On the Non-Premixed Counterflow Ignition of Alternative Fuels at Atmospheric and Elevated Pressures

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Kyle Benjamin Brady
University of Connecticut, 2015

Critical to the development of predictive combustion models is a robust understanding of the coupled effects of chemical kinetics and convective-diffusive transport at both atmospheric and elevated pressures. This dissertation describes a new variable-pressure non-premixed counterflow ignition experiment designed to address the need for well-characterized reference data to validate such models under conditions sensitive to both chemical and transport processes. A comprehensive characterization of system behavior is provided to demonstrate boundary condition and ignition quality as well as adherence to the assumption of quasi-one-dimensionality, and suggest limitations and best practices for counterflow ignition experiments. This effort reveals that the counterflow ignition experiment requires special attention to ignition location in order to ensure that the assumption of quasi-one-dimensionality is valid, particularly at elevated pressures.

This experimental tool is then applied to the investigation of butanol isomers for pressures of 1-4 atm, pressure-weighted strain rates of 200-400 s\(^{-1}\), and molar fuel loading in nitrogen-diluted mixtures of 0.05-0.25 (i.e. 5-25%). Comparison of the parametric effects of varied pressure, strain rate, and fuel loading amongst the isomers facilitates a comprehensive evaluation of the effect of varied structural isomerism on transport-affected ignition. The experimental results are simulated using isomer-specific skeletal mechanisms developed from two comprehensive butanol models available in the
Comparison of the experimental and computational results reveals that while both models largely capture the trends in ignition temperature as functions of pressure-weighted strain rate, fuel loading, and pressure, for all isomers both models over-predict the experimental data to an appreciable extent. In addition, neither model captures the experimentally-observed ignition temperature rankings. For atmospheric pressure, the experimental results show that the “ranking” of the isomers in terms of ignition temperature (lowest to highest ignition temperature) generally follows $n$-butanol$\approx$sec-butanol$<iso$-butanol$<^\star tert$-butanol. At 4 atm, this ranking switches to $n$-butanol$=iso$-butanol$<sec$-butanol$<^\star tert$-butanol. The tert-butanol isomer is consistently an outlier, exhibiting significantly higher ignition temperatures than the other isomers, which are closely grouped for all experimental conditions. In contrast, both models predict a large spread amongst the $n$/$iso$-$/sec$-butanol isomers. The model developed by Sarathy et al. [1] predicts rankings of $n$-butanol$<sec$-butanol$<iso$-butanol$<^\star tert$-butanol at atmospheric pressure and $n$-butanol$=iso$-butanol$<sec$-butanol$<^\star tert$-butanol, with significant offset between $n$-butanol and $iso$-$/sec$-butanol. The model developed by Merchant et al. [2] (excluding iso-butanol due to erroneous reaction rate descriptions for iso-butanol breakdown) predicts rankings of $n$-butanol$<sec$-butanol$=^\star tert$-butanol at atmospheric pressure and $n$-butanol$<^\star tert$-butanol$<sec$-butanol at 4 atm. While the non-premixed counterflow system is found to exhibit large sensitivities to changes in fuel diffusivity, within reasonable bounds errors in the transport model cannot account for disparities between the experimental and numerical results. Further sensitivity and path analyses reveal that significant differences exist between the fuel breakdown descriptions of the two butanol models, suggesting that further work is required to better define these pathways, particularly the branching ratios from the hydroxybutyl radicals and the breakdown chemistry of the butene isomers.

In addition, this dissertation describes experimental and computational results on the non-premixed counterflow ignition of nitrogen-diluted $n$-butanol/hydrogen mixtures.
against heated air for pressures of 1-4 atm and hydrogen molar percentages in the binary fuel blends ranging from $\xi_{H}=0\%$ (pure $n$-butanol) to $\xi_{H}=100\%$ (pure hydrogen). The experimental data show that hydrogen addition results in a non-linear decrease in ignition temperatures that can be broken into two regimes; the hydrogen-enhanced regime of $\xi_{H}=0-40\%$ where the addition of more hydrogen significantly decreases ignition temperature, and a hydrogen-dominated regime in the range of $\xi_{H}=40-100\%$ that displays little sensitivity to further hydrogen addition. The experimental results are also simulated using $n$-butanol-specific skeletal mechanisms developed from two comprehensive butanol models available in the literature. These mechanisms are used to assess their ability to predict the variation of ignition temperatures as a result of hydrogen addition to the $n$-butanol “base” fuel. Comparison of the experimental and computational results reveals that both chemical kinetic models capture the two-regime behavior associated with hydrogen addition, though both models over-predict experimental ignition temperatures. Further chemical kinetic analysis of the mechanisms reveals that the two-regime behavior is controlled by the production of hydroperoxyl radicals, with production via the reaction of formyl radicals and oxygen molecules dominating at low hydrogen addition levels, and production via the third body $H+O_{2}+M$ reaction dominating at high hydrogen addition levels.
On the Non-Premixed Counterflow Ignition of Alternative Fuels at Atmospheric and Elevated Pressures

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APPROVAL PAGE

Doctor of Philosophy Dissertation

On the Non-Premixed Counterflow Ignition of Alternative Fuels at Atmospheric and Elevated Pressures

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“No man is an island, entire of itself; every man is a piece of the continent, a part of the main ....” - John Donne

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_Dedicated to those who couldn’t make it to the finish line with us._

_Paul_

_June 14, 2008 – July 18, 2015_
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Chapter 1: Introduction

1.1 Motivation

As the impacts of fossil fuel usage on energy security, climate, and human health become increasingly tangible, the need for near- and intermediate-term alternative transportation energy solutions has been recognized as a national priority. Any potential alternative fuel must provide significantly improved tailpipe emissions and reduced lifecycle carbon footprint, while requiring a minimum of changes to existing supply infrastructure. While novel engine designs and alternative fuels promise to provide efficiency gains and emissions improvements, their success is predicated upon a robust understanding of the coupled effects of chemical kinetics and convective-diffusive transport, and their accurate representation in a predictive reactive-flow model under engine relevant conditions.

Chemical kinetic model development to date has relied heavily upon homogenous experimental systems such as flow reactors, jet-stirred reactors (JSRs), shock tubes, and rapid compression machines (RCMs), primarily due to their suppression of spatial dependencies, elimination of transport effects, and ability to be relatively conveniently modeled even with large kinetic schemes [3]. As a result, such homogenous systems have undergone appreciable improvements and modifications to better facilitate computational modeling and improve the fidelity of experimental data, as recently reviewed by Dryer et al. [4] for flow reactors, Hanson and Davidson [5] for shock tubes, and Sung and Curran [6] for RCMs. However, in practical devices combustion occurs within environments that often involve significant gradients in velocity, temperature, and species concentration, necessitating the validation of combined chemical kinetic and transport models against
computationally accessible, well-characterized experimental data. To address this need for transport-affected validation data, a number of low-dimensional laminar flame experiments have been developed including counterflow and stagnation flames, burner-stabilized flames, and spherically-expanding flames, which have provided insights into flame structure, ignition, propagation, and extinction. Of these, ignition and extinction provide unique opportunities to investigate both kinetics and transport due to the relatively high sensitivity of such limit phenomena to each. However, as recently pointed out by Egolfopoulos et al. [3], they have received relatively less attention for model development compared to laminar flame speeds, in part due to the computational difficulty associated with modeling limit phenomena, but also due to the higher sensitivity resulting in greater uncertainties when boundary conditions are not well-defined. This is particularly true of transport-affected, diffusive ignition experiments, where a high-temperature boundary results in significant thermal gradients across the test section, and can lead to unquantified deviations from ideal behavior [3]. Nonetheless, the sensitivity of diffusive ignition experiments - particularly non-premixed configurations - to both chemical kinetics and transport phenomena make non-premixed ignition studies an attractive and stringent option for complete model validation.

Such stringent validation is vital in light of recent research aimed at the development and implementation of alternative transportation fuels. Alternative fuel research has encompassed a diverse range of molecule classes, however as part of a push towards renewable fuels and reduced emissions, alcohols have emerged as a leading prospect both for near-term performance and sustainability improvements, and for the long-term replacement of fossil fuels in ground transportation applications. Ethanol, the most
successful of these to date, currently comprises up to 10% of all gasoline purchased in the United States and has facilitated the elimination or phase-out of both tetra-ethyl lead (TEL) and methyl tert-butyl ether (MTBE) as anti-knock additives. Through its long history, ethanol has received significant research attention and has been investigated in shock tube, flame, and reactor experiments (cf. [7]). However, the fermentation process by which the majority of ethanol is produced has been criticized for both its use of food-grade feedstocks as well as its low conversion efficiency, and second generation production from cellulosic plant waste has yet to be proven commercially viable. Partly as a result, so-called “second generation” alcohol-based alternative fuels such as butanol have recently received significant research attention. As a stand-alone alternative transportation fuel or as a fuel blend with gasoline, butanol offers several advantages over ethanol. Whereas ethanol is fully miscible with water, both \( n \)- and \( iso \)-butanol isomers exhibit limited solubility with water and are less corrosive, opening up the possibility of more efficient distribution methods though pipelines. In addition, its higher energy density allows higher blending ratios with gasoline without engine modifications, and its lower vapor pressure would greatly reduce evaporative emissions. Aside from its potential impact as a transportation fuel, the chemical kinetics of butanol is scientifically interesting as it represents the smallest alcohol exhibiting all forms of structural isomerism. As a result, by comparing the behavior of the butanol isomers in well-defined combustion configurations, the impacts of molecular structural variations on combustion chemistry can be better understood and broadly applied to the modeling of alcohol-based transportation fuels.
While alternative fuels such as butanol may be introduced into the marketplace as part of fuel blends in current engine technology, their primary benefit may be the facilitation of advanced engine concepts such as low temperature combustion (LTC), which have been proposed for the purpose of reducing emissions while simultaneously maintaining or improving performance. For example, the homogeneous charge compression ignition (HCCI) concept has been discussed extensively as a potential way to reduce emissions and increase fuel economy by combining a high compression ratio with a nearly homogenous fuel-air charge. However, despite a long track record of related research, this effort has not resulted in a commercially-viable engine due to a wide variety of technical hurdles including difficulties in ignition timing, low-load efficiency, a limited operability range, and high heat release rate at high-load conditions (cf. [8–10]). Reactivity controlled compression ignition (RCCI) - an offshoot of the HCCI concept - attempts to resolve these issues via the staggered injection of two or more fuels of differing reactivity to control the timing and magnitude of the combustion event. In general, a low-reactivity fuel is injected into the cylinder prior to compression to create a well-mixed charge of fuel and air. Just prior to ignition, a high-reactivity fuel is injected directly into the cylinder to promote and control the ignition event. As recently reviewed by Reitz and Duraisamy [11], the RCCI concept has shown significant promise in terms of enhanced efficiency, significantly improved emissions characteristics, and controllable ignition timing with a variety of fuel configurations including gasoline/diesel, natural gas/diesel, methanol/diesel, and gasoline/gasoline+additive. With an octane rating similar to gasoline, butanol may have promise as the low reactivity fuel in an RCCI-type engine, while an in-situ system to reform some existing on-board butanol fuel may be used to
provide hydrogen as the high reactivity fuel. By doing so, the complications of hydrogen distribution and on-board storage may be circumvented, while providing the operability benefits, improved efficiency, and reduced emissions of the RCCI concept. Such reforming has been demonstrated extensively for ethanol [12], while butanol reforming has also been investigated by several studies [13–15].

With the preceding discussion in mind, the aim of the present work is to progress three objectives. First, a new non-premixed, elevated-pressure, counterflow ignition experiment is developed and comprehensively validated in an effort to address experimental validity concerns such as those mentioned previously, as well as to provide a detailed system characterization to afford a complete understanding of the system behavior and suggest “best practices” for future studies utilizing this configuration. Limitations and suggestions for improvements of the experimental system are also discussed. Second, the counterflow ignition temperatures for all four butanol isomers (n-/iso-/sec-/tert-butanol) are compared to investigate the impact of structural isomerism. Butanol isomers have received significant research attention in recent years, and numerous fundamental studies have been conducted using a variety of experimental systems (e.g. [1,2,16–29]). Despite the research attention butanol isomers have garnered, there is relatively little data exploring limit phenomena for these fuels. In fact, the only available diffusive ignition data come from the stagnation-pool study of Liu et al. [30] for n- and iso-butanol, while flame extinction data are limited to the n-butanol studies of Veloo et al. [31] and Hashimoto et al. [32], and the n-, iso-, and sec-butanol study of Mitsingas and Kyritsis [19]. As such, this dissertation explores the impact of ambient pressure, strain rate, fuel loading, and structural isomerism on counterflow ignition
temperatures of the butanol isomers. The experimental results obtained are simulated using comprehensive butanol models available in the literature and used to validate and assess the performance of these chemical kinetic models. Analysis of these simulations allows for insights into the causes of the disparate behaviors observed amongst the butanol isomers. Third, the effect of hydrogen addition on the ignition of \( n \)-butanol is explored to assess the performance of two literature butanol models for predicting ignition temperatures of \( n \)-butanol/hydrogen mixtures. As a method for achieving emissions and efficiency gains, hydrogen addition has been shown to improve the performance of a number of engine configurations including spark-ignited engines [33–36], diesel engines [37,38], and gas turbine engines [39–42]. However, hydrogen addition has not been explored extensively in the counterflow ignition configuration - only the methane/hydrogen study of Fotache et al. [43] has thus far explored this issue - and hydrogen addition to butanol has not been addressed previously in the literature. As a result, this dissertation explores the impact of various levels of hydrogen addition to \( n \)-butanol under atmospheric and elevated pressure conditions. The experimental results are simulated using \( n \)-butanol skeletal mechanisms developed from two comprehensive butanol mechanisms available in the literature. Chemical kinetic analysis of the simulated results is performed to understand the controlling chemistry causing changes in fuel blend reactivity due to hydrogen addition.

1.2 Organization of this dissertation

Chapter 2 describes in detail the experimental apparatus and procedures used in this work, as well as the computational codes used for the accompanying simulations. In addition,
the concepts of the ignition kernel and thermal mixing zone are discussed, and a detailed description and justification is given for the global strain rate model used to characterize the counterflow system. In addition, experimental uncertainties and the radiation correction methodology for air boundary temperature measurements are discussed in detail.

Chapter 3 provides a detailed characterization of the newly-developed counterflow ignition experiment. Fuel concentration, as well as velocity and temperature profiles are measured to ensure that the boundary conditions are properly defined, and to experimentally demonstrate the quasi-one-dimensionality of the counterflow ignition system. In addition, the importance of the ignition location is discussed and demonstrated to occur in a manner consistent with quasi-one-dimensional assumptions. Finally, representative data for a gaseous fuel is compared against experimental data from a related experimental system so that the present data may be understood in the context of similar data sets.

Chapter 4 describes detailed results for the counterflow ignition of $n$-butanol. The trends as functions of pressure, fuel loading, and pressure-weighted strain rate are described. The experimental results are simulated using isomer-specific skeletal mechanisms derived from two contemporary comprehensive butanol mechanisms. Subsequent analysis of the numerical results reveals that although both mechanisms predict the ignition temperature trends observed experimentally, the two mechanisms predict significantly different ignition temperatures due to substantial differences in the controlling chemistry of $n$-butanol breakdown.
Chapter 5 further explores butanol ignition by comparing the ignition results of the four butanol isomers to systematically investigate the impact of structural isomerism. While $n$-, $iso$-, and $sec$-butanol exhibit largely similar ignition temperatures, $tert$-butanol exhibits consistently higher ignition temperatures than the other three isomers. Isomer-specific skeletal mechanisms created from the comprehensive butanol models largely fail to capture the experimentally-observed ranking of the isomers. Detailed analysis of the numerical results suggests that the butene isomers may play a significant role in determining the relative levels of reactivity between the butanol isomers, and that differing butene chemistry may account for the disparate predictions between the two models.

Chapter 6 describes the effects of hydrogen addition on nitrogen-diluted $n$-butanol ignition against heated air, showing that small amounts of hydrogen addition can dramatically reduce ignition temperatures. Two ignition regimes are observed, termed the “hydrogen-enhanced” regime and “hydrogen-dominated” regime. The numerical results are found to closely follow the trends observed experimentally, and further analysis suggests the controlling chemistry behind the observed two-regime behavior.

Chapter 7 summarizes the conclusions reached in this dissertation, and suggests future research that may take advantage of the counterflow ignition configuration to further contribute to the understanding of ignition under convective-diffusive conditions.

Finally, the appendix contains information regarding the skeletal mechanisms developed in the course of this study.
1.3 List of publications

Publications associated with this dissertation:


2. K.B. Brady, X. Hui, C.J. Sung, Comparative study of the counterflow forced ignition of the butanol isomers at atmospheric and elevated pressures, Combustion and Flame, in press.


Other publications:


Chapter 2: Experimental and Numerical Specifications

2.1 Experimental apparatus

As this is the first time that data from this newly built experimental system is being reported, it is described here in detail, and shown schematically in Fig. 2.1. Flow control is accomplished through the use of sonic nozzles for all gases, with high-pressure gauges and regulators providing a wide operational flow rate range. The air stream is synthesized by a 21%/79% $O_2/N_2$ mixture by mole, while the fuel stream is comprised of nitrogen-diluted $n$-butanol with fuel loading varying between 5-25% by mole percentage. To control chamber pressure and aid in moving combustible gases out of the combustion chamber, pressurized gas is extracted from a liquid nitrogen tank and metered to diffusers in the bottom of the combustion chamber. The flow rate of liquid fuel is controlled using a precision Teledyne Isco 1000D high-pressure syringe pump, with fuel vaporization accomplished through a heated spray system. Liquid fuel flowing through a capillary tube is broken up at the injector tip by a nitrogen stream heated to near the boiling point of the liquid fuel, and angled to produce a spray cone. This spray injector is inserted into a stainless steel cylinder electrically heated to just above the boiling point of the liquid fuel to prevent surface condensation - for the current study, ~140 °C. The remainder of the fuel line is maintained at the same temperature as the vaporization chamber. To ensure proper vaporization, the partial pressure of the fuel is maintained well below the saturation vapor pressure, calculated using the correlation from Yaw’s Chemical Handbook [44] at the temperature/pressure conditions within the fuel line.
As shown in Fig. 2.1, optical accessibility is facilitated by four lateral ports enclosed by UV-grade fused-silica windows. Water-cooling is provided on the exterior of the top lid to regulate the chamber surface temperature, while chamber pressure is regulated and monitored using a needle valve and digital pressure gauge on the chamber exhaust. The counterflow burner consists of a quartz straight-tube upper section directing heated air downward against a nitrogen-diluted fuel stream emanating from a stainless steel lower section. The air and fuel streams are surrounded by concentric nitrogen co-flow to isolate the test section from the ambient atmosphere and maintain a high quality flow field. The air and fuel tubes have 19 mm inner diameters and the co-flow tubes have 28 mm inner diameters. The air and fuel streams are separated by 20 mm, resulting in an L/D ratio - based on the air and fuel stream diameters - of 1.05. Contained within each main stream is a customized flow-straightening device consisting of extreme-temperature Hastelloy-X honeycomb and nichrome mesh with 40 openings per inch, located approximately 40 mm from each tube exit. These devices provide important flow straightening and laminarization, aid in establishing symmetrical flow profiles, and sufficiently flatten the velocity profile across the tube radius. The symmetry and flow balancing accomplished by these inserts are a critical factor that determines ignition location, especially at elevated pressures. A discussion of the importance of ignition location is provided in Chapter 3. Heating on the oxidizer side is accomplished using an internal helical SiC heater, capable of heating the airflow to 1250-1300 K at the tube exit depending on operating conditions. In addition, an external Omegalux radiant heater surrounds the air and co-flow tubes to reduce radial heat loss. Both heaters are manually controlled using independent variable transformers to maintain constant power. The fuel tube surface
temperature is controlled automatically using a flexible rope heater and temperature controller, while the gas temperature is monitored continuously by an in-line bare-wire K-type thermocouple located 50 mm from the tube exit. Testing has shown that placing the thermocouple at this location minimizes flow disturbances and that the difference between the gas temperatures at the exit and 50 mm upstream is negligible since the fuel tube is temperature-controlled along its length.

To fully describe the ignition state in the counterflow system, the oxidizer exit temperature must be known. Since the oxidizer side is heated to typical values of 1000-1250 K to ignite the fuels of current interest, special care must be taken to accurately describe this temperature. While thermocouples are able to measure such elevated air temperatures, they can be quickly destroyed by the flame that evolves post-ignition. A customized thermocouple mount consisting of a thermocouple holder, 90-degree rotary solenoid, and motorized translation stages is used, which provides the capability for two-axis motion. To avoid flame-related damage to the thermocouple, the thermocouple holder that serves as a mounting point for an Omega Engineering K-type bare-wire thermocouple - with a wire diameter of 0.125 mm (0.005 in) - is attached to a rotary solenoid that is electrically activated from outside the combustion chamber. The solenoid is itself attached to a two-axis motorized translation stage that facilitates motion in the axial and radial directions, providing for the detailed temperature characterization discussed in Section 3.3. In addition, the thermocouple itself is subject to radiative heat transfer under high temperature conditions, necessitating a correction model to maintain fidelity of the measured thermocouple value to the actual gas temperature. The impact of radiative heat transfer is discussed in detail in Section 2.7.
Also required to accurately determine counterflow ignition temperatures is knowledge of the location of the ignition event. Humer et al. [45] recognized the need to determine the ignition location to ensure that ignition occurs near the experimental centerline, consistent with quasi-one-dimensional assumptions. Though only atmospheric pressure experiments were conducted in [45], determination of the ignition location becomes critically important at elevated pressures, where buoyancy may cause the edges of the stagnation plane to come in close proximity to the air duct and cause ignition to occur on or near the duct rim at a different boundary air temperature than would otherwise be the case. This issue is discussed in more detail in Chapter 3. To facilitate monitoring the ignition location, a Vision Research Phantom v710 high-speed camera is used to acquire visible-light images of the ignition event at a frame rate of 3000 Hz for all butanol ignition data in Chapters 4 and 5, while a Photron SA5 high-speed camera acquiring visible-light images at frame rates ranging from 60 to 3000 Hz is used for the hydrogen addition data in Chapter 6. A frame rate of 3000 Hz is sufficient to capture and resolve the onset of ignition, and facilitates determining its precise location within the test section. While such frame rates are desirable and necessary for burner alignment, for high hydrogen content cases the extremely low luminosity associated with the ignition event precludes such imaging. Nonetheless, even relatively low frame rate data can be useful for ensuring consistent ignition positions - albeit with significantly less precision - when ignition has otherwise been observed to ignite at a central location for more visible fuel loading conditions. During normal operation, the camera is located at one position relative to the combustion chamber. However, during the burner alignment process the
camera views the ignition event from two perpendicular angles to locate ignition in three dimensions.

2.2 Experimental procedure

In the present experiments, the oxidizer boundary temperature at the onset of ignition is denoted as the ignition temperature ($T_{ig}$). The procedure for acquiring this temperature is as follows: (1) The internal, external, and flow system heaters are brought up to a steady-state temperature close to the ignition state, the desired gaseous mass flow rates (excepting any fuel) for a given strain rate condition are set on the flow system, and the chamber is pressurized to the desired setpoint. (2) Fuel is introduced through the flow system and allowed to come to steady state. (3) The high-speed camera begins acquiring data, and the air temperature is gradually raised by increasing power to the internal heater until a flame ignites. (4) The fuel supply is shut off to extinguish the flame. (5) The thermocouple solenoid is activated, rotating the thermocouple bead to the center of the air duct and the air temperature, along with the fuel-side gas temperature, is recorded. (6) The images acquired from the high-speed camera are checked to verify that ignition occurs at or near the longitudinal axis, and that it occurs near the middle of the test section, ±2 mm. If ignition occurs too far towards the fuel or oxidizer exits, the flow rates are adjusted to move the stagnation plane in the appropriate direction while maintaining a constant global strain rate (to be defined in Section 2.3). As the strain rate is defined based upon the ignition state, an iterative trial ignition process - prior to data acquisition - is required to determine the proper flow settings such that the ignition location and
desired strain rate conditions are met. Steps 2-6 are repeated a minimum of three times to ensure a consistent value for $T_{ig}$.

