Autoignition chemistry of liquid and gaseous fuels in non-premixed systems

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ABSTRACT

Autoignition Chemistry of Liquid and Gaseous Fuels in Non-premixed Systems

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Heat-release in CI engines occurs in the presence of concentration and temperature gradients. Recognizing the need for a validation of chemical kinetic models in transport-affected systems, this study employs non-premixed systems to better understand complex couplings between low/high temperature oxidation kinetics and diffusive transport. This dissertation is divided into two sections.

In the first section, a two-stage Lagrangian model compares model prediction of ignition delay time and experimental data from the KAUST ignition quality tester, and ignition data for liquid sprays in constant volume combustion chambers. The TSL employed in this study utilizes detailed chemical kinetics while also simulating basic mixing processes. The TSL model was found to be efficient in simulating IQT in long ignition delay time fuels; it was also effective in CVCC experiments with high injection pressures, where physical processes contributed little to ignition delay time.

In section-two, an atmospheric pressure counterflow burner was developed and fully validated. The counterflow burner was employed to examine the effects of molecular structure on low/high temperature reactivity of various fuels in transport-affected systems. These effects were investigated through measurement of conditions of extinction and ignition of various fuel/oxidizer mixtures. Data generated were used to validate various chemical kinetic models in diffusion flames. Where necessary, suggestions were made for improving these models.
For hot flames studies, tested fuels included C3-C4 alcohols and six FACE gasoline fuels. Results for alcohols indicated that the substituted alcohols were less reactive than the normal alcohols. The ignition temperature of FACE gasoline was found to be nearly identical, while there was a slight difference in their extinction limits. Predictions by Sarathy et al. (2014) alcohol combustion model, and by the gasoline surrogate model (Sarathy et al., 2015), agreed with the experimental data. For cool diffusion flames studies, tested fuels included butane isomers, naphtha, gasolines and their surrogates. Results revealed that the addition of ozone successfully established cool flames in the fuels at low and moderate strain rates. Numerical simulations were performed to replicate the extinction limits of the cool flames of butane isomers. The model captured experimental trends for both fuels; but over-predicted their extinction limits.
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LIST OF ABBREVIATIONS

SI                 spark ignition engine
CI                 compression ignition engine
HCCI              homogeneous charge compression ignition engine
PPCI              partially premixed compression ignition engines
GDCI              gasoline direct-injection compression ignition engines
LTC               low temperature chemistry
HTC               high temperature chemistry
NTC               negative temperature coefficient
KHP               ketohydroperoxide radical
RCM               rapid compression machine reactor
JSR               jet-stirred reactor
ST                shock tube
RCM               rapid compression machine
DME               dimethyl ether
PMT               photomultiplier
MFC               mass flow controller
LDV               single-point laser doppler velocimetry
PLIF              planar laser-induced fluorescence
$\tau_r$          chemical reaction time
$\tau_d$          diffusion time
$a$               global strain rate
$U_O$             oxidizer uniform velocity from oxidizer nozzle
$U_F$             fuel uniform velocity from fuel nozzle
$L$               separation distance between fuel and oxidizer nozzles
$a_2$             local strain rate of oxidizer side
$X_{f,1}$  fuel mole fraction  
$T_1$  temperature of fuel jet  
$\rho_1$  density of fuel jet  
$V_1$  fuel flow velocity normal to stagnation plane.  
$X_{O2,2}$  oxidizer mole fraction  
$T_2$  oxidizer jet temperature  
$\rho_2$  density of oxidizer jet  
$V_2$  oxidizer flow velocity normal to stagnation plane  
IQT  ignition quality tester  
TSL  two-stage Lagrangian  
CVCC  constant volume combustion chamber  
ECN  engine combustion network  
LLNL  Lawrence Livermore National Laboratory  
CFD  computational fluid dynamic  
$\tau_f$  first-stage ignition delay time  
$\tau_s$  second-stage ignition delay time  
$\tau_t$  total ignition delay time  
$T_{ef}$  temperature at the end of first-stage ignition delay time  
$A$  jet cross-sectional area  
$Y_k$  mass fraction of species k  
$K$  number of species  
$h_k$  enthalpy of species k  
$\omega_k$  species molar production rate  
$W_k$  molecular weight of species k  
$\rho$  density  
$\rho_0$  jet source density  
$m$  mass flow rate in the jet
\( m_o \)  \( m_o \)  initial jet mass flow rate

