux case is resolvable both in one (Cantera) and two (Fluent) dimensions. Near the axis, the two dimensional model should approximate steady state, and axial solution parameters can extracted as comparable to Cantera solutions. Figure 4.10 presents juxtaposed curves of temperature and the reaction rate of \( \text{VIIc/Xa} \) in the flame zone. The two dimensional temperature profile contains a much sharper gradient its Cantera counterpart, and the maximum temperature reaches in excess of the one dimensional adiabatic prediction. The reaction \( \text{VIIc/Xa} \) reveals some seemly random oscillations in the reactions rate. Further investigation of these discrepancies revealed differences in the implementation of the inlet diffusion boundary condition, while the oscillations remained unexplained. Figure 4.11 compares mole fractions of hydrogen found by either simulation, with particular emphasis placed at the inlet. Hydrogen is noted to be highly diffusive [69], and so the errors introduced through diffusion terms will be more evident. Fluent simulations are shown to incorrectly
Figure 4.11: One dimensional H\textsubscript{2} mole fraction profiles for Fluent and Cantera, where a) shows the entire domain and b) illustrates mass/mole fraction discrepancies at the inlet.

implement the inlet diffusion of hydrogen, where the mole fraction becomes approximately zero at the inlet. Other species show the same trend, such that the inlet mixture is forced to that specified by the user. Furthermore, mass and mole fractions do not correlate with one another at the inlet. The two should be proportional; however, when compared, the value computed from the mass fraction is shown to be zero while the mole fraction shows that H\textsubscript{2} is present (Fig. 4.11b). After the inlet boundary point, the two are shown to match for the entirety of the domain. It should be noted that inlet diffusion was specified in the Fluent user-interface, while the documentation is ambiguous at best. Since Fluent is a commercial software, the code could not be examined and the issue may not be resolved. An attempt to solve the oscillations observed in reaction rates was unsuccessful. Spatial refinement provided by the alternative second refinement did not show any qualitative damping, nor did a reduced time-step over the same grid. Regardless, the simulations have been proven to be incompatible with one another, and the focus should be on global and qualitative conclusions only, i.e. not on flame structure.

4.3.2 Medium Mass Flux

The medium mass flux case is considered as a control for the local laminar burning flux and flame behavior. The flame should remain flat; however, heat losses into the burner should be at a minimum. In fact, this type of flame In fact, these flames have been studied as “quasi-adiabatic” in experimental studies [22]. In Figure 4.12, the flame bows outward only slightly, indicating that it is stabilized more at the boundary. The temperature profile shows less of a gradient between inlet and flame zones; however, the flame still shows some heat losses to the burner. Thus, this flame is not truly adiabatic. An analysis
Figure 4.12: Contours of a) temperature and b) flow speed (with streamlines), for medium inlet mass flux.

Figure 4.13: Stand-off distance of the predicted medium mass flux flame \((\dot{m} = 0.2190 \frac{kg}{m^2 \cdot s})\) as a function of \(r\).
Figure 4.14: Contours of a) temperature and b) flow speed (with streamlines), for the two dimensional inlet mass flux.

of the stand-off distance in Figure 4.13 shows a slightly bowed flame, where stand-off distance decreases towards the edges. Since this flame approximates adiabatic, the surface area, as found from the stand-off distance may be used to find the laminar burning flux from the original mass flow rate. Since the stand-off distance curve contains vertical as well as radial components, each non-radial cell length is approximated as the surface area of a cone, unless flat. Using this methodology, the total surface area may be calculated up to the point where the reaction zone falls off. The laminar burning flux via this method is found to be $0.2101 \frac{kg}{m^2 \cdot s}$, in error by only 4.1%.

4.3.3 High Mass Flux

Flames stabilized at a mass flux greater than the adiabatic flux are expected to be inherently three dimensional. The local mass flux exceeds the laminar burning flux, and so the flame expands its surface area through wrinkling, similar to a premixed Bunsen flame [66]. A wrinkled flame, well-removed from the burner surface is illuminated in Figure 4.14. As predicted, the flame has increased its surface area to accommodate local mass fluxes in excess of the laminar burning flux. The pattern appears random, but generally the flame bows outward significantly. Temperature profiles up until these structures are generally flat; thus, the flame is stabilized from the boundaries. These structures are also shown to bend
the streamlines of the flow due to the variance in temperatures in both axial and radial directions. While these structures are three dimensional in reality, the two dimensional model is shown to readily predict a burner-stabilized flame greater than the adiabatic limit. To verify that it correctly resolves the burning flux, a similar analysis is applied to the stand-off distances of Figure 4.15 to determine the laminar burning flux of the flame. The stand-off distances shown greater inconsistency in this flame; however, a burning flux of $0.1962 \frac{kg}{m^2 \cdot s}$ is found, in error by 10.4%, due to unresolved grid points.