### 2.3 Definition of characteristic strain rate

As has been discussed previously by Fotache et al. [46], defining a characteristic strain rate for the counterflow ignition configuration that exhibits a clear, monotonic relationship with ignition temperature can prove somewhat troublesome. Two general options were described in [46]: the strain rate may be defined by a measured velocity gradient (i.e., local strain rate) or by the boundary conditions (i.e., global strain rate). As laid out by Fotache et al. [46], the ideal definition would describe the strain rate at the precise axial location where ignition occurs. However, this local definition requires prior knowledge of its location. An alternative local strain definition was adopted by Fotache et al. [46] in the form of the maximum measured strain rate on the oxidizer side, which was shown to behave similarly to the kernel-based definition due to its description of the strain rate in the vicinity of the ignition kernel. The choice of the oxidizer side is the result of their observation that ignition occurs on this side due to its exponential dependence on temperature compared to a linear dependence on fuel concentration. However, for the current apparatus, the solid seeding particles necessary to perform velocimetry in high-temperature flows would quickly clog the oxidizer-side mesh insert described in Section 2.1. A similar local definition could be applied on the fuel side of the stagnation plane, where cooler temperatures allow the use of liquid seeding particles, similar to Liu et al. [47]. However, the fuel-side strain rate does not maintain a constant relationship with the oxidizer-side strain rate as the temperature - and thus density - of the
oxidizer stream varies. As can be readily demonstrated computationally by keeping total mass flux constant for each stream, as the oxidizer boundary temperature varies, the resultant strain rate near the stagnation plane on the oxidizer side also varies, whereas the fuel-side strain rates are indistinguishable. Since counterflow ignition inherently involves variation of the oxidizer temperature, this behavior suggests that the fuel-side strain rate is not an appropriate strain rate definition for counterflow ignition.

Alternatively, the strain rate near the ignition kernel may be estimated from the boundary conditions. Such a global definition, while simple to apply, invokes assumptions regarding the nature of the boundary conditions, which may or may not accurately describe those observed experimentally. As such, it is critical to understand the nature of the velocity boundary conditions in order to select an appropriate flow model, namely potential flow or plug flow. A comparison of axial velocities measured by Particle Image Velocimetry (PIV) along the stagnation streamline to the commensurate potential- and plug-flow models is provided in Fig. 2.2. For atmospheric pressure and room temperature boundaries, it is immediately apparent that the measured profile does not exactly match either flow model, but instead represents an intermediate between the two. While this result is not unexpected for a practical counterflow device [48], it is seen from Fig. 2.2 that the plug flow model clearly better matches the measured velocity profiles near the boundaries.
In addition to choosing the correct flow model, it is imperative to capture the effects of varying density due to the large temperature gradients inherent to counterflow ignition. This can be accomplished using the relations of \(^1\)Seshadri and Williams [49]:

\[
k = \frac{2V_0}{L} \left(1 + \frac{V_F \sqrt{\rho_F}}{V_O \sqrt{\rho_O}} \right),
\]

Eqn. 2.1

where \(k\) is the strain rate, \(V\) is the bulk velocity at the boundary, \(L\) is the separation distance, \(\rho\) is the density, and the subscripts \(F\) and \(O\) represent the fuel and oxidizer boundaries, respectively. It is worth noting that the strain rate calculated from Eqn. 2.1 refers to the estimated characteristic strain rate on the oxidizer side of the stagnation plane. For the case in Fig. 2.2, the measured maximum strain rate is 126 s\(^{-1}\) as compared to an estimated 150 s\(^{-1}\) using Eqn. 2.1, demonstrating the adequacy of this global strain rate definition.

Finally, as is noted in the work of Kreutz and Law [50], the width of the mixing layer in the counterflow arrangement scales as a function of \((\rho k)^{-1/2}\), such that for a constant strain rate, ambient pressure/density changes will result in appreciable variations in the relevant spatial scales. Thus, in order to isolate the chemical effect of pressure variations from the effect of varied spatial structure, the anatomy of the flow field (in terms of temperature and concentration profiles) is kept approximately constant through the use of the pressure-weighted strain rate \((k')\), as used experimentally in the work of Fotache \textit{et al.} [46] and defined in Eqn. 2.2:

---

\(^1\) It is worth noting that Eqn 2.1 is uniformly attributed in the literature to the referenced work of Seshadri and Williams, however this equation does not directly appear in that publication. As a result the origins of Eqn. 2.1 are somewhat unclear. Nonetheless, this equation can be readily shown to accurately describe the strain rate for a plug flow condition using computational codes such as the OPPDIF package included in CHEMKIN.
\[ k' = \frac{P_C}{P_{\text{ref}}} k, \]  

Eqn. 2.2

where \( P_C \) is the chamber pressure, \( P_{\text{ref}} \) is a reference pressure, taken throughout this work as 1 atm, and \( k \) is the oxidizer-side global strain rate as defined in Eqn. 2.1. Thus, when the pressure-weighted strain rate is held constant the width of the pre-ignition mixing layer is expected to be approximately invariant with pressure. By measuring temperature and velocity as functions of axial position within the test region, this invariance is borne out experimentally in Chapter 3.

2.4 Computational specifications

In order to assess the fidelity of existing combustion models to experimentally-derived counterflow ignition temperatures, the ignition state is modeled based on the work of Kreutz et al. [51], with the ignition temperature corresponding to the turning point of the lower-branch ignition response curve with respect to oxidizer boundary temperature. The formulation of the counterflow non-premixed configuration follows that of Smooke et al. [52], while the navigation of the ignition turning point is achieved using the flame-controlling continuation method developed by Nishioka et al. [53]. The current code utilizes the CHEMKIN chemical kinetics and transport properties libraries [54,55]. Throughout this dissertation, the H radical is chosen as the controlled species due to its physical significance to ignition, although, as shown by Kreutz and Law [50], ignition response curves could be generated using other key radical species as well. Typically, absolute and relative tolerances are set as \( 10^{-9} \) and \( 10^{-6} \), respectively; variation of these values has no impact on the computed ignition temperature. The solution is computed on a non-uniform grid consisting of 227 points that have been adaptively placed to achieve a
dense grid within the thermal mixing zone/ignition kernel. The gradient and curvature parameters of the resulting solution typically have values of 0.05 or less.

It is important to recognize that the flow description used in Smooke et al. [52] is potential flow, while experimentally the strain rate is described by a plug-flow global formulation. Despite the varying description of the velocity boundary conditions, as demonstrated by Sung et al. [56], the scalar structures of different flow descriptions - potential, plug, or an intermediate flow - collapse onto each other within the thermal mixing zone for appropriately chosen boundary velocities. Fotache et al. [57] further indicated the insensitivity of the ignition process to the flow model used. As a result, since both models describe the expected strain rate near the stagnation plane, the choice of flow model should have a minimal effect on the ignition temperatures computed.

A number of detailed kinetic mechanisms for butanol isomers have been developed in recent years, including the mechanisms of Frassoldati et al. [28], Merchant et al. [2], and Sarathy et al. [1], hereafter referred to as the Frassoldati mechanism, Merchant mechanism, and Sarathy mechanism, respectively. The Frassoldati mechanism, which is an update of the mechanism of Grana et al. [22], includes all four isomers and was validated primarily against low-pressure flame speciation data. The Merchant mechanism, which includes all four isomers and was based upon the comprehensive mechanism of Van Geem et al. [29], was validated against pyrolysis, laminar flame speed, low-pressure flame structure, and shock tube data. The Sarathy mechanism was validated against laminar flame speeds, low-pressure flame structure data, RCM and shock tube ignition delays, and JSR species profiles. Unfortunately, the inclusion of non-integer stoichiometric coefficients in the Frassoldati mechanism makes it incompatible with the
current CHEMKIN-based ignition code. Hence, only the Sarathy and Merchant mechanisms are included and compared in the present study.

An important limitation in the current study - and indeed in combustion modeling in general - is the size of the chemical kinetic model and its accompanying computational cost. While the sizes of the Sarathy (426 species, 2335 reactions) and Merchant (372 species, 8723 reactions) mechanisms are modest compared to many mechanisms for fuels of practical interest, they are nonetheless prohibitively large for use in computing ignition turning points. As a result, isomer-specific skeletal mechanisms are created using the Directed Relation Graph with Error Propagation (DRGEP) implementation of the Mechanism Automatic Reduction Software (MARS) package of Niemeyer and co-authors [58–61]. Each mechanism is reduced using constant-volume ignition delays for equivalence ratios of 0.5-2, pressures of 1-40 atm, and temperatures of 1000-1800 K, using butanol, N₂, and O₂ as target species. In addition, the reduction procedure utilizes perfectly stirred reactor (PSR) extinction profiles for inlet temperatures of 400 and 500 K, covering the same range of pressure and equivalence ratio as the autoignition results. The error limit - defined in terms of autoignition delay and PSR extinction turning point - is set at 10%. The resulting isomer-specific skeletal mechanisms are referred to hereafter as SN, SI, SS, and ST (referring to the n-, iso-, sec-, and tert-butanol skeletal mechanisms derived from the Sarathy detailed model), and MN, MS, and MT (referring to the n-, sec-, and tert-butanol skeletal mechanisms derived from the Merchant detailed model). Due to some issues arising from iso-butanol-relevant reactions in the Merchant model, which are detailed in Section 2.5.1, the skeletal reduction cannot be conducted for iso-butanol, and
hence “MI” is lacking here. Information regarding the skeletal mechanisms can be found in the appendix.

While the Merchant and Sarathy skeletal mechanisms have been validated under both homogenous and flame conditions, it is important to ensure that they also adequately follow the behavior of the detailed mechanisms for the conditions in this study. To that end, Fig. 2.3 demonstrates the degree of matching between the predicted ignition turning points for the skeletal and detailed mechanisms at 1 and 5 atm conditions. At both pressures, the skeletal Sarathy mechanism results differ negligibly from those of the detailed mechanism, with a maximum difference in the predicted turning point temperature of 2 K at the 5 atm pressure. The skeletal Merchant mechanism exhibits a larger difference of 4 K at 1 atm and 14 K at 5 atm; however this difference, 0.3-1% of ignition temperature, is deemed small in a relative sense.

2.5 Modifications to combustion models

In the course of investigating the butanol isomers numerically, several important issues with the Merchant and Sarathy models have become apparent, and have necessitated modification of the mechanisms and the exclusion of certain data. Due to the significant impact of these changes and their implications on future modeling studies, these modifications are detailed in the following sections and are incorporated into the respective skeletal mechanisms.

2.5.1 Merchant model

In the course of mechanism reduction, it was discovered that the Merchant model contains several reactions in the PLOG format that contain negative pre-exponential
factors. The PLOG format provides the flexibility to describe reaction rates in different pressure ranges by different Arrhenius coefficient sets. For pressures intermediate between two reaction rate descriptions, a linear interpolation for \( \ln(\Psi) \) is used to obtain the reaction rate:

\[
\ln\Psi = \ln\Psi_i + (\ln\Psi_{i+1} - \ln\Psi_i) \left[ \frac{\ln P - \ln P_i}{\ln P_{i+1} - \ln P_i} \right],
\]

Eqn. 2.3

where \( \Psi \) is the interpolated reaction rate, \( \Psi_i \) and \( \Psi_{i+1} \) are the reaction rates at pressures bracketing the pressure for which \( \Psi \) is desired, and \( P \) is the pressure, with the subscripts following an identical nomenclature. The above definitions break with convention by using \( \Psi \) instead of \( k \) for reaction rate for the sake of clarity, as \( k \) is used elsewhere in this work to define strain rate. Since the logarithm of a negative number is undefined, the PLOG interpolation cannot be evaluated for negative values of \( \Psi_i \)'s. Such a situation arises for the iso-butanol decomposition reaction R2.1, where the formatting of this reaction as a “declared duplicate” forces interpolation using a negative reaction rate.

\[
iBuOH \Leftrightarrow CH_3 + C_3H_7O - N2
\]

R2.1

As a result, both the ignition code and the mechanism reduction code fail. It is worth noting that when the same mechanism is used in CHEMKIN-PRO [62], the calculation neither fails nor displays any warning messages. Given the nature of the interpolation, it is unclear what allows CHEMKIN-PRO calculations to proceed.

For the purposes of the present study, reaction R2.1 is problematic in that its reaction rate cannot be evaluated. In order to facilitate as broad a mechanism comparison as possible, this reaction is manually removed so that skeletal mechanisms for \( n-, sec-, \) and \( tert- \) butanol can be obtained and used in the ignition code. This methodology is deemed valid for these isomers given that the reversed R2.1 should at most represent a minor
recombination pathway in these cases. However, given that this reaction defines one possible pathway for iso-butanol destruction, R2.1 cannot be removed from the mechanism \textit{a priori} without potentially significant impacts to the fidelity of an iso-butanol skeletal mechanism. As a result, no computational data for iso-butanol from the Merchant model is shown in this work.

2.5.2 \textit{Sarathy model}

In the course of evaluating the impact of transport parameters on the ignition temperature of the butanol isomers, it was discovered that while the Lennard-Jones parameters for \textit{n}-butanol were quite similar between all three models [1,2,28], the parameters for \textit{iso}-, \textit{sec}-, and \textit{tert}-butanol within the Sarathy model differed significantly from the parameters used in both the Frassoldati and Merchant models. While nitrogen-fuel binary diffusion coefficients for \textit{n}-butanol differed between the Merchant and Sarathy models by only \textasciitilde5\%, the computed diffusion coefficients for the other three isomers were as much as 125\% larger in the Sarathy model. In fact, the stated values for collision diameter were almost half that of similar C$_4$-species, and even smaller than those of the oxygen and hydroxyl radicals. Following the procedures laid out in Sarathy \textit{et al}. [1,18] for the estimation of transport parameters, values more similar to those found in the Frassoldati and Merchant models were obtained, suggesting that these parameters included in the transport database of Sarathy \textit{et al}. [20] were questionable. It is worth noting that different transport parameters for the butanol isomers are included in a recent hierarchical C$_1$-C$_5$ alcohol model developed by Sarathy \textit{et al}. [63]. These values result in closer agreement with the Merchant transport model (~15\% larger fuel-N$_2$ diffusion coefficients), however this change is not described by the authors, and the new
parameters do not appear to coincide with the stable-species transport parameter correlation methodology stated in [1]. Thus it is unclear how these parameters are derived.

As will be shown in detail in Chapter 5, the effect of such large discrepancies in diffusion coefficients is significant. As a result, the transport parameters for the three butanol isomers - as well as all species which use the identical parameters - are modified to the corresponding parameters used in the Merchant model and the resulting transport database is used to compute all numerical results presented for this mechanism. Since the transport properties are otherwise similar, this change not only modifies the parameters to more realistic values, but also facilitates a more direct comparison of the underlying chemistry of the two models.

2.6 Mixing zone and ignition kernel structure

To provide a basis for understanding the behavior of the counterflow ignition system, Fig. 2.4 demonstrates typical spatial profiles at the ignition turning point for velocity, temperature, and the mole fractions of $n$-butanol, oxygen, and H, O, OH, and HO$_2$ radicals, computed using the skeletal Sarathy mechanism. Several important features are evident. First, the “ignition kernel” - taken throughout this work to refer to the localized region of maximum H, O, OH, and HO$_2$ radical mole fractions - is located on the oxidizer side of the stagnation plane at a region with temperatures near that of the oxidizer boundary. This position is the result of the high activation energies of the chain branching reactions that are primarily responsible for production of these radicals. Since the rate of radical production is exponentially dependent on temperature and linearly related to fuel concentration, the ignition kernel is located on the oxidizer side for all conditions in the
present study. Second, the fuel transports towards the oxidizer side and the radicals generated within the ignition kernel must be transported towards/across the stagnation plane to react with fuel. This spatial separation results in a fuel-lean condition at the ignition kernel, and is responsible for the counterflow ignition experiment’s relatively high sensitivity to transport properties. Third, thermal mixing between the hotter oxidizer and colder fuel streams occurs over nearly the same region as \( n \)-butanol/oxygen mixing and encompasses the ignition kernel. This zone taken as a whole is referred to as the thermal mixing zone throughout the following discussions.

2.7 Thermocouple radiation correction methodology

In a high-temperature environment, such as the exit of the hot-air duct in the current counterflow arrangement, one major source of uncertainty in the measurement of ignition temperature is the correction for radiation, closely followed by the assurance that simplifying assumptions made about the nature of the flow are accurate. The following discussion addresses the various factors impacting the fidelity of the measured temperature to the gas temperature.

The first important consideration is the temperature uniformity of the thermocouple bead, such that the entire bead may be considered to be at a single temperature. This assumption is critical so that spatial variations in temperature within the thermocouple need not be considered. This is accomplished by evaluating the Biot number, \( \text{Bi} \):

\[
\text{Bi} = \frac{hL_C}{k_w} = \frac{\text{Nu} k_g}{\beta k_w},
\]

Eqn. 2.4

where \( h \) is the convective heat transfer coefficient, \( L_C = \frac{d_{b}}{\beta} \) is a characteristic length defined as the bead volume divided by the bead surface area, \( \beta \) is a geometric factor (\( \beta = \)
6 and 4 for a spherical bead and a cylindrical bead, respectively), \(d_b\) is the bead diameter, \(\frac{h d_b}{k_g}\) is the Nusselt number, and \(k_g\) and \(k_w\) are the gas and wire thermal conductivities, respectively. The Nusselt number is calculated from Eqn. 2.5 using the correlation for a cylinder developed by Collis and Williams [64], following the suggestion of Shaddix [65] for thermocouple configurations where the ratio between bead and wire diameters \(d_b/d_w\) is less than 3:

\[
\text{Nu} = (0.24 + 0.56 \text{Re}_b^{0.45}) \left(\frac{T_m}{T_g}\right)^{0.17}.
\]

Eqn. 2.5

In Eqn. 2.5, \(\text{Re}_b\) is the Reynolds number around the thermocouple bead with \(d_b\) as the length scale and \(T_m\) refers to the arithmetic mean of the gas temperature \((T_g)\) and the thermocouple bead temperature \((T_b)\). The gas viscosity needed for \(\text{Re}_b\) in Eqn. 2.5 and the gas thermal conductivity needed for Eqn. 2.4 are calculated from the relations of Scadron and Warshawsky [66], similar to the analysis of Fotache et al. [46]:

\[
\mu = \mu_0 \left(\frac{T_g}{T_0}\right)^{0.69} \quad k_g = k_{g,0} \left(\frac{T_g}{T_0}\right)^{0.78}.
\]

Eqn. 2.6

where \(\mu_0\) and \(k_{g,0}\) refer to the gas viscosity and gas thermal conductivity at \(T_0 = 300\) K.

Assuming a larger-than-typical value for Nusselt number of 2.5, a chromel wire conductivity of \(k_w = 19.24\) W/m-K, and typical gas conductivities in the range \(k_g = 0.06-0.08\) W/m-K, Biot number is of the order \(10^{-3}\) that is \(<< 1\), indicating that the bead temperature may indeed be assumed uniform.

Under the assumption of steady-state temperature, an energy balance around the thermocouple bead may be written as the sum of conductive (subscript cond), convective (subscript conv), radiative (subscript rad), and catalytic (subscript cat) heat gain/loss:

\[
m_b c_{p,b} \frac{dT}{dt} = 0 = \dot{q}_{\text{cond}} + \dot{q}_{\text{conv}} + \dot{q}_{\text{rad}} + \dot{q}_{\text{cat}}.
\]

Eqn. 2.7
where $m_b$ and $c_{p,b}$ are the bead mass and the bead specific heat, respectively. Catalytic effects may be neglected \textit{a priori} due to the choice of a K-type chromel/alumel thermocouple, whose materials can be considered non-reactive under the present conditions [46]. However, conduction through the thermocouple wires may or may not be negligible depending on the nature of the support structure and its proximity to the thermocouple bead. To address these issues, an analysis following that of Shaddix [65] is followed, wherein conduction losses may be neglected under the criterion that the length $l_w$ of the lead wires extending from any support structure to the thermocouple bead should obey $\frac{l_w}{l_c} > 10$, where:

\begin{align*}
    l_c &= \sqrt{\alpha \tau_{\text{conv}}} , \quad \text{Eqn. 2.8} \\
    \tau_{\text{conv}} &= \frac{\rho_w c_{p,w} d_w}{4h} , \quad \text{Eqn. 2.9} \\
    \alpha &= \frac{k_w}{\rho_w c_{p,w}} , \quad \text{Eqn. 2.10}
\end{align*}

Here, $l_c$ is a critical wire length, $\alpha$ is the thermal diffusivity of the wire, and $\tau_{\text{conv}}$ is a characteristic convective time constant for the wire. The properties used in this calculation are those of chromel wire, and are given as wire density $\rho_w = 8.73$ g/cm$^3$, wire specific heat $c_{p,w} = 447.6$ J/kg-K, and wire diameter $d_w = 0.11$ mm. Using Eqns. 2.8-10 and substituting a Nusselt number for the convective transfer coefficient $h$, the minimum length criterion may be re-expressed as:

\[ l_w \geq 10 \frac{l_c}{l_c} = 10 \sqrt{\frac{d_w^2 k_w}{4N_u k_g}} , \quad \text{Eqn. 2.11} \]

This criterion results in minimum lengths ranging from 9-20 mm for flow conditions of practical interest. As a result, the length of bare thermocouple wire protruding from the support structure is set at 20 mm.
The above simplifications result in the reduction of Eqn. 2.7 to a balance between radiative and convective heat transfer, with the radiative transfer a complex function of the rates of transfer between the various surfaces contained within the pressure chamber. To simplify the analysis, the configuration factor method is used, with the geometry approximated by that shown in Fig. 2.5. It is worth noting that the co-flow “gap” (surface 3) is a simplification of the actual geometry (cf. Fig. 2.1) and models the region between the inner wall of the air duct to the outer wall of the co-flow duct as a flat surface. The radiative energy gain/loss from the bead can therefore be written as the sum of net radiative transfer between the thermocouple bead and its surroundings. The resulting equation, after invoking Kirchoff’s Law to substitute emissivities for absorptivities and using the configuration factor reciprocity relation $A_1 F_{1-2} = A_2 F_{2-1}$, gives the air temperature as:

$$T_g = T_b + \frac{\epsilon_b \sigma d_b}{\text{Nu} k_g} (T_b^4 - \epsilon_1 F_{b-1} T_1^4 - \epsilon_2 F_{b-2} T_2^4 - \epsilon_3 F_{b-3} T_3^4 - \epsilon_\infty F_{b-\infty} T_\infty^4), \quad \text{Eqn. 2.12}$$

where $\sigma$ is the Stefan-Boltzmann constant, $\epsilon$ is the emissivity, the subscripts $g$ and $b$ refer to the gas and bead, numbers 1-3 refer to each surface given in Fig. 2.5, and $\infty$ refers to the remainder of the interior surfaces of the pressure chamber, taken here as the emissivity properties of aluminum. The configuration factors needed for Eqn. 2.12 are taken from Siegel and Howell [67]:

$$F_{b-1} = \frac{1}{2} \left\{ 1 - \frac{1}{\left[ 1 + \left( \frac{d_1}{\frac{1}{2} (z + H)} \right)^2 \right]^{1/2}} \right\}, \quad \text{Eqn. 2.13}$$

$$F_{b-2} = \frac{1}{2} \left\{ \frac{1}{\left[ 1 + \left( \frac{d_1}{\frac{1}{2} (z + H)} \right)^2 \right]^{1/2}} - \frac{1}{\left[ 1 + \left( \frac{d_1}{z^2} \right)^2 \right]^{1/2}} \right\}, \quad \text{Eqn. 2.14}$$
Referring to Eqn. 2.12, it is immediately evident that the chamber temperature \( T_\infty \) as well as the surface temperature of surfaces 1-3 are necessary. While \( T_\infty \) can be reasonably approximated to the fuel-side boundary temperature as the chamber is cooled to limit its temperature rise (cf. Fig. 2.1), the surface temperature of the quartz tubes (surfaces 2 and 3 in Fig. 2.5) would be difficult to accurately quantify. Noticing, however, that the configuration factors for surfaces 1 and 3 for a normal operating position of \( z = 1 \text{ mm} \) are 0.013 and 0.026, respectively, their contributions to the radiation correction are negligible. In addition, as surface 2 is in direct contact with heated air, it can be expected to be of similar temperature, and thus the net contribution to the radiation correction is quite small; less than 5 K for typical ignition temperatures in the present study and reasonable estimates of wall temperature. Due to these factors, the net radiative transfer between surfaces 1-3 and the thermocouple bead can be neglected and Eqn. 2.12 may be simplified to:

\[
T_g = T_b + \frac{\varepsilon_b \sigma d_b}{\text{Nu} k_g} (T_b^4 - \varepsilon_{\infty} F_{b-\infty} T_b^4).
\]

Eqn. 2.17

Equation 2.17 is used to correct for radiation for all experimental data presented in this work, with bead diameter \( d_b = 0.15 \text{ mm} \), \( \text{Nu} \) and \( k_g \) computed from Eqns. 2.5 and 2.6, respectively, and \( \varepsilon_b(T) \) linearly extrapolated from the chromel emissivity data of Sasaki \textit{et al.} [68]. The magnitude of this correction ranges from 25 K to 60 K for the conditions investigated in the present study, with larger corrections corresponding to higher ignition temperatures.
In closing this section, it is worth emphasizing the sensitivity of the temperature measurement to both the emissivity of the thermocouple bead and the Nusselt number. These quantities rely upon significant assumptions regarding the surface condition of the thermocouple bead and the flow around the junction, respectively, and as a result uncertainties in these values have been constrained as much as possible. Nonetheless, some uncertainties remain and are worth stating explicitly given their potential impact on the interpretation of both the present data as well as the data evolved from similar experimental systems. With regards to thermocouple emissivity, Shaddix [65] stated the problem succinctly:

Unfortunately, experimental data on the emissivity of the most common high-temperature thermocouple wires are quite scarce. Compounding this difficulty is the fact that the emissivity of a given metal is strongly dependent on the surface characteristics, including roughness, oxidation layer, and any other coating of the metal, whether intentional or not. [65]

The effect of these uncertainties can be quite large; arbitrarily increasing the emissivity from typical values of $\varepsilon_b = 0.17-0.19$ to $\varepsilon_b = 0.3$ results in temperatures 20-35 K higher than presently stated. While no discernable thermocouple “ageing” - in terms of variability in ignition temperature measurements separated in time by several weeks - has been observed, and appropriately adjusted measurements using thermocouples of varying size have resulted in highly similar ignition temperature measurements, this merely indicates that the overall methodology is reasonably robust and that the thermocouple’s condition is quite stable. As a result, it is very difficult to determine whether the emissivity value used is accurate, and what range of values would constitute “reasonable” degrees of uncertainty. Since any error estimate for emissivity would be purely conjecture, the issue of uncertainty in emissivity is neglected in the temperature
uncertainty estimation in Section 2.8. Nevertheless, it is noteworthy that, in order to match the simulated results for the butanol isomers shown in Chapters 4 and 5, emissivity values of 0.7 or higher would be required. Since such values are more commensurate with surfaces such as alumina, concrete, and fully-oxidized copper, they should be considered entirely unreasonable for an uncoated, clean thermocouple bead, suggesting that the disparities observed in Chapters 4 and 5 cannot be sufficiently explained by errors in the emissivity of the thermocouple bead.