\( c_p \)  \( c_p \)  specific heat (at constant pressure)

\( q_R \)  \( q_R \)  radiation loss

\( f \)  \( f \)  fuel mixture fraction

\( a_{j,k} \)  \( a_{j,k} \)  number of atoms of element \( j \) in species \( k \)

\( M_j \)  \( M_j \)  atomic mass of element \( j \)

\( \varepsilon \)  \( \varepsilon \)  number to avoid the singularity where \( f_h \) passes stoichiometric

\( B \)  \( B \)  expression that controls the homogeneous stream entering the flame-sheet reactor
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1 Chapter 1: Introduction

1.1 Background and motivation

Global demand for energy is on the rise, yet more than a billion people are living without electricity and cars. According to the British Petroleum forecast [1], a significant portion of this energy demand originates in the transportation sector, which is largely supplied by hydrocarbon-based fuels (see Fig. 1-1). With this trend expected to continue for at least the next few decades, the best way to comply with stringent emission regulations is to enhance the efficiency of the internal combustion engine.

![Figure 1-1: Global energy forecast; total energy consumption by sector; shares of primary energy-right [2]](image)

The last few decades have witnessed a dramatic advancement in engine design and operation strategies that ensure better fuel and engine interaction. This progress has led to the development of numerous advanced combustion engines (ACE) strategies, such as the gasoline direct injection
(GDCI) engines and the partially premixed compression ignition (PPCI) [3, 4]. These technological advancements are increasingly becoming attractive because they deliver high efficiency with less NOx and particulate emissions [5]. The success of combustion research in ACEs and advanced fuels depends on comprehensive understanding of chemical kinetics. It has been previously reported [6] that heat release and other chemical processes in these engines depends largely on autoignition kinetics of the fuel-air mixture. Therefore, a better understanding of autoignition chemistry of the fuel/oxidizer mixture is also important for the co-optimization of these engines. This can be facilitated by designing accurate chemical kinetic models.

Development of chemical kinetic models relies on well-defined fundamental experiments for validation. These canonical experiments can be classified either as homogeneously mixed or non-homogeneously mixed experiments. Homogeneous experimental setups include facilities such as the shock tube (ST) [7], jet-stirred reactor (JSR) [8, 9] and the rapid compression machine (RCM) [10, 11]. As reviewed recently [12], many studies have been performed on autoignition chemistry in these systems, partly because they are easily modeled–even using detailed kinetic models as they are defined in terms of time-scale only. This benefit influenced the advancement in building chemical mechanisms used in modelling homogeneous facilities. However, these systems are mostly limited to premixed gas phase studies. Ignition and combustion events in homogeneous systems occur mainly due to radical growth and temperature increases as a result of heat release from exothermic reactions, without considering additional effects from the flow field and molecular diffusion. In practical combustion engines however, in-homogeneity exists in both temperature and mixture composition. And as noted by C.K Law et al. [13] when flow and mixing times scales are comparable to the chemical reaction time scale, convective-diffusive processes are strongly coupled, and these can affect the evolution of
radicals, modifying product distribution and ignition processes. It is important therefore, to validate chemical kinetic models against well-characterized non-homogeneous experiments. This dissertation will include the use of non-homogeneous systems, the ignition quality tester, spray ignition in constant volume combustion chambers and diffusion flames to study autoignition of various fuels and generate experimental data for validation of chemical kinetic models.

Ignition delay time is a widely used parameter to validate chemical kinetic models. It usually describes the global effect of all the chemical processes in combustion and product formation; thus, it is often used as a measure of the overall global reactivity of the fuel. Therefore, validating chemical kinetic models against ignition delay time data can aid in understanding overall global performance of mechanisms. In practical combustion systems, ignition delay time is the time difference between the start of injection (SOI) to the start of combustion (SOC). It consists of a physical ignition delay (atomization, vaporization and mixing of fuel and air) and a chemical ignition delay. The chemical ignition delay period of the overall ignition delay occurs once the gaseous fuel/air mixture (with a suitable temperature and mixture ratio) is obtained, so that a rapid chemical reaction can be initiated [14, 15].