### 4.3.4 Summary of Results

The Fluent results altogether lead to several conclusions on two-dimensional flame behavior. First and foremost, a model with detailed chemistry is limited by the coarseness of a two dimensional grid and the computation time required. Additionally, errors in commercial software voided any quantitative comparisons with one dimensional simulations or experiments. However, qualitative and global properties predicted by the simulations may still be considered. The boundaries do show the “cupping” effect seen experimentally, and the simulations show that the expansion of reactants into ambient air leads to dilution and lower local laminar burning fluxes. Medium and high inlet mass flux cases demonstrate two dimensional structures that occur after the laminar burning flux is reached. The quasi-adiabatic nature of this type of flame allows for an accurate prediction of the laminar burning flux. However, it should be noted that the three dimensionality of these structures in experimental realizations does not make it compatible for experimental determination of flame speeds.
Chapter 5
Conclusions

In this study, lean and rich flames, particularly in the ultra-lean/rich regimes have been studied in detail. Adiabatic simulations were completed along the entire breadth of available equivalence ratios and inlet temperatures for two mechanisms, GRI 3.0 and San Diego. As a whole, this data set demonstrates the effects of each parameter on the laminar burning flux $\dot{m}_{ad}$. Lean and rich flames both show a sharp drop in laminar burning flux. Increasing the inlet temperature induces an increase in the burning flux, which allows for equivalence ratios not attainable at standard ambient temperature to be reached. Detailed analyses of flame structures in lean flames showed that $\text{HO}_2$ reactions provide an important early pathway for methane oxidation, although it competes with the main chain-branching reaction. Other reactions were shown to play key roles in both determining the burning flux and releasing heat. A regression analysis linked flame behavior to a characteristic temperature $T^*$, which defines the transition between preheating and reaction layers. At lean conditions, the maximum curvature of the main chain-branching reaction was shown to be indicative of this location. Similar analysis in the rich regime showed that the $\text{C}_2$ chain delays the combustion process, which results in the maximum gradient being indicative of $T^*$. Mechanism comparison in both cases illustrated the shortcomings of the San Diego mechanism which still confirmed GRI results. The adiabatic findings on combustion characteristics were linked to non-adiabatic conditions through the simplest non-adiabatic configuration, the burner-stabilized flat flame. The regression, as applied to flat flame simulations, showed that heat loss generally affects the temperature of $T^*$, but not the indicators themselves. Experiments using a high temperature, uncooled flat flame burner showed that mechanism uncertainties exist, in addition to unmodeled heat transfer. However, flat flames were established at numerically predicted inlet conditions and correctly reflected expected trends in the stand-off distance. Furthermore, a two dimensional model analogous to the one dimensional simulations showed boundary phenomena and features of flame stabilization beyond the laminar burning flux.

Future work is recommended in the experimental determination of laminar burning fluxes in ultra lean/rich regimes. In order to confirm the numerical results, experiments should be performed on the
entire range of equivalence ratios for both ambient temperature (to validate the apparatus with accepted experimental data) and preheated flames. Additionally, the experiments should be performed using two different methodologies to confirm the independence of the method to preheating and ultra-lean/rich conditions. The effect of environmental radiation on the mixture temperature should be considered, particularly if the experiments are performed using the single plate, zero strain rate method [67] or the heat flux method on a flat flame burner [7]. The results will show the accuracy of the mechanism and any changes that need to be considered therein to better reflect actual preheated flame behavior.
References


Appendix
LabVIEW VI

The front panel of the LabVIEW Virtual Interface (VI) is shown in Figure 5.1. The user inputs a desired ambient temperature mixture velocity, i.e. at the mass flow controllers. This value is converted into respective fuel and air mass flow rates based on equivalence ratio $\phi$, also user-specified. The front panel then contains monitoring of actual values, both velocities and voltages. At the burner surface, the mixture velocity will have increased in response to the density decrease, modeled by the ideal gas law. Thus, a separate value is provided utilizing the temperature measurements from just below the porous plug, named “mixture temperature” on the panel. Additionally, monitoring of guard and preheater temperatures is provided. The corresponding LabVIEW block diagram is included in Figure 5.2 while corresponding subVIs are included in Figure 5.3.
Figure 5.1: Front panel.
Figure 5.2: LabVIEW Virtual Interface.
(a) flow2volt: converts user-specified ambient temperature velocity and φ into voltages for mass flow controllers (MFC).

(b) volt2flow: converts feedback voltage from MFC into actual flow data.

(c) addname1: attaches name stamp to signals for data file identification.

Figure 5.3: LabVIEW SubVI’s.
Figure 5.4: National Instruments USB-6218 Data Acquisition (DAQ).
Vita

Joseph Edward Gibson was born in Vidalia, GA, USA to Edward and Meridee Gibson on May 12, 1988. He graduated high school from Oak Mountain High School in Birmingham, AL. Immediately following graduation, he enrolled at the United States Air Force Academy, completing Basic Training and one semester before transferring to Auburn University. He graduated Summa Cum Laude from Auburn with a Bachelor of Mechanical Engineering degree in May 2010. He was married to Jennifer Lynne Jennings of Baton Rouge, LA on July 17, 2010 and enrolled at Louisiana State University in August 2010 to pursue a Master of Science in Mechanical Engineering degree under Dr. Ingmar Schoegl. He is a candidate for graduation in the Spring Commencement of 2012 for his research, Numerical and Experimental Evaluation of Preheated Premixed Flames at Lean and Rich Conditions. After graduation, he will begin work in the Career Development Program of Air Products and Chemicals, Inc. in June 2012.