Nusselt number correlations also present a significant problem. While the present study follows the suggestion from Shaddix [65] to use a cylindrical correlation, other authors have followed significantly different methods such as a constant \( Nu = 2 \) assumption [45] - essentially an implicit assumption of spherical geometry - or an average of the spherical and cylindrical predictions [46]. This disparity can have a significant impact on the magnitude of the radiation correction, as will be clearly demonstrated in Section 3.6. To the extent possible, this uncertainty is taken into account in this work (cf. Section 2.8) and is the primary source of systematic uncertainty in ignition temperature measurements. However, it should be understood that the error bars provided for ignition temperatures are based upon estimated uncertainties only within the context of a presumed cylindrical Nusselt number formulation (per Shaddix [65]), and do not consider the effect of varied junction geometry.

The combined effect of uncertainties in both thermocouple emissivity and Nusselt number are potentially significant when considering that the ignition data generated from this experiment is expected to guide model development. Certainly it becomes difficult to interpret the meaning of differences between experimental and numerical data when the
estimated uncertainty in experimental values is exceedingly large. However, it is worth considering that even the Sarathy mechanism [1] - which exhibits the closest agreement with experimental ignition temperatures - is shown in Chapters 4 and 5 to over-predict experimental ignition temperatures by a minimum of 80 K. This suggests that even in the worst-case event that Nusselt number is significantly smaller than anticipated while bead emissivity is simultaneously larger, the resulting increase in the magnitude of the radiation correction would still not fully account for the differences observed between the experiment and the model. As a result, the conclusions of the present study are independent of the details of the radiation correction.

2.8 Experimental uncertainty

The proper estimation of errors in dependent or independent variables is critical to the interpretation of any experimental data. Recognizing that insufficient or inappropriate consideration of errors and error propagation can lead to serious misinterpretations of data, the following sections describe the methodology for estimating the errors associated with parameters of interest reported in this work.

2.8.1 Systematic versus random errors

From the outset, it is important to note that two types of error are important in the interpretation of the present data set. Systematic (or bias) errors result from defects in a parameter model (e.g. Nusselt number) or measuring equipment (e.g. pressure gauges) which cause deviations from the true behavior in a given system. Such errors result in reproducible inaccuracies that tend to impact the entire data set in a largely equivalent manner. Random errors, on the other hand, are fluctuations in measured data based upon
the precision of the measurement device. Such errors are statistical in nature, and can be minimized through averaging multiple observations. These definitions are important to the present analysis because, while the total uncertainty (including both systematic and random errors) is relevant for the comparison of the present data set to other experimental data or numerical predictions, only the random error is applicable when comparing data points within the current data set since all data should be affected essentially equally by systematic errors (if any). Moreover, this random error is particularly relevant to the measured ignition temperatures, where it represents the variability associated with repeated measurements at the same operating conditions. The random error can be estimated by finding the standard error of the mean ($SE_x$):

$$SE_x = \frac{\sigma}{\sqrt{n}},$$  \hspace{1cm} Eqn. 2.18

where $\sigma$ is the standard deviation of the set of measurements and $n$ is the number of measurements at a given condition. Using this estimate, the maximum random error observed for any ignition temperature measurement is 5 K. Therefore, when comparing any two ignition temperatures within the current experimental dataset, the relevant uncertainty should be considered as $\pm 5$ K.

The total uncertainty in each of the four system variables/responses - i.e., pressure, fuel loading, strain rate, and air boundary temperature - is estimated in terms of the uncertainty in the variable’s constituent components, added in quadrature. This simple approach is demonstrated in Ref. [69]. The general form for this relation is:

$$\delta q = \sqrt{\left(\frac{\partial q}{\partial x_1}\delta x_1\right)^2 + \left(\frac{\partial q}{\partial x_2}\delta x_2\right)^2 + \cdots + \left(\frac{\partial q}{\partial x_n}\delta x_n\right)^2},$$  \hspace{1cm} Eqn. 2.19
where $\delta q$ is the uncertainty in a system variable, $\frac{\partial q}{\partial x_n}$ is the partial derivative of the relation for $q$ with respect to the $n^{th}$ independent variable $x_n$, and $\delta x_n$ is the estimated uncertainty in the independent variable $x_n$. Thus, as long as a closed-form, differentiable relationship can be defined between $q$ and $x_n$, the uncertainty in $q$ can be readily obtained. Representative total estimated uncertainties are plotted with experimental ignition temperatures in the main text.

### 2.8.2 Estimated error in pressure

Since chamber pressure is a directly-measured quantity by way of the chamber pressure gauge, the estimated error in pressure is quite simple, and is only a function of the instrument uncertainty and readout resolution. As provided by the manufacturer (Cecomp), the uncertainty in the pressure measurement is $\pm 0.25\%$ of full-scale range, in this case resulting in an uncertainty of $\pm 0.75$ psi. Added in quadrature with a readout resolution of 1 psi, the resulting estimated uncertainty in pressure is $\pm 1.25$ psi, and is included where applicable in the following analyses.

### 2.8.3 Estimated error in fuel loading

The experimental fuel loading is calculated based upon Eqn. 2.20:

$$X_F = \frac{M_F}{M_F + M_N},$$  \hspace{1cm} \text{Eqn. 2.20}

where $X_F$ is the fuel loading, $M_F$ is the molar flow rate of fuel, and $M_N$ is the molar flow rate of nitrogen. The uncertainty in fuel loading based upon Eqn. 2.20 is:

$$\delta X_F = \sqrt{\left(\frac{\partial X_F}{\partial M_F} \delta M_F\right)^2 + \left(\frac{\partial X_F}{\partial M_N} \delta M_N\right)^2},$$  \hspace{1cm} \text{Eqn. 2.21}
where $\delta X_F$, $\delta M_F$, and $\delta M_N$ are the uncertainties in fuel loading, fuel molar flow rate, and nitrogen molar flow rate, respectively. The individual uncertainties $\delta M_F$ and $\delta M_N$ thus need to be defined. The uncertainty in fuel flow rate is related to the accuracy of the syringe pump, and over the flow rates of interest for the present study, the pump has been found to have a maximum deviation of 2% from the expected value based upon average measurements of total fluid flow over extended time periods at various flow rates, measured by a precision digital mass balance. As a result, $\delta M_F$ is estimated as 0.02$M_F$.

The uncertainty in the molar flow rate of nitrogen is related to the uncertainty in the fit line created from experimentally obtained flow rate data during the calibration of the sonic nozzles used to meter the flow rates of gaseous components, as well as the uncertainty associated with readout resolution. The fit line takes the form of Eqn. Eqn. 2.22, with the overall uncertainty given as Eqn. Eqn. 2.23:

$$M_N = mx + b,$$

Eqn. 2.22

$$\delta M_N = \sqrt{\left(\frac{\partial M_N}{\partial m}\delta m\right)^2 + \left(\frac{\partial M_N}{\partial b}\delta b\right)^2 + \left(\frac{\partial M_N}{\partial x}\delta x\right)^2},$$

Eqn. 2.23

The uncertainties in the slope ($\delta m$) and intercept ($\delta b$) of the fit line are taken as the standard error in the fit coefficients as calculated by the Excel function LINEST, while $\delta x$ is the readout error of $\pm 1$ psi. Strictly speaking, both $\delta m$ and $\delta b$ are dependent on the readout error ($\delta x$), however the inclusion of such a dependence would require an alternative error treatment and is not expected to significantly alter the estimated uncertainty in fuel loading. It should also be noted that since the sonic nozzles are calibrated with the same pressure gauges used for experiments, unlike the pressure measurements in Section 2.8.2 only the readout error is relevant to $\delta x$. The resulting
uncertainties in fuel loading ($\delta X_F$) range from ±0.0025 at the lowest fuel loading to ±0.01 at the highest.

2.8.4 Estimated error in global strain rate

The strain rate is calculated from the estimated densities and bulk velocities issuing from both the fuel and oxidizer sides, as given in Eqn. 2.1. The uncertainty in strain rate is thus:

$$\delta k = \sqrt{\left(\frac{\partial k}{\partial V_O} \delta V_O\right)^2 + \left(\frac{\partial k}{\partial V_F} \delta V_F\right)^2 + \left(\frac{\partial k}{\partial \rho_F} \delta \rho_F\right)^2 + \left(\frac{\partial k}{\partial \rho_O} \delta \rho_O\right)^2 + \left(\frac{\partial k}{\partial L} \delta L\right)^2}, \quad \text{Eqn. 2.24}$$

with nomenclature definitions similar to that previously described in Section 2.8.3. Since each of these quantities - with the exception of $L$ - is itself a calculated value based upon a number of uncertain values, each uncertainty is likewise determined through an identical procedure. For the sake of brevity in the following discussion, the subscripts $N$ and $O$ refer to the properties associated with nitrogen and oxygen gases, respectively, and when used in conjunction with the linear fit parameters for sonic nozzles, refer to the values specific to the nitrogen or oxygen nozzle used in the relevant - i.e., fuel or oxidizer side - flow. In addition, it is worth noting that Eqn. 2.24 represents an estimation of the uncertainty in the global strain rate only, and does not include any estimation of the uncertainty associated with the differences between a global estimation and a direct measurement near the stagnation plane. The latter estimate would require knowledge of the measured strain rate near the stagnation plane which, as described in Section 2.3, is not possible for the present experimental system.

The bulk velocity issuing from the fuel side is described by Eqn. 2.25:

$$V_F = \frac{(m_N X_N + b_N) \rho_{ref-N} T_{ref-N}^{2/3} + m_F \rho_{ref-F} T_{ref-F}^{2/3} + m_P \rho_{ref-P} T_{ref-P}^{2/3}}{2D^2}, \quad \text{Eqn. 2.25}$$
where $m_N$ and $b_N$ are the nitrogen nozzle linear fit parameters as described previously, $x_N$ is the pressure gauge readout for the nitrogen nozzle, $\rho_{\text{ref},N}$ is a reference density of nitrogen at a given chamber operating pressure and 300 K, $T_{\text{ref}}$ is 300 K, $T$ is the temperature of the stream in question, $\dot{m}_F$ is the mass flow rate of the fuel issuing from the fuel pump, $R_{sp}$ is the specific gas constant for vaporized fuel, $P$ is the chamber pressure, and $D$ is 19 mm, the inner diameter of the fuel and oxidizer ducts. The resulting estimated uncertainty in fuel-side bulk velocity is therefore:

\begin{align*}
(\delta V_F)^2 &= \left( \frac{\partial v_F}{\partial m_N} \delta m_N \right)^2 + \left( \frac{\partial v_F}{\partial x_N} \delta x_N \right)^2 + \left( \frac{\partial v_F}{\partial b_N} \delta b_N \right)^2 + \left( \frac{\partial v_F}{\partial \rho_{\text{ref},N}} \delta \rho_{\text{ref},N} \right)^2 + \ldots \\
&\quad \ldots + \left( \frac{\partial v_F}{\partial T} \delta T \right)^2 + \left( \frac{\partial v_F}{\partial \dot{m}_F} \delta \dot{m}_F \right)^2 + \left( \frac{\partial v_F}{\partial P} \delta P \right)^2 + \left( \frac{\partial v_F}{\partial D} \delta D \right)^2,
\end{align*}

Eqn. 2.26

Equation 2.26 shows the squares of the uncertainties for the purposes of visual clarity given the overall length of the equations. It should be noted that both $R_{sp}$ and $T_{\text{ref}}$ are constants and therefore have no uncertainty. While the nitrogen reference density is also a constant, the uncertainty in pressure results in an uncertainty in the accuracy of the reference density. Based upon the uncertainty in pressure the uncertainty in reference density for all $\rho_{\text{ref}}$ terms is estimated as $\pm 0.08 \text{ kg/m}^3$. The uncertainty in temperature is variable and calculated based upon the results of Section 2.8.5; however, this uncertainty does not play a significant part in the overall uncertainty in strain rate. In a similar fashion, the bulk velocity of the oxidizer stream, consisting of purely gaseous components, may be described by:

\begin{align*}
V_O &= \frac{(m_N x_N + b_N) T_{\text{ref}}}{\frac{D^2}{4}} + \frac{(m_G x_G + b_O) \rho_{\text{ref},O} T_{\text{ref}}}{\frac{D^2}{4}},
\end{align*}

Eqn. 2.27

Thus, the resulting estimated uncertainty in oxidizer-side bulk velocity is:
\[(\delta V_o)^2 = \left(\frac{\partial V_o}{\partial m_N} \delta m_N \right)^2 + \left(\frac{\partial V_o}{\partial x_N} \delta x_N \right)^2 + \left(\frac{\partial V_o}{\partial b_N} \delta b_N \right)^2 + \left(\frac{\partial V_o}{\partial \rho_{ref,N}} \delta \rho_{ref,N} \right)^2 + \ldots
\]

\[\ldots + \left(\frac{\partial V_o}{\partial m_o} \delta m_o \right)^2 + \left(\frac{\partial V_o}{\partial x_o} \delta x_o \right)^2 + \left(\frac{\partial V_o}{\partial b_o} \delta b_o \right)^2 + \left(\frac{\partial V_o}{\partial \rho_{ref,o}} \delta \rho_{ref,o} \right)^2 + \ldots
\]

\[\ldots + \left(\frac{\partial V_o}{\partial T} \delta T \right)^2 + \left(\frac{\partial V_o}{\partial D} \delta D \right)^2, \tag{Eqn. 2.28}\]

with the sole difference being the presence of an additional set of sonic nozzle fit parameters for the oxygen sonic nozzle.

The remaining uncertainties needed are the uncertainties in fuel- and oxidizer-stream densities:

\[\rho_F = X_F \frac{R_p T}{p} + (1 - X_F) \rho_{ref,F} \frac{T_{ref,F}}{T}, \tag{Eqn. 2.29}\]

\[\delta \rho_F = \sqrt{\left(\frac{\partial \rho_F}{\partial X_F} \delta X_F \right)^2 + \left(\frac{\partial \rho_F}{\partial T} \delta T \right)^2 + \left(\frac{\partial \rho_F}{\partial \rho_{ref,F}} \delta \rho_{ref,F} \right)^2}, \tag{Eqn. 2.30}\]

\[\rho_O = X_O \rho_{ref,O} \frac{T_{ref,O}}{T} + (1 - X_O) \rho_{ref,O} \frac{T_{ref,O}}{T}, \tag{Eqn. 2.31}\]

\[\delta \rho_O = \sqrt{\left(\frac{\partial \rho_O}{\partial X_O} \delta X_O \right)^2 + \left(\frac{\partial \rho_O}{\partial T} \delta T \right)^2 + \left(\frac{\partial \rho_O}{\partial \rho_{ref,O}} \delta \rho_{ref,O} \right)^2 + \left(\frac{\partial \rho_O}{\partial \rho_{ref,N}} \delta \rho_{ref,N} \right)^2}, \tag{Eqn. 2.32}\]

In Eqns. Eqn. 2.31 and Eqn. 2.32, the term \(X_O\) refers to the mole fraction of oxygen in the oxidizer stream, set as 0.21 for all experiments. It should be noted that the dominant term driving uncertainty in strain rate \((k)\) is \(\delta \rho_{ref,N}\) as a direct result of the prevalence of nitrogen in both streams. The resulting uncertainty in \(k\) ranges from \(\pm 7\) to \(12\) s\(^{-1}\) for the range of strain rates used in the present study.

### 2.8.5 Estimated error in boundary temperatures

Two temperatures are important in the above discussion: the fuel and oxidizer boundary temperatures. The former, being a relatively low temperature measurement, is not subject
to appreciable radiative heating, and therefore the error in said measurement may be described simply as a function of the stated accuracy of the thermocouple, or 0.75%. For both measurements, the precision error associated with the readout resolution is sufficiently small to be neglected.

As described in Section 2.7, the gas temperature of the air stream is described by

Eqn. 2.17. The estimated error in the gas temperature is then given by:

\[
(\delta T_g)^2 = \left(\frac{\partial T_g}{\partial T_b} \delta T_b\right)^2 + \left(\frac{\partial T_g}{\partial \varepsilon_b} \delta \varepsilon_b\right)^2 + \left(\frac{\partial T_g}{\partial d} \delta d\right)^2 + \left(\frac{\partial T_g}{\partial \varepsilon_\infty} \delta \varepsilon_\infty\right)^2 + \ldots
\]

\[
\ldots + \left(\frac{\partial T_g}{\partial \Delta T_\infty} \delta \Delta T_\infty\right)^2 + \left(\frac{\partial T_g}{\partial \text{Nu}} \delta \text{Nu}\right)^2 + \left(\frac{\partial T_g}{\partial k_g} \delta k_g\right)^2.
\]

Eqn. 2.33

The error in \(T_b\) and \(T_\infty\) is taken as 0.75% of the measured value per manufacturer’s specifications and the error in bead diameter \(d_b\) is taken as 0.01 mm. Since the value of the gas conductivity \(k_g\) is a calculated value based upon an experimental fit [66], it is difficult to ascertain an appropriate estimate of the error. Thus a highly conservative estimate of 20% of \(k_g\) is used. It should be noted that this choice does not appreciably impact the estimated error in \(T_g\).

As mentioned in Section 2.7, emissivity values for any practical surface are exceedingly difficult to define, and even more so in high-temperature oxidizing environments. The uncertainty in \(\varepsilon_\infty\) can be neglected \textit{a priori} as its effect on the magnitude of the radiation correction is negligible. However, varying the value of \(\varepsilon_b\) will significantly alter the magnitude of the radiation correction. Unfortunately, as described in Section 2.7, there is no accessible methodology for defining either a precise value or bounds on the uncertainty of the bead emissivity. As a result, any estimation of uncertainty would be purely conjecture; this uncertainty is therefore neglected, and it is
merely stated that significant changes in emissivity will result in appreciable, but largely uniform, changes in the magnitude of the radiation correction.

The remaining uncertainty, that of the Nusselt number $\text{Nu}$, is ultimately the most significant factor in the estimation of error in the gas temperature measurement, and is simultaneously quite difficult to define. The Nusselt number is a surrogate for the convective heat transfer coefficient needed to define the energy balance around the thermocouple bead. Since this coefficient cannot be defined directly, the Nusselt number is used instead. However, numerous correlations exist to estimate Nusselt number, and each depends upon the specific geometry of the object in question. For the case of a thermocouple bead, Shaddix [65] reviewed several correlation options, and compared the results for spherical and cylindrical treatments, concluding that a cylindrical treatment was more appropriate for the thermocouple geometry at issue in the present study. However, even within the domain of cylindrical correlations, the relations shown by Shaddix [65] differ by as much as 20% in the low Reynolds number regime. To fully account for this disparity, the estimated error $\delta\text{Nu}$ is taken as double the largest deviation in observed by Shaddix [65], or 40% $\text{Nu}$. The resulting error estimate for the gas temperature based upon the above assumptions is 20-35 K for typical ignition conditions.
Figure 2.1: Diagram of the flow control, heating, and measurement systems for the counterflow ignition apparatus.
Figure 2.2: Comparison of experimentally measured axial velocities to plug- and potential-flow models under unheated, $P = 1$ atm, $k' = 150$ s$^{-1}$ conditions.
Figure 2.3: Ignition turning point validation comparing the results computed from the isomer-specific skeletal mechanisms to those of the detailed Sarathy et al. [1] and Merchant et al. [2] mechanisms. Turning points for (a) n-butanol (b) iso-butanol (c) sec-butanol, and (d) tert-butanol are computed at $X_f=0.15$ for 1 atm, $k'=300 \text{ s}^{-1}$ and 5 atm, $k'=500 \text{ s}^{-1}$. In (b), only the results based on the Sarathy model are shown (cf. Section 2.5.1).
Figure 2.4: Typical thermal mixing zone/ignition kernel structure at the ignition turning point for 1 atm, $k' = 350 \text{ s}^{-1}$, $X_f = 0.15$, and fuel stream temperature of 380 K computed using the skeletal $n$-butanol mechanism derived from Sarathy et al. [1].
Figure 2.5: Simplified diagram of the air duct near the thermocouple bead, used for the determination of configuration factors for the radiation correction.
Chapter 3: Validation of Experimental Facility

3.1 Introduction

As mentioned in Chapter 1, the first goal of the present study is to provide a comprehensive characterization of the newly developed counterflow ignition apparatus, both to ensure reasonable adherence to quasi-one-dimensional assumptions made in the numerical model and to better aid in comparison amongst other similar experimental systems. Several studies have used the counterflow ignition configuration to characterize ignition properties of gaseous and liquid fuels. Fotache et al. [46] developed and used a counterflow ignition experiment to investigate the non-premixed hydrogen-air system for ambient pressures of 0.1-6 atm and characteristic strain rates of $k' = 50-400 \text{ s}^{-1}$, measured locally using Laser Doppler Velocimetry (LDV). The authors experimentally verified three-limit behavior in the hydrogen-air system that had been previously observed in computational works [50,51]. Subsequent investigations by various groups in a non-premixed counterflow configuration studied a wide variety of fuels [45,47,57,70–85], and efforts have been extended to related configurations including premixed counterflow [86,87] and liquid-pool stagnation flows [30,88–90]. Of note, however, is that large variations in the level of description of the experimental apparatus and experimental procedure exist amongst the various systems and researchers. As an example of good practice, Fotache et al. [46] provided a quite detailed validation of their experimental system and procedure, including velocity and temperature gradient information along with details of their radiation correction methodology for thermocouple measurements.
Reliance upon assumptions about flow quality, and presuming a priori quasi-one-dimensionality, can lead to crucial deviations from expected system behavior and thus it is important for any experimental system to provide a detailed characterization to demonstrate the underlying flow quality or boundary conditions. Without providing such characterization results, the application of counterflow ignition data to model development and validation is significantly hampered.