Ignition temperature and extinction measurements in counterflow diffusion flames provide additional experimental data to validate and improve chemical kinetic models. These two properties are sensitive to both transport and chemistry. However, as recently outlined [16], these combustion properties received less attention, due mainly to the difficulty associated with modelling these systems, especially if the boundary conditions are not well-defined. Also, modelling ignition and extinction of diffusion flames is quite difficult, requiring both time and length scales. Therefore, in this dissertation, chemical kinetic models will be validated against ignition delay time data from the IQT, and ignition temperature/extinction conditions from
diffusion flames. In the sections that follow, a detailed description of the IQT and diffusion flames is provided.

1.2 **The IQT and constant volume combustion chambers**

Constant volume combustion chambers (CVCC), such as the KAUST ignition quality tester (IQT) [3], or spherical combustion chambers at [17, 18], offer a good platform for exploring the ignition properties of liquid sprays. An IQT is a constant volume combustion chamber with a spray injection system. It is designed to measure the ignition delay time of various fuels, including low volatility fuels [19-21]. The temperature, pressure, mass of fuel injected and charge oxygen concentration in an IQT can be well controlled, making it a useful system for experimental data on the validation of chemical kinetic models, provided that appropriate simulation tools are available. As reported in [20], the small fuel mass requirement of an IQT makes it an excellent system for the study of ignition delay times in fuels not readily available in large quantities. Figure 1-2 shows a schematic diagram of the KAUST IQT [3]. Briefly, it is a constant volume combustion chamber with capacity of 0.21L. The chamber is initially filled with an oxidizing agent, which can be pressurized up to 21bar. Temperatures within the chamber are maintained around 670-860K. A liquid spray is injected inside the hot chamber using a single hole s-type injector.

Ignition delay time data from the IQT has been used previously by [22] to validate n-heptane, iso-octane, and multi-component mixtures of different hydrocarbons. The majority of these studies used either detailed chemical kinetic models and closed reactor models in chemkin-pro software, or reduced chemical kinetic models in computational fluid dynamic (CFD codes) for simulation. Reduction of detailed chemical kinetic models for use in CFD codes is sometimes accompanied by a loss in the fidelity of the models in capturing ignition events. On the other
hand, closed-reactor models do not take into account mixing with surrounding gasses, and they assume ignition to be mainly a function of initial conditions, such as the mixture composition and temperature. As mentioned in the previous sections, in practical combustion systems the mixture rate of jets with surrounding gasses also affects ignition delay time of the fuel air mixture. Therefore, to accurately predict ignition processes and validate models in the IQT and the CVCCs, it is necessary that a modeling code encompass both mixing and the ability to handle detailed chemistry.

The two-stage Lagrangian model (TSL) employed in this study describes mixing as a two-stage process observed in a frame moving downstream with the normal fluid motion. The model can adopt detailed chemical kinetics while also simulating basic mixing processes important in turbulent gaseous jet diffusion flames [15, 23-28]. So far, few studies have reported using the TSL model. These include the works of Pickett et al. [26], Broadwell et al. [27], and Han et al. [28]. Though these studies provided insight into how the TSL works, they based their focus on soot and NO\textsubscript{x} emission, without an emphasis on ignition. These studies used a network of two reactors; but in the present work, only the homogeneous reactor, which represents the initially fuel-rich mixture in the spray jet, was employed. Entrained mass from the ambient mixed with the jet fluid in a stoichiometric amount at the flame sheet of the diffusion region; then, products from the flame sheet region moved to the homogeneous core reactor where they mixed homogenously with the incoming fuel jet, starting from the jet nozzle and moving downstream in a Lagrangian framework. This procedure continued to the flame tip, where the remaining fuel was consumed [25-27]. The rate of entrainment was given by a well-established correlation developed for jet mixing. Detailed explanation, including the conservation energy equations describing the flow field, is given in Chapter 2.
Figure 1-2: Schematic illustration of the KAUST ignition quality tester (IQT) [3]