To this end, the following sections describe a detailed characterization at atmospheric and elevated pressures in an effort to thoroughly describe the current experimental apparatus’ behavior and the extent to which it adheres to quasi-one-dimensional assumptions.

3.2 Velocity

While a global estimate is used to describe strain rate in the current work, the counterflow ignition experiment has been rigorously examined using PIV to observe the nature of the flow field as functions of strain rate, pressure, and - to a limited extent - temperature variations. The counterflow velocity field is obtained by cross-correlating time-delayed image pairs obtained from a Dantec Dynamics digital PIV system. The interrogation sub-region size was set at $32 \times 32$ pixels with 50 percent overlap. Pulse delays were set to follow the “¼ rule” such that the average inter-frame particle movement near the region of interest did not exceed one quarter of the sub-region size. Particle seeding is accomplished using an Oxford Lasers 10Bar MicroSeeder, which is capable of operating at elevated pressures and provides 50 cSt silicone oil droplets with sizes ranging from 0.5-5 µm. It is worth noting that, since the boiling point of the silicone oil is ~570 K, it is
not possible to use the current setup to obtain velocity fields at typical operating temperatures. While solid particles could overcome this problem, this is not feasible in the current setup as described in Chapter 2. Despite this limitation, the salient issues of quasi-one-dimensionality, velocity boundary conditions, and the impact of pressure variations may still be explored at temperatures below the seed fluid boiling point.

To begin to address the issue of quasi-one-dimensionality in the flow field, it is most informative to observe the axial velocities measured across the diameter of the top and bottom ducts. Figure 3.1 shows the axial velocity at each duct exit as a function of radial distance under 1 and 3 atm with a pressure-weighted global strain $k' = 150 \, \text{s}^{-1}$. At both atmospheric and elevated pressures, a large and nearly flat core region representing approximately 60% of the tube diameter exists near the experimental centerline. It is also apparent from Fig. 3.1 that the fuel and oxidizer velocity profiles are reasonably well balanced at varying pressures, as the extent of the core regions for both streams is quite comparable. One feature of note on the oxidizer side is the presence of a small velocity deficit near the central axis. This deficit is due to the internal heater in the oxidizer flow, which terminates just upstream of the flow-straightening mesh. However, at elevated temperatures, as demonstrated in Fig. 3.2, the effect of heat addition along the centerline by the internal heater cancels the effect of this velocity deficit, and results in an improved - and rather flatter, albeit slightly smaller - core region.

In addition to radial profiles, the axial velocity along the experimental centerline is valuable not only for its ability to determine correspondence to a given flow model (cf. Fig. 2.2), but it also facilitates a validation of the pressure-weighted strain rate concept. Figure 3.3 shows the results at unheated conditions, for pressures of 1 and 3 atm and $k' =$
150 s$^{-1}$. While the absolute magnitude of the 1 and 3 atm axial velocity profiles are quite different, when the 3 atm results are weighted to account for the density difference by a method similar to Eqn. 2.2, the spatial structure of the pressure-weighted velocity profile corresponds well to the measurements at 1 atm. Therefore, Fig. 3.3 demonstrates that comparison across pressures at a given pressure-weighted strain rate is in fact valid.

### 3.3 Temperature

It is also critical to the fidelity of the ignition data to ensure quasi-one-dimensional behavior with respect to temperature in addition to the velocity validation demonstrated in the previous section. This may be accomplished by observing the temperature field within the test section as a function of radial and axial position. Figure 3.4 shows the radial profiles of temperature at the oxidizer duct exit (denoted as $z = 20$ mm) - not corrected for radiative losses - for a pressure-weighted strain rate $k' = 300$ s$^{-1}$ at 1 and 3 atm chamber pressures. At both 1 and 3 atm, the symmetry of the temperature profile is maintained, as is the overall shape and size of the radial profile at several axial locations. In addition, a core region with only limited temperature gradient in the radial direction can be observed in the range of ±5 mm from the centerline for each pressure condition.

Figure 3.5 further demonstrates the temperature profiles along the centerline by keeping heater power constant while varying the stagnation plane location through the changes in oxidizer duct mass flow rate, for a pressure-weighted strain rate $k' = 300$ s$^{-1}$ at chamber pressures of 1 and 3 atm. Two critical features of the counterflow arrangement are validated in Fig. 3.5. First, the three 1 atm cases clearly show that the location of the stagnation plane does not impact the overall structure of the thermal mixing zone. This
feature is important as it clearly demonstrates that the mixing zone is unaffected by changes in the stagnation plane location so long as it is not excessively close to either boundary. Second, this structure is maintained when the chamber pressure is raised to 3 atm, with the width and temperature gradient being nearly identical to that of 1 atm, as is more clearly demonstrated with position-shifted temperature profiles in the inset to Fig. 3.5 by collating the thermal mixing zone. Hence, the inset of Fig. 3.5 shows that the thermal structure similarity of the test section is maintained at constant pressure-weighted strain rate.

An additional important observation derived from Fig. 3.5 is a slight axial temperature gradient at the oxidizer exit, which increases for elevated pressures. This observation is important due to the fact that the temperature associated with ignition is characterized by the oxidizer boundary temperature, while ignition occurs in the thermal boundary layer. As such, if the distance between the mixing zone and oxidizer boundary changes, the temperature gradient implies that the relationship between the temperature at the “leading edge” of the mixing zone and the boundary temperature will also change. This can lead to small, but noticeable (on the order of 10-15 K for stagnation plane variations of the order seen in Fig. 3.5), differences in measured ignition temperatures. As a result, for all experiments the location of the onset of ignition (observed by the high-speed camera) is maintained at the center of the test region ± 2 mm to ensure that the relationship between ignition temperature and oxidizer boundary temperature is as consistent as possible.
3.4 Fuel concentration

To fully characterize the boundary conditions of the counterflow system, the concentrations of reactants must be known. For liquid fuels such as butanol, the fuel must first be completely vaporized and mixed with its nitrogen diluent, and then must remain vaporized as it travels to the combustion chamber. This necessitates elevated temperatures along the entirety of the fuel line in order to avoid condensation; however, excessive temperature may foster premature fuel breakdown such that the composition on the fuel side consists of diluted fuel and fuel fragments. Thus, a balance must be struck between the juxtaposed needs of ensuring complete vaporization and preventing fuel decomposition in order to establish an accurate description of the fuel stream concentration boundary condition.

To ensure that no condensation or decomposition occurs at local cold or hot spots, a gas chromatograph/mass spectrometer (GC/MS), Shimadzu GC-QP2010S, is employed to allow for simultaneous identification and quantification of species present within a gas sample. Typical n-butanol GC/MS results are shown in Fig. 3.6 for samples retrieved from the fuel supply line just prior to entering the combustion chamber. A single n-butanol peak is observed, with nitrogen eluting prior to the detector start time. No secondary peaks are observed within the measured baseline, as demonstrated through magnification of the baseline in the left inset to Fig. 3.6. The lack of additional peaks prior to n-butanol indicates that no measurable fuel decomposition occurs within the fuel stream prior to the combustion chamber. The n-butanol isomer is chosen for this analysis as it represents a “worst-case” in terms of condensation, exhibiting the lowest vapor pressures amongst the four isomers. Since no condensation was observed for the n-
butanol concentration validation, the fuel line settings can be presumed adequate for all butanol isomers.

In addition to demonstrating adequacy with respect to fuel breakdown, it is also necessary to show that the concentration matches the expected value based upon the flow rate of the fuel pump. This can be readily evaluated via the \( n \)-butanol peak areas. The right inset of Fig. 3.6 shows peak areas from successive samples of \( n \)-butanol/nitrogen from the fuel stream. As is visually apparent, such runs are highly consistent in terms retention time, peak shape, and total area. Using a pooled standard deviation of samples taken from multiple sample bottles, the resulting standard deviation in peak area is calculated as 1.57% of the mean, indicating a high degree of repeatability across all samples, with the mean sample concentration falling within 11% of expected values based on flow settings. Given that typically-quoted values of estimated uncertainty lie between 7-15% for similar GC/MS analyses [91–93], this level of matching between expected and measured fuel loading, combined with the degree of observed repeatability in ignition results, suggests that the fuel mole fraction settings are in fact representative of the real boundary conditions.

3.5 Ignition location

The preceding discussions of velocity, temperature, and concentration validations have focused on understanding the steady-state behavior of the counterflow ignition apparatus, and ensuring that the system behaves - to within a reasonable approximation - quasi-one-dimensionally. However, ignition is inherently a transient process; the fidelity of any experimental data hinges on the assumption that ignition itself behaves in a quasi-one-
dimensional manner. This does not happen automatically. Even for a flow field with no obvious defects in boundary conditions, ignition may still occur at unexpected locations for any of a variety of reasons, including insufficient or uneven shroud flow, local velocity imbalances, and small (almost imperceptible via flame observation or PIV measurements) duct misalignments.

Figure 3.7 demonstrates an out-of-bounds ignition event for $k' = 350 \text{ s}^{-1}$, $n$-butanol mole fraction in the fuel stream $X_f = 0.15$, fuel stream temperature of 380 K, and $P = 4 \text{ atm}$. At $t = 0 \text{ ms}$, a flame becomes just visible in the top-left corner of the frame, and proceeds to propagate along the mixing layer between the air and fuel streams until it reaches a nearly steady-state form $\sim 23 \text{ ms}$ later. It is readily apparent from this progression that the onset of ignition occurs far away from the well-characterized core-region, at a location where the relationship between the oxidizer boundary conditions and the ignition kernel conditions is unclear. In addition, this process occurs quickly enough that it is not possible to observe in the absence of high-speed imaging. Thus, without a method of determining ignition location, it is not possible to ascertain whether ignition has occurred prematurely due to an ignitable state being reached in the outer regions of the flow field before an ignitable state was reached within the core region. This can result in several problems when collecting ignition data, including an underestimation of ignition temperatures or an inability to repeat previously collected datasets. It is important to note that this problem is most critical when attempting to collect ignition data at elevated pressures, and is a direct reflection of the fact that buoyancy plays a significant role in the ignition location/stagnation plane location due to the temperature gradients inherently involved in this type of experiment. This becomes immediately
apparent when one calculates the Richardson number, a dimensionless comparison between potential and kinetic energy:

\[ Ri = \frac{gh}{u^2} \]  
Eqn. 3.1

where \( g \) is the acceleration due to gravity, \( h \) is a characteristic vertical length taken in this case as the distance between the stagnation plane and the oxidizer duct exit that is \( \sim 10 \) mm here, and \( u \) is a characteristic velocity, taken as the bulk velocity. For the conditions in Figs. 3.4 and 3.5, the Richardson number is calculated on the order of 0.02 at 1 atm, and 0.2 at 3 atm, showing an order of magnitude difference between 1 and 3 atm. The largest value stands at 0.37 for the highest pressures tested in this dissertation (4 atm). Importantly, the Richardson number at elevated pressures indicates that natural convection is becoming non-negligible at these conditions. One of the effects of this increase is that the “wings” of the stagnation plane move closer to the co-flow tube wall, resulting in an increased likelihood of hot surface ignition, well away from the axial centerline and the thermal mixing layer. It is for this reason that the upper limit for ignition data derived from the current system is set at 4 atm; within this pressure limit ignition has been found to reliably occur within the core region. In addition, for elevated pressures the location of the stagnation plane - and thus the ignition location - will tend towards the oxidizer duct in the absence of an increased oxidizer mass flow. This is important due to the fact that - as was observed in Section 3.3 - a slight axial temperature gradient exist at the oxidizer exit. If the ignition location varies in the axial direction, the relationship between the boundary oxidizer temperature and the temperature in the thermal mixing layer will also vary, leading to small but noticeable variability in measured ignition temperatures. Thus, for the sake of consistency the ignition location is
intentionally located at the middle of the test section for all data contained in this dissertation.

Typical ignition sequences for pressures of 1 and 3 atm are shown in Fig. 3.8. In contrast to Fig. 3.7, ignition in Fig. 3.8 occurs along the centerline of the experiment, well within the core region and centered between the fuel and air boundaries. Once initiated at $t = 0$ ms, the flame propagates outwards in a largely symmetrical manner and reaches its steady-state form in approximately 9 ms. The consistent ignition location instills an additional degree of confidence for the reported datasets.

### 3.6 Comparisons with previous ignition data

For the purposes of providing a comparison between the results of the current experimental system and those derived from other similar systems, a comparison of ethylene ignition temperatures at atmospheric pressure, fuel loading $X_f = 0.15$, and fuel stream temperature of 300 K is provided in Fig. 3.9 based on the data of Humer et al. [45]. This dataset is chosen as a basis for comparison since it is directly comparable due to the authors’ identical global strain rate definition. To provide a more complete comparison, and to demonstrate the effect of differing radiation correction models, two corrected ignition temperature results are presented. The first represents the radiation correction used for all subsequent data derived from this system, which is described in detail in Section 2.7. The second correction method is similar to the procedure of Humer et al. [45]; the salient feature of which is the assumption of a constant Nusselt number about the thermocouple bead $\text{Nu} = 2$. As is readily observed, for similar radiation correction procedures the present data closely follows the trend observed by Humer et al.
and also compares favorably in terms of ignition temperature values, falling 29-36 K below the values reported by Humer et al. [45]. While the source of the discrepancy between the two Nu = 2 datasets is not known, one possible cause is differing thermocouple designs and support structure, as is described in Section 2.7. When a variable Nusselt number formulation based on the bulk velocity is used, the magnitude of the radiation correction is larger and the resulting ignition temperature results are commensurately higher. Figure 3.9 clearly demonstrates the impact of varied radiation correction on the derived ignition temperature data, and serves to underline the necessity of describing the radiation correction methodology in detail. Such a detailed description for the present experiments is provided in Section 2.7.

In addition to the comparison shown in Fig. 3.9, it is informative to compare hydrogen ignition results from the present study to those obtained by Fotache et al. [46]. While a direct comparison between the data sets would not be readily applicable given the differences in the operating conditions (X_f = 0.15, fuel boundary temperature of 380 K, and globally-defined k'_glob = 350 s^{-1} in the present study, versus X_f = 0.2, fuel boundary temperature of 300 K, and locally-defined k'_LDV = 225 s^{-1} in Fotache et al. [46]), the ignition temperature in general is not a strong function of strain rate for the conditions investigated herein - as will be shown in Chapters 4 and 5 - and hydrogen’s ignition temperatures specifically are relatively insensitive to fuel loading above X_f = 0.15 as shown in previous work by Fotache et al. [94]. With this in mind, the comparison in Fig. 3.10 demonstrates that the ignition temperatures in the present study fall somewhat below those obtained by Fotache et al. [46] whereas, in the absence of any other factors, one would expect to observe slightly higher ignition temperatures based upon the lower fuel
loading and higher strain rate, despite the slightly higher fuel boundary temperature. The disparity between the sets of results appears to be the result of differing magnitudes of the radiation correction. In previous work, Fotache et al. [46] demonstrated a comparison of measured temperature versus radiation-corrected temperature as a function of thermocouple location, showing a difference of 42 K at the oxidizer boundary for $P = 2$ atm, $X_f = 0.2$, and $k_{LDV} = 152 \text{ s}^{-1}$. For similar temperature and flow conditions, the radiation correction in the present study is only 16 K. Under the assumption that this disparity in radiation correction is roughly consistent across the operating range of Fig. 3.10, the raw thermocouple results from the present study are uniformly shifted to coincide with the radiation correction magnitude of 42 K shown in Fotache et al. [46]. The resulting data corresponds much more closely to the data of Fotache et al. [46], suggesting that the disparity between the results can be accounted for by the radiation correction. Given the complexities associated with the calculation of the radiation correction, the present results and those of Fotache et al. [46], as compared in Fig. 3.10, are deemed to match reasonably well.
3.7 Figures

Figure 3.1: Axial velocity as a function of radial distance from the experimental centerline at $k' = 150 \text{ s}^{-1}$, 1 and 3 atm, measured at 1 mm axial distances from air and fuel duct exits. Results are obtained for room temperature flows.
Figure 3.2: Comparison between air duct axial velocity profiles across the air duct radius for unheated (air boundary temperature $T_O = 298$ K) and slightly heated ($T_O = 538$ K) cases at 1 atm using identical mass flow rates to those used in Fig. 3.1.
Figure 3.3: Axial velocity profiles (raw and pressure-weighted) along the experimental centerline for $P = 1, 3$ atm, $k^* = 150$ s$^{-1}$. 
Figure 3.4: Radial profiles of uncorrected temperature at varying axial locations for $k' = 300 \text{ s}^{-1}$, $P = 1$ and 3 atm, and a centrally-located stagnation plane. Open symbols represent 3 atm chamber pressure, while filled symbols represent 1 atm pressure. The oxidizer duct exit is located at $z=20 \text{ mm}$. 
Figure 3.5: Axial profiles of uncorrected temperature at $P = 1$ and 3 atm, $k' = 300 \, \text{s}^{-1}$, and constant heater power. Various stagnation plane locations corresponding to varied oxidizer-side mass flow rates are shown for 1 atm. Inset: position-shifted temperature profiles demonstrate the similarity in the axial profile of temperature for a constant pressure-weighted strain rate.
Figure 3.6: GC/MS results for $X_f = 0.15$ at 1 atm. Main graph: typical peak for $n$-butanol. Peak area shows agreement within 11\% of expected peak area. Left inset: expanded y-axis showing a lack of additional peaks, and hence indicating no fuel breakdown. Right inset: representative measurements from successive sampling, demonstrating repeatability of flow system and sampling procedure.
Figure 3.7: Example of an out-of-bounds ignition event at 4 atm, $k'=350$ s$^{-1}$, $X_f = 0.15$ fuel loading, and fuel stream temperature of 380 K. Arrow indicates the location where the flame enters frame (not readily visible at $t = 0.0$ ms).
Figure 3.8: High-speed imagery of the ignition event using \( n \)-butanol at \( k' = 350 \text{ s}^{-1} \), \( X_f = 0.15 \) fuel loading, and fuel stream temperature of 380 K for 1 atm (left) and 3 atm (right) chamber pressures. The slight asymmetry observed in the third and fourth frames of the 3 atm history are the result of slightly off-centerline ignition, both left-to-right and front-to-back.
Figure 3.9: Comparison between the ethylene ignition results from Humer et al. [45] and the present study. Ignition temperatures from the present study are given using the radiation correction method presented in Chapter 2, as well as using the constant Nu = 2 assumption in keeping with the methodology of Humer et al. [45]. Error bars represent estimates of total uncertainty. Experimental conditions: P = 1 atm, fuel loading X_f = 0.15, and fuel stream temperature of 300 K.
Figure 3.10: Comparison between the hydrogen ignition results from Fotache et al. [46] and the present study. Ignition temperatures from the present study are given using the radiation correction method presented in the Chapter 2, as well as shifted values from the raw thermocouple data with the total radiation correction corresponding to the 2 atm correction, i.e. 42 K, of Fotache et al. [46]. Error bars represent estimates of total uncertainty. Experimental conditions for the present study: P = 1-4 atm, fuel loading X_f = 0.15, pressure-weighted strain rate k' = 350 s^{-1}, and fuel stream temperature of 380 K.
Chapter 4: Boundary Condition and Pressure Effects on Non-premixed Ignition of $n$-Butanol in Counterflow

4.1 Introduction

As described in Chapter 1, the butanol isomers have received significant research attention in recent years, and numerous fundamental studies have been conducted using a variety of experimental systems (e.g. [1,2,16–29]). Despite the research attention butanol isomers have garnered, there is relatively little data exploring limit phenomena for these fuels. In fact, to the authors’ knowledge, the only available diffusive ignition data comes from the stagnation-pool study of Liu et al. [30] for $n$- and iso-butanol, while flame extinction data are limited to the $n$-butanol studies of Veloo et al. [31] and Hashimoto et al. [32], and the $n$-, iso-, and sec-butanol study of Mitsingas and Kyritsis [19]. As such, this chapter explores the impact of ambient pressure, strain rate, and fuel loading on counterflow ignition temperatures of $n$-butanol in detail. The experimental results are simulated using skeletal mechanisms developed from comprehensive butanol models (SN and MN mechanisms) available in the literature, and used to validate and assess the performance of these chemical kinetic models for prediction of ignition in a convective-diffusive environment.

4.2 Effects of aerodynamic strain rate

Figure 4.1 demonstrates the impact of varied strain rate on the experimentally-derived ignition temperature of $n$-butanol, as well as the results of the numerical simulations using SN and MN skeletal mechanisms (cf. Chapter 2) for the same imposed conditions.
For 1 and 3 atm ambient pressures, $X_f = 0.15$, fuel stream temperature of 380 K, and $k' = 200-400 \text{ s}^{-1}$, the ignition temperature increases monotonically by ~20 K, at essentially the same rate regardless of the ambient pressure. However, the increase in pressure does result in a downward shift in ignition temperature by approximately 100 K. Similar strain rate effects have been observed previously by Fotache et al. [57,70] for short-chain alkanes and is attributable to the thinning of the ignition kernel width and commensurate reduction in characteristic residence times associated with increasing strain rate, resulting in increased convective/diffusive losses of heat and radicals. Turning to the numerical results, the SN and MN mechanisms produce nearly identical trends, slightly over-predicting the experimental rate-of-change of ignition temperature with increasing strain rate. It is worth noting that a similar over-prediction of the effect of strain rate - namely, uniformly higher predicted ignition temperatures at 1 atm and for pressure-weighted strain rates of 250-450 s$^{-1}$ at 3 atm - was observed by Liu et al. [30] using a previous version of the Sarathy mechanism [18] in their liquid-pool stagnation study for $n$-butanol, where strain rate was defined locally via LDV measurements. Even with different experimental configurations, this consistent over-prediction despite varied strain rate definitions suggests that the discrepancy is unlikely to be due to how the strain rate is characterized. It is further noted that the primary discrepancy between the experimental and numerical results is an upward shift of 80-100 K for the Sarathy mechanism and 130-160 K for the Merchant mechanism. In absolute terms this deviation of ~7-14% is comparable to the effect of changing the fuel loading from $X_f = 0.05$ to 0.25 (cf. Section 4.2) or ambient pressure from 1 to 4 atm (cf. Section 4.3). Thus, this degree of
discrepancy is consistent across all conditions investigated and should be considered significant within the context of the experimental results.

4.3 Effects of fuel loading

Figure 4.2 demonstrates the effects of varied fuel loading for $X_f = 0.1-0.25$ for 1 atm and $X_f = 0.05-0.2$ for 3 atm, by keeping $k'$ constant at 350 s$^{-1}$ and fuel stream temperature fixed at 380 K. As is most clear from the 3 atm results, at low fuel concentrations the ignition temperature is significantly affected by small changes in fuel concentration, while at higher concentrations the ignition temperature becomes progressively less sensitive to increases in fuel concentration at the fuel boundary. Because of constant $k'$, the characteristic mixing zone thickness remains similar when varying $X_f$. As fuel loading increases, the effective fuel flux to the ignition kernel increases, resulting in lower ignition temperatures. In addition, the ignition temperature begins to plateau as fuel loading surpasses $X_f = 0.2-0.25$, showing that the effective fuel flux becomes progressively less limiting to ignition. The observed “plateau” is similar to the behavior observed by Fotache et al. [57,70] for C$_1$-C$_4$ alkanes and Liu et al. [47] for C$_3$-C$_{12}$ alkanes. Furthermore, as is the case for strain rate variations, both the SN and MN mechanisms capture the experimentally observed trend with increasing fuel concentration, but the simulated results are uniformly shifted upward by ~100 K for the SN mechanism, and ~140-160 K for the MN mechanism.
4.4 Effects of pressure

The impact of elevated pressure in the range of 1-4 atm is shown in Fig. 4.3 for $X_f = 0.15$, fuel stream temperature of 380 K, and $k' = 350$ s$^{-1}$. As pressure is increased at constant fuel loading and pressure-weighted strain rate, ignition temperature monotonically decreases, dropping by ~120 K over the pressure range. This indicates enhanced reactivity with increasing pressure. While the mechanism predictions are shifted upward to a similar extent as seen in Figs. 4.1 and 4.2, the ignition temperature trend is largely captured by both mechanisms, with the MN mechanism slightly over-predicting the pressure sensitivity.

To begin to explore the important chemistry and transport controlling $n$-butanol’s pressure behavior, sensitivity analyses are conducted for reaction rates (by perturbing pre-exponential factors, $A_i$’s) and binary diffusion coefficients (by perturbing the zeroth-order coefficients of the polynomial fits for $D_{jk}$’s) defined as $S_{A_i} = \frac{\partial \ln T_{ig}}{\partial \ln A_i}$ and $S_{D_{jk}} = \frac{\partial \ln T_{ig}}{\partial \ln D_{jk}}$, respectively. As such, sensitivity coefficients with positive signs suggest that ignition temperature increases with an increase in reaction/diffusion rates, while a negative result suggests a decrease in $T_{ig}$ (i.e., promoting ignition). Results of such an analysis are shown in Fig. 4.4 for the ten reactions and diffusion pairs of greatest magnitude at $k' = 350$ s$^{-1}$, $X_f = 0.15$, and pressures of 1 and 4 atm. The results from the SN mechanism are shown in Figs. 4.4 (a)-(c), while those obtained utilizing the MN mechanism are demonstrated in Figs. 4.4 (d)-(f). It is seen from Fig. 4.4 that both mechanisms yield highly similar sensitivity results. For the purposes of clarity in exploring the ignition temperature’s pressure-dependency, the following discussion will focus on the results from the SN mechanism except where explicitly noted. A discussion
of the differences between the SN and MN mechanisms for non-premixed ignition follows in Section 4.5.

A general observation immediately apparent upon inspection of Fig. 4.4 is the dominant effect of transport properties on the ignition temperature. Comparing the axes of Figs. 4.4 (a) and (b)/(c), it is clear that the nitrogen-fuel diffusivity exhibits sensitivities almost two orders of magnitude larger than that of the most sensitive chain branching reactions in Fig. 4.4 (b) or (c). As has been observed previously in similar systems [47,89], the non-premixed structure of the mixing zone results in large sensitivities of the n-butanol-related binary diffusivities due to the necessity for fuel to diffuse across the stagnation plane to the ignition kernel. Thus, an enhancement of the binary diffusion rates of fuel with nitrogen and oxygen will tend to promote ignition. In addition to the intuitive importance of fuel transport, the binary diffusion rates of several intermediate products exhibit equal or greater ignition sensitivities compared to the most sensitive reaction rates. As the peak mole fractions of these intermediates are offset towards the fuel side from the peak concentrations of the O, OH, and H radicals, the ability for intermediates to diffuse towards the ignition kernel plays an important role in the diffusive ignition systems.

Also of interest in Fig. 4.4 (a) is the significant change in the sensitivity of hydrogen peroxide transport at elevated pressure. Whereas at atmospheric conditions ignition is minimally affected by its diffusion rates, at 4 atm ignition temperature is predicted to be three times more sensitive to nitrogen-hydrogen peroxide diffusion rates than the rate of chain branching reactions. This difference is attributed to the significant changes in the fuel chemistry over this pressure range. While the chain-branching reaction R4.1 exhibits
the largest negative sensitivity at atmospheric pressure (cf. Fig. 4.4 (c)), ignition becomes primarily sensitive to hydrogen peroxide scission (R4.2) at 4 atm, as shown in Fig. 4.4 (b).

\[
\begin{align*}
\text{H + O}_2 & \rightleftharpoons \text{O + OH} & \text{R4.1} \\
\text{H}_2\text{O}_2(+M) & \rightleftharpoons \text{2OH}(+M) & \text{R4.2}
\end{align*}
\]

This transition in chain branching mechanism mirrors that of the hydrogen ignition limits [46], where the system transitions between the second limit (with chain branching dominated by R4.1) and the third limit (typified by reactions involving hydroperoxyl and hydrogen peroxide, e.g., R4.2) at pressures of 3-4 atm. Since R4.2 is a high activation energy reaction, and the peak hydrogen peroxide mole fraction is shifted towards the cooler fuel side of the ignition kernel (cf. Fig. 4.5), enhanced diffusion of hydrogen peroxide would promote its losses to a low-temperature region where this reaction would not be favored and thus inhibit ignition (positive sensitivity).

Further inspection of Fig. 4.4 highlights several other interesting features within the n-butanol chemistry. First, when sorted by the sensitivity magnitude at 4 atm (Fig. 4.4 (b)) it is apparent that destruction of the parent fuel by hydroperoxyl plays an appreciably more prominent role at elevated pressure than atmospheric pressure. A flux analysis comparison between these two conditions reveals that the reaction R4.3:

\[
\text{nC}_4\text{H}_9\text{OH + HO}_2 \rightleftharpoons \alpha\text{C}_4\text{H}_8\text{OH + H}_2\text{O}_2
\]

accounts for ~10.4% of fuel consumption at 4 atm, and only 3.6% at 1 atm. Similar behavior is observed from the MN mechanism, albeit for H-abstraction from the β-site (cf. Fig. 4.4 (e)). In addition, taken together R4.2 and R4.3 are chain-branching and grow the radical pool at 4 atm. Under atmospheric conditions R4.2 is relatively inactive and hydrogen peroxide serves primarily as a radical sink.
Second, when sorted by the sensitivity magnitude at 1 atm (Fig. 4.4 (c)), several of the more sensitive reactions involve the formyl radical:

\[ \text{C}_2\text{H}_4 + \text{O} \leftrightarrow \text{CH}_3 + \text{HCO} \quad \text{R4.4} \]

\[ \text{HCO} + \text{O}_2 \leftrightarrow \text{CO} + \text{HO}_2 \quad \text{R4.5} \]

\[ \text{HCO} + \text{M} \leftrightarrow \text{H} + \text{CO} + \text{M}, \quad \text{R4.6} \]

which are minimally important at 4 atm. Again, similar results are obtained from the MN mechanism, with the exception of R4.4, which does not appear in the present sensitivity analysis shown in Fig. 4.4 (f).

The underlying causes of both of the above features are evident in Fig. 4.5, which compares the spatial profiles of important radical species and hydrogen peroxide at 1 and 4 atm corresponding to the open circles in the SN mechanism results in Fig. 4.3 (T_{ig} = 1310 and 1173 K, respectively). While the peak mole fractions of H, O, OH, and formyl radicals are lower at 4 atm than 1 atm by an order of magnitude or more, hydroperoxyl mole fractions remain relatively constant, and hydrogen peroxide mole fractions increase with pressure. As a result, the relative importance of reactions R4.2 and R4.3 is enhanced at elevated pressure. Conversely, appreciably less formyl radical is present in the ignition kernel at 4 atm, and path flux analysis reveals that additional carbon monoxide formation pathways involving the ethynyloxy and vinyloxy radicals become important at elevated pressures, thus reducing the importance of formyl to the reduction of fuel intermediates to carbon monoxide.
4.5 *Sources of combustion model disagreement*

Observing Figs. 4.1-4.3, two obvious trends emerge. First, both the SN and MN mechanisms over-predict the experimental data to an appreciable extent. Second, while each mechanism predicts similar trends, the MN mechanism uniformly predicts higher ignition temperatures by ~50-80 K. This raises two corresponding questions: what is the source of the discrepancies between the models and experimental data, and what is responsible for the disparity between the two models? As such, the following discussion attempts to address both of the aforementioned questions.

Recalling the sensitivity results of Fig. 4.4, a handful of reactions and diffusion pairs exhibit large sensitivities, suggesting they may play a predominant role in determining the ignition turning point for a given mechanism. Regarding the transport properties, it is noted that the two mechanisms employ similar databases. The effect on the ignition turning point of manually changing important transport parameters of \( n\)-butanol, \( \text{C}_2\text{H}_4 \), and \( \text{C}_2\text{H}_3\text{OH} \) (selected based on the sensitivity results) in the Merchant model to their corresponding values in the Sarathy model is first examined. For the conditions tested, modification of these transport properties cannot account for the ignition temperature difference predicted by the two mechanisms, with \( n\)-butanol leading to a ~5 K decrease, \( \text{C}_2\text{H}_4 \) further reducing ignition temperature by ~2 K, and \( \text{C}_2\text{H}_3\text{OH} \) increasing the turning point temperature by ~1 K. Hence, the disparity between the two mechanisms cannot be attributed to differences in the transport parameters for key diffusion pairs. Moreover, as will be shown in more detail in Section 5.4, even when the diffusivity of the fuel species is more than doubled, the simulated results still predict appreciably higher ignition temperatures than are seen experimentally. Considering that for stable, non-polar species
typical errors in transport property predictions are 5-10% [95], errors of such magnitude for mildly-polar butanol isomers are unreasonably large. As a result, errors in the transport model are unable to account for the large disparities observed either between models or between simulated and experimental results, suggesting that the observed disparities must result from the kinetic mechanism.

As shown in Fig. 2.3, while the ignition temperatures predicted by the Merchant and Sarathy mechanisms differ by 62 K at 1 atm and 43 K at 5 atm, for each pressure their peak H-radical mole fractions at the respective turning points are of similar size. In fact, the atmospheric ignition kernel structures in terms of important radicals (and hydrogen peroxide) are remarkably similar when the structure at the respective ignition turning points are compared, with peak O, OH, H, and HO₂ mole fraction predictions within a factor of two of each other. Although each mechanism predicts an ignition kernel with a roughly equivalent radical pool size, the MN mechanism reaches this critical size more slowly (and hence exhibits higher ignition temperature) relative to the SN mechanism. The likely cause of this behavior is demonstrated in Fig. 4.6 for P = 1 atm, \( k' = 350 \text{ s}^{-1} \), \( X_f = 0.15 \), and fuel stream temperature of 380 K through a path flux analysis for the destruction of \( n \)-butanol. After an initial H-abstraction reaction leading to hydroxybutyl radicals, the SN mechanism (Fig. 4.6 (a)) predicts further reactions proceeding primarily through unimolecular decomposition pathways. In contrast, the MN mechanism (Fig. 4.6 (b)) predicts that nearly half of the hydroxybutyl radicals are consumed through H-abstraction reactions to form enols or butyraldehyde. These intermediates are themselves consumed through various H-abstraction pathways, forming additional products that are primarily consumed in the same way. As a result, significantly more O, OH, and H
consumption is involved in fuel breakdown in the MN mechanism relative to the SN mechanism, and likely accounts for the slower radical pool growth and thus the overall higher predicted ignition temperatures.

Similarly, it is possible that the growth rate of the radical pool is also responsible for the disparity between experimental and numerical results. If overall slower growth of the radical pool is responsible for the large disparity between mechanisms, a similar under-prediction of radical pool growth rate could also account for the discrepancy between the models and the experimental results. Along these lines, a recent review of alcohol combustion chemistry by Sarathy et al. [63] suggested several potential areas for model improvement that may favorably impact agreement with experiment. Rosado-Reyes and Tsang [96] conducted single-pulse shock tube experiments to derive unimolecular decomposition rate expressions for \( n \)-butanol, concluding that previous estimates for these reactions were not in agreement with their experimental rates. In addition, Rosado-Reyes and Tsang [96] observed a lack of pressure dependence for these reactions. Vasu and Sarathy [97] investigated the impact of modifying these reaction rates contained within the Sarathy model [1] to the rates of Rosado-Reyes and Tsang [96], along with a faster rate for hydrogen abstraction from formaldehyde via the H radical. The improved model exhibited slightly better agreement with the shock tube data of Stranic et al. [26].

For limited conditions, the mechanism updated by Vasu and Sarathy [97] has been tested in the present counterflow ignition study for \( n \)-butanol. It is found that although this updated mechanism leads to reductions in ignition temperature of \(~15\) K, thereby indicating a small improvement, it nonetheless still results in appreciable over-predictions of the present experimental data. Sarathy et al. [63] also suggested other avenues of
improvement, including better estimates of the site-specific branching ratios for H- abstraction via OH and HO₂, the latter of which has not been determined experimentally. Furthermore, Sarathy et al. [63] identified reactions between the hydroxybutyl radicals and molecular oxygen as important at temperatures below 1000 K. These reactions are largely unexplored and their rate coefficients rely on theoretical calculations and analogies with low-temperature alkane oxidation mechanisms. As can be seen from Fig. 4.6, the Merchant model [2] predicts such pathways to be significant under the current experimental conditions, but results in ignition temperatures that are appreciably further from the current experimental dataset than those of the Sarathy model [1].

4.6 Conclusions

In this chapter, the non-premixed counterflow ignition experiment is used to investigate the ignition temperature trends of n-butanol as a function of strain rate, fuel loading, and pressure. This data is then compared to two skeletal mechanisms developed from currently available comprehensive butanol mechanisms to investigate their ability to predict experimentally observed trends. This comparison results in a number of conclusions:

• The experimental trends in terms of strain rate, fuel loading, and pressure are largely captured by both the Sarathy et al. [1] and Merchant et al. [2] mechanisms. However, both mechanisms over-predict the experimental data to an appreciable extent, with the SN mechanism predicting uniformly lower ignition temperatures compared to the MN mechanism.
Counterflow ignition of \( n \)-butanol is shown to be sensitive to the transport of fuel and its intermediates. Normalized sensitivities of reaction rates are appreciably lower than those of binary diffusion coefficients even for the most sensitive chain-branching reactions.

The two mechanisms tested appear to largely agree on the size of the radical pool - in terms of O, OH, and H radicals - at which ignition occurs. However, the overall growth rate of the radical pool as a function of boundary temperature is much smaller in the MN mechanism, leading to higher ignition temperatures.

The source of disagreement between the two butanol mechanisms is analyzed and discussed, with the MN mechanism predicting a significant portion of the parent fuel breaking down through enol and aldehyde pathways, as compared to primarily scission reactions in the SN mechanism. The pathways considered in the MN mechanism deplete the radical pool and result in overall slower growth of the ignition kernel.

The over-prediction of experimental ignition temperatures by both mechanisms is likely attributable - at least in part - to an under-prediction of the growth rate with respect to oxidizer temperature of the radical pool.
4.7 Figures

Figure 4.1: Ignition temperatures of $n$-butanol ($X_f = 0.15$ and fuel stream temperature of 380 K) as a function of pressure-weighted strain rate at 1 and 3 atm, compared to the numerical simulation results predicted by the SN and MN mechanisms. Error bars represent total estimated uncertainty.
Figure 4.2: Ignition temperatures of $n$-butanol as a function of fuel loading at $P = 1$ and 3 atm, $k' = 350 \text{ s}^{-1}$, and fuel stream temperature of 380 K compared to the results predicted by the SN and MN mechanisms. Error bars represent total estimated uncertainty.
Figure 4.3: Ignition temperatures of \( n \)-butanol as a function of pressure at \( k' = 350 \, \text{s}^{-1} \), \( X_f = 0.15 \), and fuel stream temperature of 380 K compared to the results predicted by the SN and MN mechanisms. Error bars represent total estimated uncertainty. Circles represent the data points at which the sensitivity analyses of Fig. 4.4 are conducted.
Figure 4.4: Sensitivity analyses at 1 and 4 atm, $k' = 350 \text{ s}^{-1}$, $X_f = 0.15$, and fuel stream temperature of 380 K using the SN mechanism (a-c) and MN mechanism (d-f). (a/d): Sensitivity to binary diffusion coefficients. (b/e): Sensitivity to reaction rates, sorted by largest magnitude at 4 atm. (c/f): Sensitivity to reaction rates, sorted by largest magnitude at 1 atm.
Figure 4.5: Important species spatial profiles at the ignition turning points based on the SN mechanism compared between 1 and 4 atm at $k' = 350 \text{ s}^{-1}$, $X_f = 0.15$, and fuel stream temperature of 380 K.
Figure 4.6: Integrated path flux analysis maps computed at 1 atm, $k' = 350 \text{ s}^{-1}$, $X_f = 0.15$, and fuel stream temperature of 380 K demonstrating the differing chemical pathways predicted by the skeletal SN and MN mechanisms at their respective turning points. a) SN mechanism, evaluated at $T_{ig}=1310$ K, and b) MN mechanism, evaluated at $T_{ig}=1372$ K, with highlighted areas indicating pathways that significantly differ from those predicted by the Sarathy mechanism. “X” denotes a radical species, and a lack of a modifier denotes a unimolecular reaction.
Chapter 5: Effect of Fuel Structure on the Ignition of Butanol Isomers

5.1 Introduction

As described in Chapter 1, as a stand-alone alternative transportation fuel or as a fuel blend with gasoline, butanol offers several advantageous properties. Both \( n \)- and \( iso \)-butanol isomers exhibit limited solubility with water and are relatively non-corrosive, opening up the possibility of more efficient distribution methods though pipelines. In addition, butanol’s higher energy density allows higher blending ratios with gasoline without engine modifications, and its lower vapor pressure would greatly reduce evaporative emissions. Scientifically speaking, butanol is interesting as it represents the smallest alcohol exhibiting all forms of structural isomerism. As a result, by comparing the behavior of the butanol isomers in well-defined combustion configurations, the impacts of molecular structural variations on combustion chemistry can be better understood and broadly applied to the modeling of alcohol-based transportation fuels.

Due to the interest from both practical and scientific points of view, an appreciable body of fundamental research has been developed for butanol isomers in recent years. Though by no means a comprehensive review, numerous fundamental studies have been conducted using a variety of experimental systems including laminar flame speeds [16–18,98], flame extinction [19], pyrolysis [20], flame structure [18,21,22], species and temperature measurements in flow reactors [21] and jet-stirred reactors (JSR) [18,23], and ignition delays in rapid compression machines (RCM) [24,25] and shock tubes [26,27]. Several of these studies have investigated the impact of isomeric variations on
global combustion properties. Veloo and Egolfopoulos [98] determined atmospheric pressure laminar flame speeds of the butanol isomers in the equivalence ratio range of 0.7-1.5, finding highly similar flame propagation rates for \( n-/iso-/sec-\)butanol but significantly lower flame speeds for \( tert-\)butanol. Stranic \textit{et al.} [26] investigated ignition delay times of the butanol isomers in a shock tube at 1050-1600 K, 1.5-43 atm, and equivalence ratios of 0.5 and 1.0, finding that the butanol isomers exhibited noticeably different ignition delay times, with the relative rankings changing as a function of pressure. At 1.5 atm, \( n-\)butanol exhibited the shortest ignition delay times, followed by \( iso-\) and \( sec-\)butanol, with \( tert-\)butanol exhibiting considerably longer ignition delays, whereas at 43 atm the rankings followed \( n-\)butanol \( \approx \) \( iso-\)-butanol \( < \) \( sec-\)-butanol \( < \) \( tert-\)-butanol. In an RCM configuration Weber and Sung [25,99] found quite different ignition delay trends for stoichiometric mixtures at 715-910 K and 15 and 30 bar pressures. At both pressure conditions \( n-\)butanol exhibited significantly faster ignition delay times than other isomers, additionally finding that the ignition delay ranking followed \( n-\)butanol \( < \) \( iso-\)-butanol \( \approx \) \( sec-\)-butanol \( < \) \( tert-\)-butanol at 15 bar, but \( n-\)butanol \( < \) \( tert-\)-butanol \( < \) \( sec-\)-butanol \( < \) \( iso-\)-butanol at 30 bar.

Based on the utility of ignition and extinction data in convective/diffusive systems from both practical and scientific perspectives, the present work compares the impact of ambient pressure, strain rate, and fuel loading on the counterflow ignition temperatures of all four butanol isomers in order to understand the isomeric structural effects on diffusive ignition. The experimental results are further simulated using isomer-specific skeletal mechanisms derived from comprehensive butanol models available in the literature. A
comparison of experimental and simulated results is then used to validate and assess the performance of these literature butanol models.

5.2 Structure of the butanol isomers

As described in Chapter 1 and detailed in the preceding section, the butanol isomers represent an interesting target fuel from both an applied and fundamental perspective. From an applied engineering perspective, all of the isomers have some commercial significance, with \( n \)-, \( iso \)-, and \( sec \)-butanol representing possible candidates as second-generation biofuels for blending with or replacement of gasoline\[100\], and \( tert \)-butanol commonly acting as an octane enhancer. Fundamentally, these fuels are also interesting as they represent the smallest alcohol exhibiting all four types of structural isomers. Structural isomers, while retaining the same chemical formula, can exhibit quite different combustion properties. As a result of structural differences, relative bond strengths between atoms can change, and certain fuel destruction pathways may become more or less probable or even be cut off entirely. Skeletal structures for the four butanol structural isomers are shown in Fig. 5.1, with the carbons labeled according to their distance from the hydroxyl functional group. As is clear from this figure, the arrangements of the constituent carbon atoms and alcohol functional group can vary quite substantially, and can be broken into two subgroups; the positional isomers (\( n \)- and \( sec \)-butanol) and chain isomers (\( iso \)- and \( tert \)-butanol). The positional isomers vary in terms of the location of the alcohol functional group (either an end or interior carbon) while the chain isomers vary in terms of the structure of the carbon backbone.
5.3 Experimental results

Figure 5.2 demonstrates the effect of strain rate on the ignition temperature of the four butanol isomers at 1 and 3 atm. Only a single data point for tert-butanol is included at 1 atm due to the difficulty in igniting this fuel under atmospheric conditions. All isomers respond similarly to varied strain rate within the range of \( k' = 200-400 \text{ s}^{-1} \), with the differences between the isomers narrowing slightly as strain rate increases. However, two interesting features with regards to isomer ranking are apparent. First, tert-butanol exhibits significantly higher ignition temperatures relative to the other three isomers. This ignition temperature difference amounts to 43-57 K at 1 atm, and 64-83 K at 3 atm. Second, the relationship between iso- and sec-butanol reverses between 1 and 3 atm. While iso-butanol exhibits the highest ignition temperature amongst the n/isol/sec-butanol group at 1 atm, sec-butanol occupies this position at 3 atm. Similar behaviors are observed when comparing the isomers in terms of the effect of fuel loading. As shown in Fig. 5.3 for \( k' = 350 \text{ s}^{-1} \), while all isomers exhibit highly similar behavior as a function of fuel loading, the relative ranking between iso- and sec-butanol again changes between 1 and 3 atm and is consistent across the fuel loading range investigated. It is worth noting that while the differences amongst the n/isol/sec-butanol group are relatively small (on the order of 5-20 K), in general the noteworthy trends involve ignition temperature differences in excess of the maximum random error estimated from repeated measurements at the same operating conditions (±5 K). In addition, the aforementioned trends are consistent across a wide range of strain rate and fuel loading conditions, suggesting that they are unlikely to be the result of experimental variability and therefore merit further investigation.
Figure 5.4 provides a clearer demonstration of the \textit{iso/sec}-butanol ranking switch by plotting ignition temperature as a function of pressure at $k'=350 \, \text{s}^{-1}$ and $X_f=0.15$. A clear crossover point for these isomers exists between 2 and 2.5 atm; below this pressure \textit{sec}-butanol is the more reactive one of the pair, while above this pressure \textit{iso}-butanol becomes more reactive. Throughout the pressure range, \textit{tert}-butanol exhibits significantly higher ignition temperatures than the other three isomers. It is worth noting that similar “crossover” behavior has been observed in homogenous experiments involving similar temperature ranges. The shock-tube study of Stranic \textit{et al.} [26] found that at 1.5 atm, the ignition delay times of \textit{iso}- and \textit{sec}-butanol were quite similar, while at higher pressures \textit{sec}-butanol exhibited noticeably longer ignition delays than \textit{iso}-butanol. In addition, in line with the results of the present study, \textit{tert}-butanol manifested significantly longer ignition delays under all pressure conditions investigated.

5.4 \textit{Effect of transport model uncertainties in the Sarathy mechanism}

As discussed in Chapter 2, the original transport data contained in the mechanism of Sarathy \textit{et al.} [1] has apparent discrepancies in the Lennard-Jones parameters for \textit{iso}-, \textit{sec}-, and \textit{tert}-butanol, as compared to those of Frassoldati \textit{et al.} [28] and Merchant \textit{et al.} [2]. The effect of changing these parameters - for both the parent fuel molecules and related C$_4$ intermediates using identical values to the respective parent fuel - to those used by Merchant \textit{et al.} [2] is exemplified in Fig. 5.5 for 3 atm, $k'=350 \, \text{s}^{-1}$ conditions. In addition to being shifted upwards by 55-100 K, the sensitivity of ignition temperature to fuel loading (i.e. rate of change as a function of fuel loading) is also increased. Comparing the original and modified transport model results, the difference between
predicted ignition temperatures at $X_f=0.05$ and 0.25 is ~60-70 K for all three isomers using the original parameters, however using the modified model this difference increases to 100-110 K.