1.3 Counterflow flame experiments and simulations

Basic understanding of the effect of a non-uniform flow field on fuel autoignition would provide a guide for modelling combustion processes occurring in practical combustion engines. This is partly because in some advanced combustion engines, such as the PPCI and GDCI engines, fuel autoignition occurs before the complete mixing of fuel and oxygen; hence there is a high occurrence of non-uniform distribution in temperature and concentration of fuel air mixtures in the engine. This in-homogeneity would result in some additional time for convective-diffusive transport for heat and mass, in addition to the chemical time scale which might affect an ignition event [4, 29]. The fuel and oxidizer stream in the counterflow are initially separated and are brought to the reaction flow field by diffusion, where mixing and reaction occur. Figure 1-3 shows a schematic diagram of the counterflow configuration with opposing nozzles.
An important parameter for information on the characteristic flow time in the counterflow diffusion flames is the velocity gradient, or global strain rate. The strain rate, \(a\) (Eq. (1-1)), is defined as the normal gradient of the normal component of the flow velocity; and this value varies from the exits of the fuel to the oxidizer duct [31]. It represents the physical effects of diffusion and transport on the thickness of the flame and mixing layer. The strain rate increases with increased flow velocity, or decreased separation distance between fuel and oxidizer nozzles.

\[
\alpha = \frac{2|V_2|}{L} \left( 1 + \frac{|V_1|\sqrt{\rho_1}}{|V_2|\sqrt{\rho_2}} \right) 
\]  
Equation (1-1)

Measurements of ignition and extinction conditions in counterflow diffusion flames provide an additional platform for validating and improving chemical kinetic models in a transport-affected environment. As mentioned earlier, these properties have received less attention in the past,
partly due to the difficulty in modeling them and the problems associated with building a counterflow experimental setup. In light of new combustion strategies, such as the GDI and PPC, rigorous validation and improvement of chemical kinetic models in diffusive systems is essential.

A limiting issue in the use of available detailed kinetic models for simulating flames is their inherently large size and computational cost when used for simulations. For this reason, a method of direct-relation graph, with expert knowledge (DRG-X) [32], together with isomer lumping, was used to generate a skeletal mechanism with fewer species and reactions from the detailed models. The skeletal models generated had similar chemical fidelity as the original detailed models and were easily used for flame simulation in this study.

1.4 Chemical kinetic models describing the combustion of hydrocarbon fuels

Development of chemical kinetic models for fuels combustion follows many reaction pathways and intermediates that are developed through several elementary steps. These pathways are divided into different classes, depending on temperature range. Combustion kinetics of hydrocarbon fuels is different at low- and high temperature conditions, as such kinetic mechanisms change continuously with the temperature [22].

1.4.1 Intermediate and high temperature combustion

Intermediate and high temperature combustion occurs at temperatures above 900K. At this temperature range, reaction occurs in a very short time scale. The reactions proceed either through unimolecular decomposition of the fuel to produce two alkyl radicals, or through H-abstraction of the fuel, to produce an alkyl radical with a H-atom. Unimolecular decomposition of the fuel is a bond cleavage at C-H or C-C bond. Breaking the C-C bond produces high
activation energy (\( \sim 90 \text{ kcal/mol} \)), and therefore can only occur at relatively high temperatures (\( \geq 1300 \text{K} \)) [33]. The reaction below illustrates an example of unimolecular decomposition:

\[
\text{RH} + (M) \rightarrow R' + R''
\]

RH is the fuel molecule, (M) is collision partner (such as AR, He), R' and R'' are alkyl radicals

At relatively lower temperatures (\( \leq 1300 \text{K} \)), fuel can be abstracted by small radicals, mainly, OH, O, HO\(_2\), CH\(_3\), etc. (see reaction below). H-abstraction reaction has lower activation energy, so it requires a lower environmental temperature to proceed. H atoms can be abstracted from primary, secondary, or tertiary carbon positions; the primary carbon site is one whose atom is bonded to a neighboring carbon atom and three other H atoms. The secondary C-site is bonded to two neighboring carbon atoms and two other H atoms; while a tertiary carbon site is attached to three carbons and one H atom. The rate constant for abstraction depends on the type of H atom being abstracted, the radical species. Primary carbon H atoms have the strongest C-H bond energies and are therefore the most difficult to abstract, while tertiary H atoms are weakest and most easily abstracted. Below is an illustration of H-abstraction reaction. OH, H and O are the most reactive radicals for abstraction; but O radicals are usually present in small quantities, except in experiments involving ozone, as can be seen shortly in this dissertation. HO\(_2\) radicals are notably less reactive; but their reaction leads to H\(_2\)O\(_2\) formation, which decomposes to two OH radicals at high temperatures:

\[
\text{RH} + (\text{OH, O, H, CH}_3, \text{HO}_2) \rightarrow R' + (\text{H}_2\text{O, OH, H}_2, \text{CH}_4, \text{H}_2\text{O}_2)
\]

Where RH-fuel molecule, \( R' \) is an alkyl radical.