Comparing the numerical results to the accompanying experimental results in Fig. 5.5, it is clear that this modification results in a greater disagreement with experimental data than the original model, with the difference between experimental and numerical data rising to between 80-120 K, depending on the isomer and operating conditions in question. While this modification could hardly be termed an “improvement” in terms of fidelity to experimental results, it does serve to illustrate two important points. First, it is imperative to include non-premixed validation data during combustion model development to provide more rigorous validation of the transport model. The larger sensitivities of non-premixed systems to transport properties can help to improve the performance of the complete combustion model in transport-affected environments, a designation encompassing most practical combustion devices. Second - and most relevantly for the present discussion - while transport parameters exhibit significantly larger sensitivities relative to individual reactions (to be discussed in due course), the fuel diffusion coefficients of the original model would have to be increased by an excessively large amount to close the gap between the numerical and experimental data. Since the resulting transport parameters would then be entirely unreasonable - as outlined in Section 2.5.2 - alternative factors must be considered to account for the differences. This observation proves valuable in the evaluation of the Sarathy and Merchant models, as modification of the fuel transport parameters - within reasonable bounds - cannot account
for the disparity between numerical and experimental results, and thus the source of the remaining disparities must lie within the chemical kinetic mechanism.

5.5 Numerical results from the Sarathy model

While the accompanying numerical results to Figs. 5.2 and 5.3 have been computed, the trends in terms of strain rate and fuel loading are highly similar amongst the various isomers within a given mechanism set, and largely capture the experimentally-observed trends. As a result, the following description and analysis will focus on the effect of varied pressure. Figure 5.6 shows a comparison between the experimentally obtained ignition temperatures and numerical results computed using the SN, SI, SS, and ST mechanisms for $k' = 350 \text{ s}^{-1}$, $X_f = 0.15$, and $P = 1-4 \text{ atm}$. Several interesting observations can be made from Fig. 5.6. First, the numerical results for all isomers over-predict the experimental results by an appreciable extent, ranging from 70 to 140 K (6-10%). While such a deviation could be considered relatively small on a percentage basis, it should be noted that the gap between numerical and experimental results is of similar magnitude to the difference between 1 and 4 atm experimental ignition temperatures. As such, the difference between numerical and experimental results should be considered significant within the context of the experimental data. Second, while the experimental ignition temperature trends for $n/iso/sec$-butanol as a function of pressure are largely well-captured by its accompanying numerical results, for tert-butanol the difference is more dramatic. At 1 atm the difference stands at 140 K, however at 4 atm the gap shrinks to just 70 K. Interestingly, the numerical results for the butanol isomers exhibit one of two behavior sets corresponding to the isomer types; the positional isomers ($n$- and $sec$-
butanol) exhibit a highly similar rate of change as a function of pressure, while the branched chain isomers (iso- and tert-butanol) also exhibit remarkable similarity but with a slightly greater pressure sensitivity. Third, unlike the experimental data where n-, iso-, and sec-butanol exhibit highly similar ignition temperatures, the results from the Sarathy model predict a noticeable offset between n-butanol and iso/sec-butanol. This behavior suggests appreciable differences in the modeled fuel breakdown chemistry, a subject that will be explored further in due course. Finally, the crossover between the iso- and sec-butanol results observed experimentally is reproduced by the numerical results, with both the crossover pressure and the difference between the two isomers at 1 and 4 atm closely matching those seen experimentally. This suggests that while overall the ignition temperatures are shifted upwards relative to the experimental data, the Sarathy model nonetheless captures some of the isomer-specific differences in terms of pressure-dependent reactions.

To begin to explore some of the above observations, a sensitivity analysis is conducted for reaction rates (by perturbing pre-exponential factors, $A_i$’s) and binary diffusion coefficients (by perturbing the zeroth-order coefficients of the polynomial fits for $D_{jk}$’s) defined as $S_{Al} = \frac{\partial \ln T_{ig}}{\partial \ln A_i}$ and $S_{Djk} = \frac{\partial \ln T_{ig}}{\partial \ln D_{jk}}$, respectively. Figures 5.7-5.10 demonstrate the ten largest reaction rate and transport sensitivity coefficients for all four butanol isomers, computed at the ignition turning points for 1 and 4 atm pressures, $k' = 350$ s$^{-1}$, and $X_f = 0.15$, ranked by the sensitivity magnitude at 4 atm. Similar to the results discussed in Chapter 4, for each isomer the sensitivity analysis of binary diffusion coefficients demonstrates significant sensitivity to the N$_2$-butanol and O$_2$-butanol transport rates as well as those of several important intermediates. Of particular note is
the consistent importance of butene isomers (1-$C_4H_8$, 2-$C_4H_8$, and i$C_4H_8$) in the transport sensitivity analysis for each of the butanol isomers. Sarathy et al. [1] attributed the lower experimental laminar flame speeds of iso- and tert-butanol relative to n-butanol to the predominance of iso-butene ($iC_4H_8$), and additionally noted that the branching ratios for isomerization and beta-scission of hydroxybutyl radicals warranted improvement to better predict the formation of butene isomers. Indeed, deficiencies were noted compared to both low-pressure flame speciation and JSR experiments. As a result, the persistent appearance of butene isomers in the present analysis suggests that further investigation of their role in counterflow ignition merits further examination, and will be discussed in more detail in conjunction with path analyses in due course.

Examination of reaction rate sensitivity analyses in Figs. 5.7-5.10 demonstrates additional differences associated with differing isomerism. Comparing amongst the positional isomers (n-butanol and sec-butanol), noticeable correspondence is apparent in terms of the sensitive reaction rates, with both isomers primarily exhibiting sensitivity to $H_2/C_1$ chemistry. In contrast, while the branched chain isomers (iso-butanol and tert-butanol) also exhibit sensitivity to $H_2/C_1$ chemistry, a number of reactions involved in the early stages of fuel breakdown also appear in the sensitivity analysis. For iso-butanol, this includes the initial H-abstraction from the $\alpha$ and $\gamma$ sites, as well as subsequent H-abstraction and scission reactions from the $\alpha$-hydroxybutyl radical. Similarly, tert-butanol displays substantial sensitivity to fuel breakdown reactions through both iso-butene and propen-2-ol ($CH_2$=COHCH$_3$) pathways. Interestingly, for both branched chain isomers the fuel breakdown reactions display appreciable pressure sensitivity in contrast to the positional isomers where - with the exception of hydrogen peroxide decomposition and
H-abstraction from the parent fuel via hydroperoxyl - most reactions display comparatively less pressure sensitivity. This difference may account for the different variation of ignition temperature with pressure between the positional and branched chain isomers observed in the numerical results.

Figures 5.11-5.14 show spatially-integrated path flux analyses at the ignition turning point for the butanol isomers at $k' = 350 \text{ s}^{-1}$, $X_i = 0.15$, and atmospheric pressure. In agreement with the sensitivity analysis, the butene isomers feature prominently in the initial fuel breakdown steps for all butanol isomers, albeit to differing extents. The path analysis for $n$-butanol (Fig. 5.11) shows that the majority of the 1-butene produced is through $\beta$-hydroxybutyl radical decomposition, with a minor pathway to 1-butene directly from $n$-butanol. In comparison, noticeably more butenes production is apparent in the flux maps of the other isomers. Approximately 6% of $iso$-butanol (Fig. 5.12) is converted directly to $iso$-butene, and ~80% of the $\beta$-hydroxybutyl radical is consumed through decomposition to $iso$-butene. The sec-butanol analysis (Fig. 5.13) shows significant paths to both 1-butene and 2-butene through the $\beta$-hydroxybutyl radicals, as well as minor pathways to each directly from the parent fuel. Finally, the overwhelming majority of tert-butanol consumption (Fig. 5.14) occurs through $iso$-butene, either directly from the parent fuel or via the hydroxybutyl radical. Interestingly, the ignition temperature ranking of the isomers at 1 atm based on the Sarathy model - $n$-butanol < $iso$-butanol < sec-butanol < tert-butanol - correlates well with the relative production of butenes by each isomer. This correspondence suggests that the butene chemistry plays a significant role in prescribing the ignition temperature trends observed amongst the butanol isomers, specifically their relative ranking in terms of ignition temperature, and
may account for the disparity observed between experimental and numerical results when comparing \( n \)-butanol with \( iso-/sec \)-butanol. This possibility will be explored in more detail in Section 5.7. In addition to differences in the importance of butene, the role of propenol changes significantly amongst the butanol isomers. For \( n \)-butanol, production of propen-3-ol (\( \text{CH}_2=\text{CHCH}_2\text{OH} \)) represents a relatively minor pathway, accounting for 5.9% of parent fuel breakdown via \( \beta \)-hydroxybutyl. In contrast, for \( iso \)-butanol 33.7% of the parent fuel decomposes through propen-1-ol (\( \text{OHCH=CHCH}_3 \)). For \( sec \)- and \( tert \)-butanol, 21.9% and 15.8% of the parent fuel decomposes through propen-2-ol. It is worth noting that, as pointed out by Sarathy et al. [1], H-abstraction from propen-2-ol results in an allylic radical which exhibits resonant stabilization characteristics and thus is expected to be relatively unreactive.

### 5.6 Numerical results from the Merchant model

Figure 5.15 compares the numerical results derived from the MN, MS, and MT mechanisms to the experimentally obtained ignition temperatures for \( k' = 350 \text{ s}^{-1} \), \( X_f=0.15 \), and \( P=1-4 \text{ atm} \). As mentioned in Section 2.5.1, \( iso \)-butanol results are not shown due to the inability of the MARS reduction package or the ignition code to interpret reaction R2.1 in its current PLOG form. The corresponding results using the skeletal Sarathy mechanisms are also shown in Fig. 5.15 for comparison. Similar to the results in the previous section, the skeletal Merchant mechanisms universally over-predict experimental ignition temperatures - in this case by \( \sim 100-190 \text{ K} \). In addition, the MS mechanism predicts \( sec \)-butanol ignition temperatures offset from the \( n \)-butanol results predicted using the MN mechanism by 20-60 K, with the disparity rising as pressure
increases. In fact, based on the skeletal Merchant mechanisms, the sec-butanol results are more similar in magnitude to those for tert-butanol, and exhibit the highest ignition temperatures for pressures above \(~ 2\) atm. This behavior runs counter to the experimental results, where tert-butanol consistently ignites at appreciably higher temperatures than the other three isomers, which ignite at largely similar temperatures for most operating conditions. Unlike the results from the skeletal Sarathy mechanisms, sec-butanol and n-butanol are not predicted to exhibit similar ignition temperature variation with pressure in the Merchant model, which in fact seems to capture a slight divergence in ignition temperature trend observed experimentally between the two isomers at elevated pressures.

Sensitivity analyses of the ten largest reaction rate and transport sensitivity coefficients for \(n\)-, sec-, and tert-butanol isomers are shown in Figs. 5.16-5.18, respectively. The results are largely similar to those obtained using the skeletal Sarathy mechanisms, with the positional isomers exhibiting sensitivity to many of the same reactions and tert-butanol showing strong sensitivity to early-stage fuel breakdown reactions. Also similar to the results of the previous section, a consistent dependence upon the transport of butene isomers is observed. However, there are some notable differences. The \(n\)-butanol results (Fig. 5.16) demonstrate sensitivity to H-abstraction from the fuel molecule via hydroperoxyl to form \(\beta\)-hydroxybutyl, as compared to the SN mechanism which exhibits sensitivity to abstraction at the \(\alpha\)-carbon. In addition, the MN mechanism is noticeably less sensitive to the chain-branching \(H + O_2 \Leftrightarrow O + OH\) reaction at \(1\) atm relative to the SN mechanism.

With regards to sec-butanol (Fig. 5.17), while the reaction rate sensitivity results are quite similar aside from minor differences in coefficient magnitude, the MS mechanism
exhibits a greater degree of sensitivity to the transport properties of both 1-butene and 2-butene. Also of interest is the presence of propen-2-ol in the transport sensitivity analysis of Fig. 5.17(b). As pointed out by Sarathy et al. [1], the allylic radical of propen-2-ol exhibits resonant stabilization characteristics and thus is expected to be relatively unreactive. Since path analysis on the MS mechanism predicts that almost a quarter of propen-2-ol is consumed to form the allylic radical at both 1 and 4 atm, the relatively large negative transport sensitivity of propen-2-ol may indicate that enhanced transport results in migration of propen-2-ol to locations where alternative pathways - e.g., tautomerization to acetone - become more prevalent, thus avoiding the less reactive allylic radical pathway.

Sensitivity results for tert-butanol (Fig. 5.18) also display significant similarities to the ST mechanism, with iso-butene, propen-2-ol, and acetone featuring prominently in the transport sensitivity analysis, and reactions related to iso-butene comprising a significant proportion of the most sensitive reaction rates. Of note in the reaction rate sensitivity analysis shown in Fig. 5.18(a) is the sign change in the sensitivity coefficient for the water elimination reaction from tert-butanol: $tC_4H_9OH \leftrightarrow iC_4H_8 + H_2O$. While at atmospheric conditions an increase in this reaction rate tends to inhibit ignition, at 4 atm this trend reverses, suggesting a significant pressure-dependent change in this important fuel breakdown reaction. This strong pressure dependence may be partially responsible for the growing disparity between the two numerical sets of tert-butanol results as pressure increases.

Furthermore, for the sensitive reactions related to H$_2$/C$_1$-C$_2$ chemistry shown in Figs. 5.7-10 and Figs. 5.16-18, their reaction rates over a temperature range relevant to the
present study are compared between the Sarathy and Merchant models. This comparison shows that the reaction rates of most of them are quite similar except that noticeable differences exist for the reactions of $C_2H_3 + O_2 \leftrightarrow CH_2CHO + O$ and $OH + C_2H_4 \leftrightarrow C_2H_3 + H_2O$. It should be highlighted that replacing the rate coefficients for these two reactions in the Sarathy model with those from the Merchant model results in better agreement between the two models. However, a significant disparity remains, suggesting that additional differences exist in the $C_2$ sub-mechanism between the Sarathy and Merchant models.

To investigate the isomeric differences further, path analyses at the ignition turning point for $n$-, sec-, and tert-butanol using the MN, MS, and MT mechanisms are shown in Fig. 5.19 for 1 atm, $k' = 350$ s$^{-1}$, and $X_f = 0.15$. As was the case in the previous section, the butene isomers figure prominently in the path analysis for each isomer, with the molar flux proceeding through butene pathways roughly correlating to the trend in ignition temperature (at 1 atm), namely $n$-butanol $<$ sec-butanol $<$ tert-butanol. However, several noteworthy differences are apparent in the path analyses of sec-butanol (Fig. 5.19(b)) and tert-butanol (Fig. 5.19(c)). First, while the MS and SS mechanisms predict a similar flux of parent fuel to the $\alpha$-hydroxybutyl radical (27% versus 29.3%, respectively) as well as the same major products (propen-2-ol and methyl radical or 2-butanone), the branching ratios from the $\alpha$-hydroxybutyl radical are nearly reversed. Whereas the MS mechanism predicts 39.4% of $\alpha$-hydroxybutyl is converted to propen-2-ol and 60% to 2-butanone (resulting in $\sim$10.6% of the parent fuel passing through propen-2-ol), the SS mechanism predicts 74.8% proceeds to propen-2-ol while only 23.1% is converted to 2-butanone (21.9% of parent fuel through propen-2-ol). It is worth noting that unlike the
MS mechanism, the SS mechanism does not contain a pathway to propen-2-ol’s allylic radical. Second, the molar flux through 1-butene and 2-butene pathways is significantly larger in the MS mechanism. Nearly 55% of the parent fuel in the MS mechanism is consumed through butene-related pathways - either directly from sec-butanol via water elimination or indirectly via the β-hydroxybutyl radicals - as compared to 12% in the SS mechanism. As other pathways are largely similar between the two mechanisms, the large difference in the level of butene involvement is likely responsible for the differences observed between the sec-butanol ignition temperatures for the MS and SS mechanisms.

Comparing the MT mechanism path analysis results (Fig. 5.19(c)) to those of the ST mechanism (Fig. 5.14), it can be seen that the MT mechanism predicts somewhat more water elimination to directly form iso-butene while forming relatively less hydroxybutyl and almost no hydroxypropyl radicals. The MT mechanism also predicts less conversion of hydroxybutyl to iso-butene, instead favoring more production of propen-2-ol; this latter pathway accounts of 27.1% of the total parent fuel consumption in the MT mechanism, compared to 15.8% in the ST mechanism. Despite this difference, the total molar flux through iso-butene pathways is fairly similar between the two mechanisms (~62% in the MT mechanism compared to ~69% in the ST Mechanism), which likely accounts for the quite similar predictions in terms of ignition temperature at 1 atm. However, as pressure increases the predicted ignition temperatures begin to diverge, with the MT mechanism predicting tert-butanol ignition temperature ~ 20 K higher than the ST mechanism at 4 atm. This difference is attributed to a significant increase in the importance of the ROOH pathway in the MT mechanism as a result of a simultaneous rise in the proportion of tert-butanol reduced to hydroxybutyl (46% at 1 atm versus
68.5% at 4 atm) and a tripling of the branching ratio from hydroxybutyl to iso-butenyl hydroperoxide (9.5% at 1 atm versus 34.8% at 4 atm), as shown in Fig. 5.19(c). The ST mechanism shown in Fig. 5.14, in contrast, does not contain this pathway from hydroxybutyl, and the branching ratios to iso-butene and propen-2-ol remain quite similar between 1 and 4 atm.

5.7 Potential areas for model improvement

The preceding discussion has highlighted a number of important points regarding the differences between the Sarathy et al. [1] and Merchant et al. [2] models. First, the transport parameters for iso-/sec-/tert-/butanol in the Sarathy model - despite describing unreasonably fast fuel diffusion - still cannot account for the disparity between the numerical and experimental data. Furthermore, despite utilizing identical butanol isomer transport parameters, significant differences remain between the Sarathy and Merchant models. These observations suggest that, while the transport model is unquestionably important to the accurate prediction of ignition temperatures, modifications to transport parameters can resolve neither the disparity between the numerical results and the experimental data, nor the differences observed between the Sarathy and Merchant models. This leads to the conclusion that these discrepancies must result from the chemical kinetics. Second, when the skeletal mechanisms from each model are compared, appreciable differences in the fuel breakdown pathways can be observed. For example, as has been discussed at length in Chapter 4, the breakdown of n-butanol differs substantially between the Sarathy and Merchant models, including significant variations in the predicted branching ratios to both γ- and δ-hydroxybutyl (cf. Figs. 5.11 and
5.19(a)) as well as the presence of additional pathways involving enols/aldehydes in the Merchant model. With regards to sec-butanol, despite describing largely similar chemical pathways and predicting mostly similar branching ratios directly from the parent fuel, path analysis reveals that approximately 5 times more sec-butanol is consumed through butene pathways in the Merchant model relative to the Sarathy model. Moreover, the butene pathways themselves differ substantially. Path analysis reveals that both the branching ratios from the butene isomers as well as the subsequent breakdown pathways are dramatically different. In fact, as a proxy for estimating reactivity, additional ignition turning point calculations for $P = 1 \text{ atm}$, $k' = 350 \text{ s}^{-1}$, and $X_f = 0.15$ using butene isomers as a fuel are conducted with both models, showing that 1- and 2-butene ignition turning points in the Merchant model occur at 88 K and 108 K higher temperatures, respectively, as compared to the Sarathy model. For the same conditions, the two models predict similar ignition turning points for iso-butene, with ignition temperatures falling within 6 K. Combined with the increased flux through butene pathways, the differing descriptions for 1- and 2-butene breakdown likely account for the sec-butanol ignition temperature disparity observed between the two models, and likely contribute to differences observed for other isomers as well. Finally, even where substantial agreement exists between the models’ ignition temperature predictions - i.e. atmospheric tert-butanol ignition (cf. Fig. 5.15) - the matching appears to be somewhat serendipitous. As demonstrated for tert-butanol by Figs. 5.14 and 5.19(c), even under atmospheric conditions the branching ratios from the hydroxybutyl radical differ dramatically, and the Merchant model even includes an additional ROOH pathway from hydroxybutyl which is absent in the Sarathy model. This ROOH pathway becomes significantly more important at elevated pressures, and
likely is a key factor resulting in the growing disparities between the two models as pressure increases.

Taken as a whole, the above observations suggest that despite reasonably matching experimental trends as functions of pressure-weighted strain rate, fuel loading, and pressure, substantial uncertainties remain in the description of combustion chemistry of the butanol isomers. Based upon the above analysis, it is likely that the disparities between the experimental and numerical results cannot be resolved without additional specification of the nature of both butanol and butene breakdown chemistry. With regards to fuel breakdown, Vasu and Sarathy [97] provided minor updates to \(n\)-butanol unimolecular decomposition reactions based on the shock tube study of Rosado-Reyes and Tsang [96], and additionally increased the rate constant for H-abstraction from formaldehyde, showing slightly improved matching with the data of Stranic et al. [26]. It should be noted that this updated mechanism has been tested for limited conditions in the present configuration, and leads to reductions in the simulated ignition temperature of \(n\)-butanol of ~15 K, thereby indicating a small improvement. In a recent review of alcohol combustion chemistry, Sarathy et al. [63] also pointed out that significant uncertainties remain in the description of H-abstraction reactions from the butanol isomers, particularly by OH and HO\(_2\). Although site-specific OH-abstraction reaction rates developed by McGillen et al. [101] were suggested as a possible avenue of improvement, these reaction rates had yet to be implemented into a combustion model. Additional uncertainties exist with regards to abstraction by HO\(_2\), for which no experimental measurements are currently available [63]. Regarding modeling of butene pathways, the butene sub-mechanism itself is an area of current research. For example, a recent study by Schenk et
al. [102] experimentally explored the behavior of the butene isomers in a low-pressure premixed flame configuration and made improvements to an existing hydrocarbon model [103] based upon their results. However, a subsequent study of the ignition of butene isomers in non-premixed counterflow by Zhao et al. [104] discovered significant discrepancies between their experimental data and the model of Schenk et al. [102], and subsequently developed their own butene model which exhibited somewhat improved performance. Taking the above into consideration, it is anticipated that further study of the isomer-specific branching ratios (particularly better understanding of H-abstraction reactions) and an improved understanding of butene chemistry and branching ratios can help to close the gap between the models, as well as resolve discrepancies between the models and the experimental data. Furthermore, recognizing that the two models do not share the same C_1–C_2 sub-mechanism, the foundation fuel chemistry could also play some role in the disparities observed between the Sarathy and Merchant models. Finally, as the role of enols (particularly propenol) appears to change appreciably between the isomers within a given model, improved understanding of appropriate branching ratios would likely aid in improving the overall fidelity of the models.

5.8 Conclusions

This chapter comprehensively explores the ignition temperature trends of the four butanol isomers as a function of pressure-weighted strain rate ($k'=200-400$ s$^{-1}$), fuel loading ($X_f=0.05-0.25$), and pressure (P=1-4 atm) in a non-premixed counterflow configuration. These trends are compared to numerical results derived from isomer-specific skeletal mechanisms developed from two comprehensive butanol models available in the
literature. While these mechanisms largely capture the experimentally-observed trends, they universally over-predict the experimental data to an appreciable extent. Additionally, for both sets of skeletal mechanisms the “ranking” of isomers in terms of predicted ignition temperatures deviates significantly from the experimental results. Whereas the experimental n-/iso-/sec-butanol results all lie in close proximity to each other, the Sarathy et al.-based [1] and Merchant et al.-based [2] skeletal mechanisms predict significant separation amongst these isomers. Both ST and MT mechanisms predict largely similar tert-butanol ignition temperatures, although the disparity increases as pressure is raised from atmospheric pressure to 4 atm. Detailed sensitivity and path analyses suggest that significant differences exist between the models, as well as between the isomers within each model, in terms of the roles of enols and butene isomers. Reactions of the hydroxybutyl radicals with molecular oxygen to form butenols appear to be the major difference between the MN and SN mechanisms, while the importance of various propenol isomers varies significantly between models and between isomers. In addition, the butene isomers may play a significant role in determining the relative levels of reactivity between the butanol isomers, as the relative reactivity of the butanol isomers correlates well with the relative amounts of parent fuel consumed through butene pathways. In particular, the major difference between the MS and SS mechanisms appears to be the branching ratios to 1- and 2-butene, where the MS mechanism predicts nearly 5 times more sec-butanol being consumed through these pathways than is apparent in the SS mechanism. Moreover, the treatment of the butene isomers itself varies between models, with the Merchant et al. [2] model predicting the 1- and 2-butene isomers to be significantly less reactive than their counterparts in the Sarathy et al. [1] model. These
trends suggest that the disparities between results from the different base chemical kinetic models may be significantly reduced by an improved understanding of the role of enols and butene in butanol combustion, and that additional work remains to better specify these pathways.
Figure 5.1: Skeletal structures of the four butanol isomers. Carbon atoms are labeled according to their position relative to the alcohol functional group.
Figure 5.2: Experimental ignition temperatures for the butanol isomers at P=1 and 3 atm, $X_f=0.15$, as a function of pressure-weighted strain rate. Ignition temperature error bars represent the random error of $\pm 5$ K, while pressure-weighted strain rate error bars represent the total estimated uncertainty.
Figure 5.3: Experimental ignition temperatures for the butanol isomers at P=1 and 3 atm, $k'=350 \text{ s}^{-1}$ as a function of fuel loading. Ignition temperature error bars represent the random error of ±5 K, while fuel loading error bars represent the total estimated uncertainty.
Figure 5.4: Experimental ignition temperatures for the butanol isomers at $X_r=0.15$ and $k'=350$ s$^{-1}$ as a function of pressure. Ignition temperature error bars represent the random error of ±5 K, while pressure error bars represent the total estimated uncertainty.
Figure 5.5: Demonstration of the effect of modifying the Lennard-Jones transport parameters for iso-/sec-/tert-butanol and C\textsubscript{4} intermediates related to the parent fuel breakdown in the Sarathy et al. [1] to the matching parameters listed in Merchant et al. [2]. Conditions: P=3 atm and \( k '=350 \text{ s}^{-1} \). Experimental data are also included for reference.
Figure 5.6: Comparison between experimental data and numerical predictions using the SN/SI/SS/ST skeletal mechanisms as a function of pressure for $X_f=0.15, k'=350\,\text{s}^{-1}$.
Figure 5.7: Normalized (a) reaction rate and (b) binary diffusion sensitivity coefficients for $n$-butanol computed at $P=1$ and 4 atm, $k=350 \text{ s}^{-1}$, $X_f=0.15$ at the ignition turning point for the SN skeletal mechanism.

Figure 5.8: Normalized (a) reaction rate and (b) binary diffusion sensitivity coefficients for iso-$n$-butanol computed at $P=1$ and 4 atm, $k'=350 \text{ s}^{-1}$, $X_f=0.15$ at the ignition turning point for the SI skeletal mechanism.
Figure 5.9: Normalized (a) reaction rate and (b) binary diffusion sensitivity coefficients for sec-butanol computed at $P=1$ and 4 atm, $k'=350$ s$^{-1}$, $X_f=0.15$ at the ignition turning point for the SS skeletal mechanism.

Figure 5.10: Normalized (a) reaction rate and (b) binary diffusion sensitivity coefficients for tert-butanol computed at $P=1$ and 4 atm, $k'=350$ s$^{-1}$, $X_f=0.15$ at the ignition turning point for the ST skeletal mechanism.
Figure 5.11: Spatially-integrated path analysis for \(n\)-butanol at \(P=1\ atm\), \(k'=350 \ s^{-1}\), \(X_f=0.15\), evaluated at the ignition turning point using the SN skeletal mechanism.
Figure 5.12: Spatially-integrated path analysis for iso-butanol at P=1 atm, $k'=350$ s$^{-1}$, $X_i=0.15$, evaluated at the ignition turning point using the SI skeletal mechanism.
Figure 5.13: Spatially-integrated path analysis for sec-butanol at P=1 atm, $k' = 350$ s$^{-1}$, $X_f = 0.15$, evaluated at the ignition turning point using the SS skeletal mechanism.
Figure 5.14: Spatially-integrated path analysis for tert-butanol at P=1 atm, $k'\approx 350 \text{ s}^{-1}$, $X_f=0.15$, evaluated at the ignition turning point using the ST skeletal mechanism. Pathways from the hydroxybutyl radical under 4 atm conditions (in bold) are also included to illustrate differences at elevated pressure, as discussed in Sections 5.6-7.
Figure 5.15: Comparison between experimental data and numerical predictions using the MN/MS/MT skeletal mechanisms as a function of pressure for $X_f=0.15$, $k' = 350$ s$^{-1}$. Results from the SN/SS/ST skeletal mechanisms are also included for comparison purposes.
Figure 5.16: Normalized (a) reaction rate and (b) binary diffusion sensitivity coefficients for n-butanol computed at P=1 and 4 atm, $k'=350 \text{ s}^{-1}$, $X_f=0.15$ at the ignition turning point for the MN skeletal mechanism.
Figure 5.17: Normalized (a) reaction rate and (b) binary diffusion sensitivity coefficients for sec-butanol computed at P=1 and 4 atm, $k^\prime$=350 s$^{-1}$, $X_f$=0.15 at the ignition turning point for the MS skeletal mechanism.
Figure 5.18: Normalized (a) reaction rate and (b) binary diffusion sensitivity coefficients for tert-butanol computed at P=1 and 4 atm, $k'=350 \text{ s}^{-1}$, $X_f=0.15$ at the ignition turning point for the MT skeletal mechanism.
Figure 5.19: Spatially-integrated path analysis at $P=1$ atm, $k'=350$ s$^{-1}$, $X_f=0.15$, evaluated at the ignition turning point (a) for $n$-butanol using the MN skeletal mechanism, (b) for $sec$-butanol using the MS skeletal mechanism, and (c) for $tert$-butanol using the MT skeletal mechanism. In (c), some important pathways under 4 atm conditions (in bold) are also included to illustrate differences at elevated pressure, as discussed in Sections 5.6-7.
Chapter 6: Effect of Hydrogen Addition on the Ignition of $n$-Butanol

6.1 Introduction

As a method for improving a wide range of combustion properties including efficiency and emissions characteristics, hydrogen addition to a base hydrocarbon fuel presents a variety of interesting opportunities. As early as the 1980s, Milton and Keck [105] and Yu et al. [106] recognized that laminar flame speed data for hydrocarbons with hydrogen addition were of both fundamental and practical interest. More recently, as a result of a significant push towards fuel-efficient, ultra-low emissions engines, numerous studies have investigated hydrogen addition for practical engines fueled by hydrocarbons. In spark-ignited engines, several studies have noted performance improvements, including extended lean operation limits, improved thermal efficiency, and reduced cycle-to-cycle pressure variations at lean operating conditions (e.g. [33–36]). Similar studies in diesel engines have noted improvements in NO$_X$ emissions and thermal efficiency (e.g. [37,38]). In addition, benefits have been observed for aviation turbine engines (e.g. [39–42]), with hydrogen addition improving flame stability and blowout under lean conditions, leading to potentially lower NO$_X$ emissions as a result of stable, fuel lean combustion.

In addition to extensive investigations using butanol as a pure fuel as outlined in Chapter 5, several fundamental efforts have explored blending butanol with other transportation-relevant fuels, focusing largely on mixtures relevant to butanol/gasoline blends. Dagaut and Togbé investigated species concentration profiles emanating from a jet-stirred reactor using butanol-gasoline surrogate mixtures [107] and butanol/$n$-heptane
mixtures [108] at 10 atm and a range of lean and rich equivalence ratios. Saisirirat et al. [109] conducted further experiments on 1:1 mixtures of ethanol and n-butanol with n-heptane in a jet-stirred reactor configuration for lean conditions. Broustail et al. [110] investigated laminar flame speeds of ethanol and butanol mixtures with iso-octane in a spherically-expanding flame configuration, observing that the addition of alcohols linearly increased the propagation velocity relative to iso-octane at atmospheric conditions as blending ratios of ethanol and butanol increased, with similar but more muted effects at elevated pressures. Similar experiments at atmospheric pressure were conducted by Zhang et al. [111], coming to similar conclusions. Using a rapid compression facility, Karwat et al. [112] explored the effects of blending n-heptane/n-butanol on ignition delays, finding that butanol slowed ignition relative to pure n-heptane. In addition, Karwat et al. [112] found that the presence of n-heptane caused n-butanol to react at temperatures it would otherwise be non-reactive. Similar behavior for n-heptane/n-butanol mixtures was observed by Zhang et al. [113] in a shock tube for pressures of 2 and 10 atm and equivalence ratios of 0.5 and 1.0. In a recent rapid compression machine study, Kumar et al. [114] studied the effect of blending n-butanol on the ignition delay times of n-heptane and iso-octane for a pressure of 20 bar and equivalence ratios of 0.4 and 1.0. For blends with n-heptane, Kumar et al. [114] showed that both first-stage and total ignition delay increased with the addition of n-butanol. However, for iso-octane/n-butanol blends, the addition of n-butanol to iso-octane was found to lead to shorter total ignition delays under fuel lean conditions [114].

Recognizing that the development of advanced engine concepts - such as those described in Chapter 1 - and their integration into practical devices will require high-
fidelity combustion models able to capture the chemical kinetic effects of fuel blending, the present study aims to progress two objectives. First, novel non-premixed counterflow ignition data exploring the effect of hydrogen addition to n-butanol for mixing ratios defined as the mole percentage of hydrogen in the hydrogen/n-butanol blends - of 0-100% and pressures of 1-4 atm are obtained. This dataset is furthermore simulated using n-butanol skeletal mechanisms (cf. Chapter 2) developed from two comprehensive butanol mechanisms available in the literature. Comparison of the experimental and simulated results is used to assess the performance of the two literature butanol models for predicting ignition temperatures of n-butanol/hydrogen mixtures. Second, chemical kinetic analysis of the simulated results is performed to understand the controlling chemistry causing changes in fuel blend reactivity due to hydrogen addition. This understanding suggests the possibility of generalized rules for estimating the effect of hydrogen addition on forced ignition temperatures for a given “base” fuel, and highlights an area for future investigation.

6.2 Effects of hydrogen addition

Figure 6.1 demonstrates the effect of hydrogen addition to n-butanol, with accompanying simulated results using the SN and MN mechanisms. For atmospheric pressure conditions, total fuel loading $X_f = 0.15$, a pressure-weighted strain rate of $k' = 350$ s$^{-1}$, and a fuel boundary temperature of 380 K, ignition temperature decreases by ~250 K as the hydrogen content in the fuel stream - characterized by $\xi_{H}$, defined as the mole percentage of hydrogen in a hydrogen/n-butanol blend, ranging from $\xi_{H} = 0\%$ (pure n-butanol) to $\xi_{H} = 100\%$ (pure hydrogen) - increases from $\xi_{H} = 0\%$ to $\xi_{H} = 40\%$. However, as the
hydrogen content increases beyond 40%, the effect of further hydrogen addition is significantly more muted, with ignition temperature decreasing by less than 40 K between $\xi_H = 40\%$ and $\xi_H = 100\%$. Similar, but less dramatic effects are observed when pressure is increased to 3 atm, where ignition temperature decreases by ~100 K from $\xi_H = 0\%$ to $\xi_H = 40\%$, and ~25 K from $\xi_H = 40\%$ to $\xi_H = 100\%$.

The reduced ignition temperature sensitivity to hydrogen addition at elevated pressure can be readily explained by considering the disparate behavior of the pure component fuels. Unlike hydrocarbon fuels, which exhibit a monotonic decrease in ignition temperature as pressure rises (e.g., previous butanol results in Chapters 4 and 5), hydrogen exhibits a unique three-limit behavior wherein ignition temperature falls with rising pressure at pressures below ~0.2 atm, increases between 0.2 and 3-4 atm, then decreases again as pressure rises further beyond 4 atm [46]. As the pressure range of 1-4 atm in the present study generally falls within the “second limit” regime for hydrogen ignition [46], the ignition temperature of n-butanol falls with increasing pressure while the ignition temperature of hydrogen rises. This behavior results in a crossover point between the two sets of fuel blend results, which is observed to occur between $\xi_H = 20\%$ and $\xi_H = 30\%$ for the present conditions.

The simulated results from both the SN and MN mechanisms are also included in Fig. 6.1 and generally capture the above trends, including the transition in behavior at ~40% hydrogen addition for a given pressure and the crossover point between the 1 and 3 atm results, suggesting that both mechanisms capture the controlling chemistry and that further analysis of the mechanisms can yield meaningful explanations of the observed trends. Several other interesting features are also worth mention. As was observed in
Chapter 4, the MN mechanism predicts ignition temperatures 50-60 K higher than those predicted by the SN mechanism for pure \( n \)-butanol ignition. However, both mechanisms converge to appreciably similar results for pure hydrogen ignition, with predictions from each mechanism at both 1 and 3 atm falling within 10 K of each other. In addition, Fig. 6.1 demonstrates that the simulated results for pure hydrogen lie substantially closer to the experimental results than the simulated results for pure \( n \)-butanol, with the simulations exceeding the experiments by 25-35 K at 1 atm and 50-60 K at 3 atm. At 1 atm, the simulated hydrogen results lie nearly within the estimated total uncertainty in experimental ignition temperature, while at 3 atm the simulated results still lie well outside these bounds. In comparison, for the same operating conditions the SN and MN mechanisms predict \( n \)-butanol ignition temperatures 90-100 K higher and 140-160 K higher, respectively, than experimental values across the pressure range.

Figure 6.2 provides additional detail on the effect of pressure for selected percentages of hydrogen addition for both experimental and simulated results. The conditions of Fig. 6.2 are a total fuel loading \( X_f = 0.15 \), a pressure-weighted strain rate of \( k' = 350 \text{ s}^{-1} \), and a fuel boundary temperature of 380 K. Focusing on the experimental results, at \( \xi_H = 0\% \) and 10\% hydrogen addition, increasing pressure results in a monotonic decrease in ignition temperature. The 10\% hydrogen addition level decreases the overall ignition temperatures relative to the pure \( n \)-butanol case and reduces the slope of the ignition temperature change with respect to pressure. Further, as was indicated in Fig. 6.1, when the hydrogen content reaches 25\% the ignition temperature is nearly invariant with pressure, with ignition temperature increasing only slightly between 1 and 2.5 atm before a small decrease above 3 atm. Hydrogen addition at 25\% therefore
delineates a point of transition from butanol-dominated behavior to hydrogen-dominated behavior. As more hydrogen is added to the fuel blend, ignition temperature behavior as a function of pressure becomes progressively more similar to that of pure hydrogen, with the 50% hydrogen addition results showing a great degree of similarity to the pure hydrogen results both in trend and in absolute ignition temperatures. The effect of the aforementioned trends is a convergence in ignition temperature amongst the various mixtures as pressure increases, indicating more clearly the pressure effects observed in Fig. 6.1. Both the SN mechanism (Fig. 6.2(a)) and the MN mechanism (Fig. 6.2(b)) capture the above trends quite well, including the transitional behavior at 25% hydrogen, although both mechanisms predict ignition temperatures exceeding those observed experimentally.

In addition to the broad trends observed in Fig. 6.2, several more subtle features are also worthy of mention. First, comparing the experimental results for $\xi_H = 25\%, 50\%, \text{ and } 100\%$, a non-monotonic response with pressure variation is exhibited in that ignition temperature reaches a maximum and then begins to decrease with increasing pressure. For the 25% hydrogen case, the maximum ignition temperature is reached at 2.5 atm, after which the experimental ignition temperatures slowly decrease. For $\xi_H = 50\%$ and 100% the maximum ignition temperature occurs between 3 and 3.5 atm. This shifting in the pressure at which ignition temperature peaks is interesting in that it suggests that the presence of $n$-butanol may impact the critical pressure of the typical second-to-third limit transition. However, such behavior is not observed in the simulated results using either the SN or MN mechanism.
Second, observing Fig. 6.2(c) - that shows the experimental and simulated results for 100% hydrogen in detail - it is apparent that the simulated results from the SN and MN mechanisms fall within 10 K of each other throughout the pressure range tested and additionally match very well with corresponding results using the recent hydrogen-oxygen model proposed by Burke et al. [115]. This suggests that despite not being specifically reduced for prediction of hydrogen ignition, the SN and MN mechanisms nonetheless capture hydrogen’s ignition behavior predicted by Burke et al. [115] quite well.

Third, it is seen from Fig. 6.2(c) that whereas the experimental results transition from the second to third limit at ~3.5 atm, all the three mechanisms predict a transition above 4 atm. Taken in conjunction with the increasing level of disagreement between the experimental and simulated results as pressure increases, the conclusion reached by Burke et al. [115] - namely that uncertainties in the model parameters for the formation and consumption of hydroperoxyl significantly impact the model’s predictive capabilities, particularly at elevated pressures and lower temperatures - would appear to be supported by the present dataset.

6.3 Controlling ignition chemistry

The results of Figs. 6.1 and 6.2 can best be understood as a transition between the thermokinetically-controlled behavior of butanol and the kinetically-controlled behavior of hydrogen. As has been described previously by Kreutz et al. [51] and Fotache et al. [57], while thermal feedback plays an insignificant role in most situations for hydrogen ignition, for hydrocarbons it is indispensable for the prediction of ignition turning point
behavior. To begin to understand what is responsible for the enhancement of \( n \)-butanol ignition with hydrogen addition, this transition is demonstrated in Fig. 6.3, which shows the ignition turning point as well as the lower branch of the characteristic “S-curve” using the MN mechanism. Since similar results are obtained using the SN mechanism, only the results from the MN mechanism are presented in this section for the sake of clarity.

As shown in Fig. 6.3, the pure butanol case (0% hydrogen) exhibits a consistent increase in temperature as the peak H-radical mole fraction increases up to the ignition turning point. However, as hydrogen is introduced, the lower branch exhibits a region of strong temperature sensitivity, what Fotache et al. [43] in their methane-hydrogen ignition study termed a “hydrogen chemistry kinetic growth” or HKG zone. At low hydrogen addition percentages (e.g., \( \xi_H = 10\% \)) this zone terminates ahead of the ignition turning point and returns to a lower temperature sensitivity more commensurate with the pure butanol case. As hydrogen addition level increases beyond 10%, the ignition turning point begins to merge with the HKG zone. This merging coincides with the end of the \( \xi_H = 0-40\% \) hydrogen addition region, after which the ignition temperature is insensitive to further hydrogen addition (cf. Fig. 6.1). As a result, the two ignition regimes observed in the previous section may be roughly described as hydrogen-enhanced (\( \xi_H = 0-40\% \)) or hydrogen-dominated (\( \xi_H = 40-100\% \)).

In order to identify the underlying cause of the ignition enhancement due to hydrogen addition, it is first useful to identify the chemistry underlying the HKG zone. Recognizing that this enhancement must be related to hydrogen consumption, a path flux analysis utilizing the MN mechanism reveals that the following four reactions account for the majority of \( H_2 \) and H radical consumption.
Reactions R6.1 and R6.2 are the primary consumption reactions for the H radical, while R6.3 and R6.4 represent the major consumption reactions for H\(_2\). To identify the controlling reactions of the HKG zone, each of the four reactions is artificially removed from the MN mechanism to create individual “test” mechanisms. The resulting solutions on the lower branch and in the region of the turning point for conditions of 10% hydrogen addition, \(X_f = 0.15\), \(k' = 350 \text{ s}^{-1}\), and a fuel boundary temperature of 380 K are shown in Fig. 6.4, with the ignition response curve for the pure \(n\)-butanol case (0% H\(_2\)) shown for comparison.

Figure 6.4 shows that the removal of reaction R6.1 results in identical solutions to the unmodified 10% case up to the HKG zone, but significantly departs from this solution thereafter, displaying no HKG zone or ignition turning point within the range of air boundary temperatures calculated. Since R6.1 represents a basic chain branching reaction, this result is not surprising. Removing R6.2, which competes for reactants with R6.1, reduces the ignition temperature while significantly enlarging the HKG zone and translating it to ~800 K, 200 K lower than the baseline unmodified 10% hydrogen case. Removal of R6.3 results in lower- and middle-branch solutions closely related to those seen in the pure \(n\)-butanol (0% H\(_2\)) case, with significant deviations occurring only near the ignition turning point. No HKG zone is observed when removing R6.3. Finally, R6.4 has a less dramatic effect, slightly reducing the size and translating the HKG zone to a
higher air boundary temperature, while exerting minimal influence on the ignition turning point. Although all four reactions impact the HKG zone to greater or lesser extents, Fig. 6.4 clearly demonstrates that R6.3 serves as a gateway reaction for the enhancement associated hydrogen addition, as it effectively isolates the effect of hydrogen addition and reverts to the pure $n$-butanol results in the lower and middle branches.

Further flux analysis considering the production and consumption of the H radical reveals that R6.3 represents the primary reaction both in consuming H$_2$ and producing H for all conditions involving hydrogen addition. The H radicals produced via R6.3 are then primarily consumed via R6.1 and R6.2, with R6.1 dominating consumption in the hydrogen-enhanced regime and R6.2 taking over as hydrogen addition levels move into the hydrogen-dominated regime. It is noted that the net effect is a significant enhancement in terms of the size of the radical pool available in the hydrogen-enhanced regime, as demonstrated in Fig. 6.5 through a spatially-resolved profile comparison between O, OH, and H radicals with 0% and 10% hydrogen addition at their respective ignition turning points. As shown in Fig. 6.1, the computed ignition temperatures using the MN mechanism for the 0% and 10% hydrogen addition cases are 1371.4 K and 1255.5 K, respectively. Figure 6.5 shows that the mole fractions of key radicals increase by more than two orders of magnitude as a result of hydrogen addition, providing a significantly larger radical pool from which $n$-butanol breakdown reactions can draw. The larger radical pool size leads to a dramatic reduction in ignition temperature, as observed in the hydrogen-enhanced regime in Fig. 6.1. In light of the observed effects on the radical pool, it is also interesting to note the greater sensitivity to hydrogen addition displayed by the MN mechanism relative to the SN mechanism in Fig. 6.1. As discussed in Chapter 4, the MN mechanism predicts that $n$-butanol consumption proceeds in large
part through enol and butyraldehyde pathways via a series of H-abstraction reactions, which require significant input from the radical pool. In contrast, the SN mechanism predicts relatively rapid breakdown via unimolecular decomposition reactions. The present results thus demonstrate the greater sensitivity of the MN mechanism to the radical pool growth, and explain the differing variations of ignition temperatures with respect to $\xi_H$ between the SN and MN mechanisms in the hydrogen-enhanced regime.

In addition to the root cause of the ignition enhancement via hydrogen, Fig. 6.1 also begs the question of what causes the ignition enhancement effect to be confined to low levels of hydrogen addition (i.e. below ~40% addition). This question is particularly interesting in light of previous work by Fotache et al. [43] on hydrogen-enriched methane mixtures, which showed the hydrogen-enhanced regime confined to a significantly smaller hydrogen addition range of approximately 0-10% for atmospheric pressure and similar total fuel loading conditions. This disparate behavior suggests that the nature of hydrogen enhancement has some dependence on molecule size, which could be a critical consideration for the application of hydrogen addition in practical engines.

A useful starting point for investigating this behavior is the observation that, somewhat counterintuitively, spatially-integrated H$_2$ consumption exhibits significant non-monotonic behavior as hydrogen addition increases, as shown in Fig. 6.6. As the mole percentage of hydrogen in the fuel blend increases from $\xi_H = 0\%$ to $\xi_H = 40\%$, H$_2$ consumption increases by an order of magnitude, reaching a peak consumption at $\xi_H \sim 40\%$ before decreasing as hydrogen content increases further. This is in contrast to the behavior of $n$-butanol, whose consumption remains nearly constant up to 20-30% hydrogen addition before dropping off as the total fraction of $n$-butanol in the fuel blend
reduces further. That the observed peak consumption coincides with the end of the hydrogen-enhanced regime suggests that increased hydrogen consumption supports and promotes radical production, which in turn leads to reduced ignition temperatures.

Figure 6.7 shows the spatially-resolved profiles of H, O, OH, and HO₂ radical species at the ignition turning point as a function of hydrogen addition for atmospheric pressure. It is clear from the profiles of H, O, and OH that low levels of hydrogen addition result in a significantly larger ignition kernel, with 10% addition raising the peak mole fraction of each radical by several orders of magnitude. However as hydrogen content is further increased, the size of the kernel does not change significantly, with peak mole fractions of O and OH remaining essentially constant, and the H radical increasing only slightly between 10% and 40% hydrogen addition. After 40%, the kernel progressively decreases in size as hydrogen percentage increases, with the kernel for pure hydrogen stabilizing at peak mole fractions two to three orders of magnitude greater than those observed in the pure n-butanol ignition kernel. The spatial profiles of HO₂ exhibit similar trends in terms of magnitude. However, the shape of the HO₂ profile changes dramatically between 50% and 80% hydrogen content. At low hydrogen addition levels a significant drop in HO₂ mole fraction is apparent near 1.2 cm from the fuel stream boundary, with the magnitude of this drop progressively decreasing from $\xi_H = 10\%$ to $\xi_H = 50\%$, and disappearing entirely by $\xi_H = 80\%$. This significant change in the shape of the HO₂ profile suggests significant changes in the production/consumption routes of HO₂ as $\xi_H$ increases.