Once formed, the alkyl radical undergo a beta scission at the abstracted C-H or C-C to form an alkene and a radical according to the reaction below:
\[ R^* \rightarrow \text{alkene} + R'(\text{OH, H, CH}_3) \]

Abstraction of hydrogen from a different C-H site (1°, 2°, or 3°) produces different radicals. For example, consider a simple propane molecule (see reactions below): when H is abstracted from the primary C-H site, it yields an n-propyl radical; while an abstraction from a secondary C-H site gives an iso-propyl radical. Further β scission of the n-propyl radical yields an alkene (C\(_2\)H\(_4\)) and a methyl (CH\(_3\)) radical. On the other hand, iso-propyl radical undergoes a β scission to produce an iso-propene (i-C\(_3\)H\(_6\)) and hydrogen (H) radical. The alkene produced is usually attacked by an O atom at the double bond, or it could undergo further H-abstraction to produce allylic compounds, which are further oxidized to produce oxygenated and non-oxygenated small species. The oxidation mechanism of these small species is described by the chemistries of H\(_2\)/CO/CH\(_4\) schemes:

\[
\begin{align*}
\text{C}_3\text{H}_8 + (\text{OH, O, H, CH}_3, \text{HO}_2) & \rightarrow \text{n-C}_3\text{H}_7 + (\text{H}_2\text{O}, \text{OH, H}_2, \text{CH}_4, \text{H}_2\text{O}_2) \\
\text{C}_3\text{H}_8 + (\text{OH, O, H, CH}_3, \text{HO}_2) & \rightarrow \text{i-C}_3\text{H}_7 + (\text{H}_2\text{O}, \text{OH, H}_2, \text{CH}_4, \text{H}_2\text{O}_2) \\
\text{n-C}_3\text{H}_7 & \rightarrow \text{C}_2\text{H}_4 + \text{CH}_3 \\
\text{i-C}_3\text{H}_7 & \rightarrow \text{C}_3\text{H}_6 + \text{H}
\end{align*}
\]

1.4.2 **Low temperature combustion**

Low temperature combustion refers to the sequence of events that occur at temperatures around 500-700K. The chemistry describing low temperature combustion is much more complicated than that of high temperature chemistry. Low temperature oxidation is of practical importance to combustion phenomena such as engine knock, autoignition and even soot formation [30]. First developed by the Soviet scientist, Nikolai Semenov [34], and later modified by Benson in 1981 [35], the simplified low temperature combustion scheme is given in Fig. 1-4. LT chemistry
begins with the addition of molecular oxygen (O2) to the alkyl radicals (R•) to produce an alkylperoxy (RO2•) radical. The fate of this radical is determined by temperature. At sufficiently low temperatures (less than 500K), the equilibrium favors RO2 propagation. RO2 isomerizes to the hydroperoxyalkyl radical (i.e., QOOH), which later reacts with another O2 molecule to form O2QOOH; this molecule isomerizes and decomposes to ketohydroperoxide (KHP), plus two OH radicals. This is the low temperature chain branching pathway. At temperatures above 500K, two other pathways compete with the LT branching pathway.

Figure 1-4: Summary of the low temperature oxidation chemistry, M. Mehl lecture slide, CCRC workshop, 2014

When the temperature is high, the RO2 radical becomes unstable and dissociates back to R and O2. The alkyl radical then undergo a β-scission cleavage that reverts to the high temperature
described above. RO₂ can also go through a concerted elimination reaction to form alkene and a hydroperoxyl radical (HO₂). These two paths compete with the RO₂ isomerization and this competition results to a reduction in OH formation, and thus a decrease in overall low temperature reactivity.

1.5 Premixed and non-premixed combustion systems

Chemical kinetic models are often validated against data from fundamental experimental facilities whose flow patterns are well known. These experimental facilities are commonly grouped as either premixed or non-premixed systems. The two terms describe the level to which the fuel is mixed and the oxidizer in the systems before reaction occurs [30]. In non-premixed systems, the fuel and the oxidizer are initially separated; the two streams are brought to the reaction zone as a result of the molecular diffusion of the reactants and radicals. Non-premixed systems are sometimes referred to as diffusive because diffusive transport is required to mix the fuel and oxidizer streams at the molecular level.

In premixed systems, the fuel and the oxidizer are fully mixed before they are brought to the reaction zone. Diffusion could still be required in premixed systems to bring the premixed fuel/oxidizer--and even heat--to the reaction zone, and to transport the products away from the reaction zone. Non-premixed systems are sometimes called non-homogeneous reaction systems, referring to the existence of temperature and concentration gradients, while premixed system are homogeneous systems, indicating the absence of such gradients. Examples of premixed fundamental experiments include the shock tube (ST) [36], jet-stirred reactors [9] and the rapid compression machine [37]. Experimental data derived from these systems offer information on reaction pathways as well as rate constants of elementary reactions [12]. Facilities for the studies of non-premixed combustion include the counterflow diffusion flames [38-44]. Premixed
combustion has a practical application in homogeneous charge ignition, while non-premixed combustion is typical in diesel and PPCI engines, and even in turbines.

In premixed combustion, mixing occurs rapidly, so the time scale for mixing is very short compared to the chemical time scale, and the role of transport in the evolution of species is usually neglected. Also, in these systems, all spatial dependencies are suppressed; thus, growth of radicals and subsequent combustion events depends only on time [12, 30]. As a result of this advantage, premixed systems can easily be modeled with fewer computational resources—even with detailed kinetic models. However, as recently noted by Egolfopoulos et al. [12] and Reuter et al. [45], the assumption of ideality, adiabaticity, absence of spatial non-uniformity, short mixing time scales, constant temperature and pressure, pre-specified initial radical concentration, and the definition of zero time—among other assumptions—generates many concerns, especially for long ignition delay time fuels at low temperatures.

Previous studies have suggested the need to validate chemical kinetic models in non-premixed environments [45-48]. In such systems, the time scales for convective-diffusive processes is nearly comparable to the chemical time scale. This results in complex interaction between species and radicals, and under this circumstance, both mixing and chemistry contribute to combustion events. The data generated from these setups enables validation of both transport and kinetics in reacting flows. Modeling combustion events in non-premixed systems is difficult, requiring both time and length scales. However, such rigorous validation of kinetic models in non-homogeneous environments is important to ensure that both chemistry and species transport data can be relied upon to predict various complex phenomena, such as heat release and other flame properties.
1.6 Outline of the dissertation research

The study which resulted in this dissertation was motivated by the need to validate chemical kinetic models in well-defined non-premixed systems where chemistry, molecular transport and mixing contribute to the evolution and progress of ignition events. For this reason, this work is divided into two parts: the first part employs the TSL to compare model prediction with experimental data from the KAUST IQT and other constant volume combustion chambers; while the second part involves the use a well characterized counterflow diffusion burner to measure critical conditions of cool and hot flame ignition/extinction. The data generated from the second part validates available chemical kinetic models in transport affected environments. Specific objectives and their respective chapters are as follows:

- Section one: In this section, TSL is employed to model the ignition quality tester and two other constant volume combustion chambers. The aim of this segment is to describe the ability of TSL to reproduce ignition events in the high pressure CVCC and IQT, using detailed kinetic models. Physical and chemical processes affecting ignition events of fuels in these CVCC’s are then compared. The first section includes chapters 1, 2 and 3.
  - Chapter 1 is a brief introduction and background of the thesis.
  - Chapter 2 describes TSL modelling of ignition processes in the ignition quality tester (IQT) and constant volume chambers (CVCC).
  - Chapter 3 deals with modelling ignition processes of palm-oil biodiesel and diesel fuels using a two-stage Lagrangian approach.

- Section two: In this section, the counterflow facility is employed to clarify the effects of fuel molecular structure on the low and high temperature reactivity of classic and alternative fuels in transport affected systems. These effects were investigated through measurements of
critical conditions of extinction and ignition of various fuel/oxidizer mixtures in hot and cool diffusion flames. The data generated was used to validate various chemical kinetic models. Where necessary, suggestions were offered to improve these models. This section comprises chapters 4-8. Chapters 4, 5 and 6 cover hot flame studies, while chapters 7 and 8 describe cool diffusion flame studies.

- Chapter 4: Chapter 4 begins with the development of a well-characterized counterflow diffusion facility for both hot and cool flame studies. The setup was comprehensively validated using previous experimental data by Humer et al. [49] and velocity profile measurements. The second section of chapter 4 describes the procedure used to generate skeletal models with fewer species.