To investigate the cause of this changing behavior, Fig. 6.8 compares the spatially-resolved molar production rates of some important HO₂-related reactions - identified via path flux analysis - accounting for the greatest proportion of HO₂ production and
consumption. For atmospheric conditions, $X_f = 0.15$, $k' = 350 \text{s}^{-1}$, and hydrogen addition levels of 10%, 40%, and 80%, it is apparent that the primary production and consumption reactions change significantly as hydrogen addition increases. At 10% hydrogen addition, the majority of HO$_2$ is produced via reaction R6.5, with reaction R6.2 playing a significantly smaller role.

$$HCO + O_2 \rightleftharpoons HO_2 + CO$$ \hspace{1cm} \text{R6.5}

As hydrogen addition increases to 40%, R6.2 becomes significantly more prominent, and overtakes R6.5 in terms of total HO$_2$ production rate. By 80% addition, R6.5 accounts for a minimal proportion of overall HO$_2$ production, while R6.2 is responsible for ~90% of its production. The major consumption reactions also change as a function hydrogen addition, with the chain branching reaction R6.6 and the chain propagating reaction R6.7 becoming relatively more important than the terminating reaction R6.8 as hydrogen addition increases.

$$HO_2 + H \rightleftharpoons 2OH$$ \hspace{1cm} \text{R6.6}

$$HO_2 + O \rightleftharpoons O_2 + OH$$ \hspace{1cm} \text{R6.7}

$$HO_2 + OH \rightleftharpoons H_2O + O_2$$ \hspace{1cm} \text{R6.8}

The drop in HO$_2$ mole fraction near 1.2 cm - and its decreasing magnitude with increasing hydrogen addition - can be explained by the spatial distribution of the production and consumption reactions shown in Fig. 6.8. At 10% hydrogen addition, the peak consumption rates of the two major consumption reactions R6.7 and R6.8 occur just after the peak production rate via R6.5, resulting in a steep drop near 1.2 cm. As hydrogen addition increases, the magnitude of this drop diminishes as reaction R6.2 becomes more prominent, due to R6.2's peak production rates occurring farther towards
the oxidizer side. Ultimately the drop disappears entirely as the relatively broadly-distributed R6.2 represents the overwhelming majority of HO₂ production.

The transition between R6.5 and R6.2 as a function of hydrogen addition are summarized in Fig. 6.9 by comparing the spatially-integrated molar production rates of total HO₂, R6.2, and R6.5. A clear crossover point between molar production rates of R6.2 and R6.5 occurs at 30% hydrogen addition, while overall HO₂ production rate peaks at 40%. As R6.2 takes over from R6.5 as the primary pathway leading to HO₂, production of HO₂ begins to compete with the critical chain branching reaction R6.1, and the reaction pathways begin to strongly resemble the competition between R6.1 and R6.2 that typifies the second limit in the hydrogen-oxygen system. Thus, the relative importance of reactions R6.5 and R6.2 determine the transition point between hydrogen-enhanced and hydrogen-dominated behaviors.

The above-mentioned phenomena can also help in understanding the cause behind the observed pressure-insensitivity of the 25% hydrogen fuel mixture in the 1-4 atm pressure range shown in Fig. 2. As the gap between the R6.5 and R6.2 production rates closes between 20-30% hydrogen content, HO₂ production is approximately evenly split between the pressure-insensitive reaction R6.5 and the pressure-sensitive reaction R6.2. After ξₜₕ = 30%, R6.2 dominates HO₂ production and the mixture begins to take on pressure behaviors similar to those of hydrogen. This counteracts the typical pressure dependency of hydrocarbon ignition - namely an increase in reaction rate with increasing pressure - and results in the largely constant ignition temperatures for 25% hydrogen addition. Finally, this competition helps to explain the differing transition behavior observed between the methane/hydrogen results of Fotache et al. [43] and the present n-
butanol/hydrogen results. As mentioned earlier, for hydrogen addition to methane, Fotache et al. [43] observed a transition to the hydrogen-dominated regime at hydrogen addition percentages near 10%, whereas the present study observes transition at much higher hydrogen addition percentages near 40%. As described above, the transition between these regimes is mediated by the competition between R6.2 and R6.5, with R6.5 relying on the availability of HCO to proceed. As methane contains only a single carbon atom, appreciably less HCO will be available with methane as compared to n-butanol for similar total fuel loading and hydrogen addition conditions. As a result, R6.2 will overtake R6.5 more quickly for the methane/hydrogen blends, resulting in earlier transition between regimes. This conclusion is further supported by the dataset of Fotache et al. [43], which examined the effect of increasing total fuel loading on methane-hydrogen blends. Fotache et al. [43] found that as total fuel loading is increased, the transition between hydrogen-enhanced and hydrogen-dominated regimes is delayed to higher hydrogen addition percentages. By adding more hydrocarbon fuel, the availability of carbon in the system will increase, thus leading to a delayed transition point. This observation further suggests that as the carbon chain length of the “base” fuel increases - with a commensurate increase in total carbon atoms - greater hydrogen addition is required to reach the hydrogen-dominated regime, and thus the effect of hydrogen in the hydrogen-enhanced regime should be more muted for longer chain hydrocarbons as compared to smaller hydrocarbons. As this suggests potentially more limited effects for longer carbon chain molecules of practical interest for transportation purposes (e.g., diesel, gasoline, kerosene), the effect of carbon chain length on the transition point should be examined in more detail in future study.
6.4 Effect of pressure variation on controlling chemistry

The preceding discussion of the controlling chemistry has focused largely on atmospheric conditions, based on the great degree of similarity between trends observed in the 1 and 3 atm ignition temperature results in Fig. 6.1, and the greater magnitude of hydrogen addition effects for atmospheric conditions. Despite the significantly more muted effect of hydrogen addition at elevated pressures, the controlling reactions under these conditions deserve attention. Figure 6.10 replicates the analysis found in Fig. 6.3 for 3 atm pressure conditions. As is particularly evident for the $\xi_H = 10\%$ result, the HKG zone at this elevated pressure is less dramatic, lacking the near-vertical region observed in Fig. 6.3 for the same $\xi_H$. However, the overall effect of hydrogen addition appears quite similar, with the ignition point merging into the HKG zone as $\xi_H$ increases.

Replicating the analysis of Fig. 6.7, Fig. 6.11 also reveals significant similarity in the effects of hydrogen addition on the ignition kernel, with all cases involving hydrogen addition replicating the trends discussed previously for atmospheric conditions. However, the $\xi_H = 0\%$ case exhibits significantly higher peak mole fractions for key radical species than are observed under atmospheric conditions. In fact, the $\xi_H = 0\%$ kernel is comparable to those predicted for the $\xi_H = 100\%$ case, in contrast to the atmospheric results where peak mole fractions of key radical species differ by as much as three orders of magnitude. Flux analysis further reveals that such an increase is supported at least in part through the increased production of OH from $H_2O_2$ via reaction R6.9.

$$H_2O_2(+M) \rightleftharpoons 2OH(+M) \quad \text{R6.9}$$
At atmospheric conditions, R6.9 is responsible for 24% of OH production, while R6.1 produces 29% and the remainder is produced via several reactions involving HO₂. However at 3 atm conditions, the production rate of OH via R6.9 is more than doubles, accounting for nearly half (48%) of OH production. Nonetheless, aside from the increase in the importance of R6.9 the controlling chemistry at 3 atm conditions are identical to those observed at atmospheric conditions, resulting in the similar - but muted - trends observed in Fig. 6.1.

In closing this section, it is worth noting that the SN and MN mechanisms predict different trends with respect to the effect of pressure on the ignition kernel. While the MN mechanism predicts increases in all major radical species as a function of pressure within the present range of interest, the SN mechanism - as has been shown previously in Chapter 4 - predicts that the peak mole fractions of H, O, and OH fall with increasing pressure, while HO₂ remains approximately constant and H₂O₂ increases slightly. The differing behavior between the two mechanisms is attributed to the MN mechanism’s increased reliance on H, O, and OH for n-butanol breakdown, as described Chapter 4.

6.5 Conclusions

The present study explores the impact of hydrogen addition to n-butanol on ignition temperatures in a non-premixed counterflow configuration for total fuel loading X_f = 0.15, a fuel stream boundary temperature of 380 K, a pressure-weighted strain rate of k' = 350 s⁻¹, pressures varying between 1 and 4 atm, and hydrogen addition ranging from ξ_H = 0% (pure n-butanol) to ξ_H = 100% (pure hydrogen). Two ignition temperature regimes are observed and are termed the hydrogen-enhanced regime and hydrogen-dominated regime.
Within the hydrogen-enhanced regime (0-40% hydrogen addition), ignition temperature is appreciably more sensitive to hydrogen addition at atmospheric pressure than at elevated pressure within the current pressure range as a result of a convergence in ignition temperatures of the two pure component fuels as pressure increases. Within the hydrogen-dominated regime (40-100% hydrogen), ignition temperature is largely insensitive to further hydrogen addition. Comparison to numerical results simulated using the SN and MN mechanisms reveals that both mechanisms capture this two-regime behavior at both atmospheric and elevated pressures. Additionally, the location of the transition between the two regimes is predicted well. Further analysis reveals that the controlling mechanism behind the reduction in ignition temperatures in the hydrogen-enhanced regime is a significant increase in the size of the available radical pool, which promotes fuel ignition. This increase in radical pool size is primarily mediated by the reaction \( H_2 + OH \leftrightarrow H_2O + H \) (R6.3), which serves as a gateway reaction to further chain branching reactions. Furthermore, flux analysis reveals that the reactions \( HCO + O_2 \leftrightarrow HO + CO \) (R6.5) and \( H + O_2(\pm) \leftrightarrow HO_2(\pm) \) (R6.2) are the primary reactions producing hydroperoxyl, which in turn provides 30-50% of the hydroxyl radicals needed by reaction R6.3. In the hydrogen-enhanced regime, R6.5 is primarily responsible for hydroperoxyl production, however as hydrogen addition levels increase, R6.2 becomes more prominent, eventually overtaking R6.5 as the mixture transitions to the hydrogen-dominated regime. While this effect is most prominent at atmospheric pressures, a more muted effect is observed at elevated pressures, and is mediated by identical chemistry. The competition between these reactions also suggests that the extent of the hydrogen-enhanced regime and the impact of hydrogen addition within that regime may be
impacted by “base” fuel molecule size, as an increase in the number of carbon atoms available will enhance R6.5 and delay the transition point between R6.2 and R6.5 to higher hydrogen addition levels. Based on the fact that many practical transportation fuels involve relatively long-chain hydrocarbons, this subject merits further investigation.
6.6 Figures

Figure 6.1: Counterflow ignition temperatures as a function of molar percentage of hydrogen in the fuel blend. Total fuel loading $X_f = 0.15$, $k' = 350$ s$^{-1}$, and fuel boundary temperature of 380 K. Solid lines represent results from the SN mechanism, while dashed lines indicate results from the MN mechanism.
Figure 6.2: Counterflow ignition temperatures as a function of pressure for varying hydrogen addition percentages in the fuel blend. Total fuel loading $X_f = 0.15$, $k' = 350 \text{ s}^{-1}$, and fuel boundary temperature of 380 K. (a) Comparison of experimental data to simulated data from the SN mechanism. (b) Comparison of experimental data to simulated data from the MN mechanism. (c) Comparison of 100% hydrogen experimental data to simulated results using the SN and MN skeletal mechanisms, as well as the $\text{H}_2/\text{O}_2$ model of Burke et al. [115].
Figure 6.3: Comparison of the ignition turning points and lower-branch “S-curve” behavior for varying levels of hydrogen addition at 1 atm, $X_f = 0.15$, $k' = 350$ s$^{-1}$, and fuel boundary temperature of 380 K. Simulated results are derived from the MN mechanism.
Figure 6.4: Comparison of the effect on the lower branch and ignition turning point of removing several key hydrogen-related reactions from the MN mechanism. Solid lines represent the unmodified MN mechanism solutions for 0% and 10% hydrogen addition. Symbols represent solutions for 10% hydrogen addition with selected reactions artificially removed from the MN mechanism. Solutions are for atmospheric conditions, $X_f = 0.15$, $k' = 350 \text{ s}^{-1}$, and fuel boundary temperature of 380 K.
Figure 6.5: Comparison of the H, O, and OH radical profiles for 0% and 10% hydrogen addition at the corresponding ignition turning point. Results computed for atmospheric pressure, $X_f = 0.15$, $k' = 350 \text{ s}^{-1}$, and fuel boundary temperature of 380 K using the MN mechanism. Axial position is relative to the fuel stream boundary.
Figure 6.6: Spatially-integrated $n$-butanol and hydrogen consumption rates as a function of hydrogen addition at atmospheric pressure, total fuel loading $X_f = 0.15$, $k' = 350 \text{ s}^{-1}$, and fuel boundary temperature of 380 K.
Figure 6.7: Spatially-resolved profiles of (a) H, (b) O, (c) OH, and (d) HO₂ radicals as a function of hydrogen content of the fuel blend. Results computed using the MN mechanism for atmospheric pressure, total fuel loading $X_f = 0.15$, $k' = 350 \text{ s}^{-1}$, and fuel boundary temperature of 380 K.
Figure 6.8: Spatially-resolved molar production rates of the hydroperoxyl radical related reactions; (a) 10%, (b) 40%, and (c) 80% hydrogen addition. Results computed using the MN mechanism for atmospheric pressure, total fuel loading $X_f = 0.15$, $k' = 350 \text{ s}^{-1}$, and fuel boundary temperature of 380 K.
Figure 6.9: Spatially-integrated molar production rates of total HO$_2$, R6.2 ($H + O_2(\pm M) \rightleftharpoons HO_2(\pm M)$), and R6.5 ($HCO + O_2 \rightleftharpoons HO_2 + CO$) as a function of hydrogen addition. Results computed using the MN mechanism for atmospheric pressure, total fuel loading $X_f = 0.15$, $k' = 350$ s$^{-1}$, and fuel boundary temperature of 380 K.
Figure 6.10: Comparison of the ignition turning points and lower-branch “S-curve” behavior for varying levels of hydrogen addition at 3 atm, $X_f = 0.15$, $k' = 350$ s$^{-1}$, and fuel boundary temperature of 380 K. Simulated results are derived from the MN mechanism.
Figure 6.11: Spatially-resolved profiles of (a) H, (b) O, (c) OH, and (d) HO$_2$ radicals as a function of hydrogen content of the fuel blend. Results computed using the MN mechanism for 3 atm, total fuel loading $X_f = 0.15$, $k' = 350$ s$^{-1}$, and fuel boundary temperature of 380 K.
Chapter 7: Conclusions and Future Directions

As the detailed conclusions relevant to each of the studies are provided in their respective chapters, only a general summary of the major conclusions is provided here, along with several recommendations for future directions for the non-premixed counterflow ignition experiment.

7.1 Conclusions

As described in Chapter 1, the development of combustion models relies upon high-quality reference data collected under diverse operating conditions. This dissertation describes the development of a new experimental system capable of acquiring novel ignition data in a convective/diffusive environment for atmospheric and elevated pressures. The advantages and limitations of the counterflow ignition arrangement are discussed in detail, and a comprehensive experimental characterization is completed to fully describe the experiment and provide confidence in the underlying quality of data derived from this system.

This system is then used to study the ignition behavior of alternative fuels. The study of the butanol isomers reported in this dissertation is the first to report experimental ignition results for all four butanol isomers in the convective/diffusive environment of the counterflow configuration. Experimental trends in terms of pressure-weighted aerodynamic strain rate, fuel loading, and ambient pressure are obtained for $k' = 200-400 \text{ s}^{-1}$, $X_f=0.05-0.25$, and $P=1-4 \text{ atm}$. While the mechanisms tested largely capture the experimental trends in terms of the effects of strain rate, fuel loading, and pressure, both
fail to capture the relative ranking of the isomers, predicting substantial separation between $n$-iso-/sec-butanol that is not present in the experimental results. Similar to previous efforts for other fuels in counterflow, the ignition of the butanol isomers is found to be highly sensitive to diffusion rates of fuel, however even exceptionally large changes to the Lennard-Jones parameters of key species are insufficient to explain the appreciable disparities observed between the two mechanisms employed or between the numerical and experimental results. Comparison between the treatments of $n$-butanol in the Sarathy et al. [1] and Merchant et al. [2] mechanisms reveals that the fuel breakdown pathways differ substantially, with the Merchant et al. [2] mechanism predicting significant pathways involving enols and butyraldehyde, while the Sarathy et al. [1] mechanism predicts breakdown primarily via unimolecular reactions. For other isomers, the primary differences appear in the treatment of the butene isomers, suggesting that closer inspection of these pathways would result in better predictions relative to the experimental results.

When hydrogen is blended with $n$-butanol, ignition behavior changes dramatically, with two regimes - hydrogen-enhance and hydrogen-dominated - becoming apparent. The crossover between these regimes is mediated by the relative importance of two hydroperoxyl formation pathways, namely via the formyl radical or via a third-body reaction. The effect of hydrogen addition is most apparent at atmospheric pressures, and diminishes as pressure increases between 1 and 4 atm. In comparison with the results from previous studies, the present data also suggests that the relative impact of hydrogen addition may depend on the carbon chain length of the “base” fuel, with longer molecules experiencing the hydrogen-enhanced regime over a wider range of molar hydrogen
percentages. This suggests that high molecular weight fuels may require more hydrogen addition to accomplish significant ignition enhancements relative to lighter fuels.

In closing this dissertation, it is worth commenting on the utility of the counterflow ignition configuration. As has been shown in the preceding chapters, the counterflow ignition experiment is capable of discerning comparatively subtle variations associated with structural isomerism, suggesting that such ignition data can be of practical use in model development. In Chapter 1 the usefulness of counterflow ignition data is couched in terms of highlighting the effects of transport on ignition, however it is worth noting that - as has been shown in the preceding chapters - this system also provides a useful complement to more conventional, homogeneous ignition data (e.g., shock tube and RCM) for kinetic mechanism validation. Such homogeneous systems have been used as a starting point for model development and validation, as such data ideally eliminates spatial dependencies, and significantly reduces the complexity of the calculations and their associated computational cost. This has the unintended implication that increased “weight” is placed on quasi-zero-dimensional data, as quasi-one-dimensional data are generally included only as an *a posteriori* mechanism validation. However, while such quasi-zero-dimensional systems are ostensibly unaffected by boundary conditions, this idealization obfuscates reality in several ways. For example, such systems are highly sensitive to initial conditions such as initial temperature and concentration, such that spatial non-uniformities in said quantities may significantly impact the results, hindering comparisons with both simulated results and other similar experimental data sets. Such issues are of course not unique to these experimental systems, and apply equally to steady flame measurements (e.g., flame speed and speciation studies) as well as the
configuration presently of interest, as is comprehensively addressed in Chapter 2. However, it is important to note that the counterflow ignition apparatus is sensitive to very different kinds of boundary/initial conditions, as compared to typical quasi-zero-dimensional experiments. As a result, when considering the potential for systematic errors in experimental data - and their impact on model development and validation - it is worth considering that two sets of experimental data using the same configuration could conceivably be influenced in comparable ways by the same kinds of systematic errors; this is much less likely for two experiments using completely different configurations. This issue is particularly relevant to the present dissertation due to the counterflow ignition experiment’s sensitivity to ignition-relevant chemical kinetics. While high-temperature kinetics and transport effects can be captured by steady flame phenomena, counterflow ignition data provides a bridge between flame and ignition data by including the influence of convective/diffusive processes while maintaining sensitivity to kinetic sets typically only investigated by quasi-zero-dimensional systems. As a result, the inclusion of counterflow ignition data during model development has the potential to significantly improve the robustness of such models, and the inclusion of additional diagnostic tools - as described in the following section - may allow this system to dramatically improve our understanding of the combustion kinetics of a range of practical fuels.

### 7.2 Future directions

In the preceding dissertation, it has been shown that the non-premixed counterflow ignition apparatus can provide useful insights into the ignition behavior of practical fuels.
Significant opportunities exist to utilize this system to make very meaningful advances in the understanding and modeling of practical fuels.

While a number of gaseous and liquid fuels have been investigated in the counterflow ignition configuration, the understanding of several molecule classes relevant to practical transportation fuels could be improved using the counterflow ignition configuration. For example, while an understanding of ester chemistry will be critical to the proper modelling of biodiesel, mechanisms for even the smallest esters are at their early stages, and high-quality reference data can make a significant impact on the fidelity of these models as they develop.

With regards to hydrogen addition, as mentioned in Chapter 6 the span of the hydrogen-enhanced regime seems to be dependent upon the carbon chain length of the “base” fuel. This suggests that high-molecular weight fuels could potentially benefit less from hydrogen addition than lower molecular weight fuels. Given that hydrogen addition may provide a pathway to improved engine performance and reduced emissions, this possibility should be explored in more detail.

Despite the fact that ignition is an inherently transient process, much can be learned from the steady-state responses prior to ignition. As has been shown in this dissertation, ignition is largely dependent on the growth of the ignition kernel. If components of this kernel can be measured, this can greatly aid in constraining the kinetic mechanisms and improve their predictive abilities. Measurements such as OH-Planar Laser-Induced Fluorescence (OH-PLIF) along the lower branch of the S-curve can help to define the ignition kernel growth rate as a function of temperature, a constraint which could significantly improve model fidelity by constraining the models in terms of ignition
kernel size. Moreover, as has been shown in this dissertation, proper predictions of intermediate species such as butene are vital for the overall fidelity of butanol models specifically, and combustion models more generally. As was shown in Chapter 5, for example, the Sarathy et al. [1] and Merchant et al. [2] models predict significantly different production rates of the butene isomers. Spatially-resolved speciation studies investigating the concentration of key intermediates along the lower branch of the S-curve may be able to resolve such disparities, and further constrain the models to improve their predictive abilities across a wide range of conditions.

Finally, as recently pointed out by Shan and Lu [116], while ignition and extinction are typically identified computationally by “static” turning points in the “S-curve” as described in Chapter 2, steady-state solutions leading up to a turning point may not necessarily be dynamically stable, such that the experimental transition state may not correspond to the computational turning point. This can result in significant inherent disparities between computational and experimental results that may be incorrectly attributed to mechanism deficiencies. Shan and Lu [116] computationally investigated methane/air and dimethyl ether (DME)/air mixtures in a PSR configuration, finding that for DME/air mixtures, multiple ignition/extinction turning points were found, and that for both extinction turning points, solutions became unstable well prior to the static extinction turning points. For methane-air mixtures, no such disparity was observed. A related analysis conducted by Sung et al. [117] on pulsating instabilities in rich hydrogen/air flames observed that pulsating extinction occurred prior to the conventional steady-state extinction state, indicating a narrower stable flame range and a corresponding discrepancy between experimental and steady-state computational
definitions of extinction. Specific to the fidelity of the results in the preceding dissertation, two points are worth highlighting. First, the transition from stable to unstable solutions corresponded with the ignition and extinction turning points for methane/air in the work of Shan and Lu [116]. A lack of correspondence was only observed for DME/air mixtures, which exhibit negative temperature coefficient (NTC) behavior. Second, the “premature” instability is only observed for extinction turning points, and Shan and Lu [116] observed no such issues with the ignition turning point. As a result, since the present study is focused on the ignition of a fuel that does not exhibit NTC behavior, such issues are not expected to affect the results presented herein. Nonetheless, due to the important implications such a disparity would have on the interpretation of the results, a stability analysis directly addressing this issue deserves attention in future efforts to conclusively determine the stability at the ignition turning point for the specific fuel in question.
References


Appendix A: Skeletal Mechanisms

The complete skeletal mechanisms are available from the publisher of the journal articles associated with this dissertation. Size information is given in Table A1 and a list of species is given in Table A2. For species nomenclature, please see the glossaries associated with the original models of Sarathy et al. [1] and Merchant et al. [2].

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