- Chapter 5: In this chapter, the effects of substitution on counterflow hot flame ignition and extinction of C₃-C₄ alcohols is examined. N-propanol, iso-propanol, n-butanol and iso-butanol fuels where investigated. An alcohol model (Sarathy et al. [50]) was used to compare model prediction with experimental measurements.

- Chapter 6: Chapter 6 investigates the counterflow hot diffusion flame ignition and extinction of FACE gasoline fuels. The high temperature reactivity of six FACE gasoline fuels, FACE (A, C, F, I, J and G), were studied under various strain rates and fuel loadings. The experimental measurements were numerically simulated using a gasoline surrogate model (Sarathy et al. [37]).

- Chapter 7: This chapter describes the cool diffusion flames of butane isomers activated by ozone addition to the counterflow configuration. It clarifies the coupled effects of heat release, low temperature oxidation chemistry and molecular transport in cool diffusion flames.
Chapter 8: Chapter 8 investigates the cool diffusion flame properties—gasolines and naphtha—with varying octane ratings and their surrogate mixtures. The effects of molecular structures and octane ratings on low temperature reactivities of the fuels in diffusion flames are examined.

Chapter 9: Chapter 9 presents a summary and conclusions reached from this dissertation and propose possible future research that may take advantage of TSL and counterflow to understand the detailed effect of fuel structure on low/high temperature reactivity of different fuels in non-homogeneous systems.

1.7 List of publications


9. A. Katoch, **A. Alfazazi**, S.M. Sarathy, S. Kumar, “Laminar Burning Velocity Of C1-C4 Alcohols at Elevated Temperatures” Submitted to *Fuel*

10. A. Katoch, **A. Alfazazi**, S.M. Sarathy, S. Kumar, “Laminar Burning Velocity of pentanol” Accepted in *Fuel*


**Journals in preparation**

12. **A. Alfazazi**, A. Secco., A. Najjar., S. Mani Sarathy, Cool diffusion flames of practical liquid fuels in the counterflow. For submission to *Combustion and Flame*.


**Conference Proceedings**


**Poster Presentations**

Chapter 2: Two-Stage Lagrangian modeling of ignition processes in an ignition quality tester and constant volume combustion chambers

In this chapter, the ignition characteristics of iso-octane and n-heptane in an ignition quality tester (IQT) were simulated using a two-stage Lagrangian (TSL) model, which is a zero-dimensional (0-D) reactor network method. The TSL model was also used to simulate ignition delay of n-dodecane and n-heptane in a constant volume combustion chamber (CVCC), results of which are archived in the Engine Combustion Network (ECN) Library (http://www.ca.sandia.gov/ecn). A detailed chemical kinetic model for gasoline surrogates from the Lawrence Livermore National Laboratory (LLNL) was utilized for the simulation of n-heptane and iso-octane. Additional simulations were performed using an optimized gasoline surrogate mechanism from RWTH Aachen University. Validations of the simulated data were also performed using experimental results from an IQT at KAUST. To simulate n-dodecane in the CVCC, two n-dodecane kinetic models from the literature were utilized. The primary aim of this study is to test the ability of TSL to replicate ignition timings in the IQT and the CVCC. Agreement between the model and the experiment was acceptable, except for iso-octane in the IQT and n-heptane and n-dodecane in the CVCC. The ability of the simulations to replicate observable trends in ignition delay times (in regard to changes in ambient temperature and pressure), allowed the model to clarify the reactions contributing to ignition. Thus, the TSL model was further employed to investigate the physical and chemical processes responsible for controlling the overall ignition under various conditions. The effects of exothermicity, ambient pressure, and ambient oxygen concentration on first-stage ignition were also studied. Increasing ambient pressure and oxygen concentration shortened overall ignition delay time but did not affect timing of the first-stage ignition.
Additionally, the temperature at the end of the first-stage ignition increased at higher ambient pressures and oxygen concentrations.

A sensitivity analysis was performed using the TSL model to define the reactions controlling the overall ignition process. The present TSL modeling approach demonstrated the suitability of detailed chemical kinetic models to clarify spray combustion processes.

2.1 Introduction
Greater understanding of physical and chemical processes that occur during autoignition is paramount to the development of advanced combustion engine technologies and future fuels. Such engines include homogeneous charge compression ignition (HCCI) engines and low temperature combustion (LTC) engines. Combustion processes in these engines are dominated by the kinetics of intermediate and low temperature ignition [51]. Autoignition is related to the increased rate of chain branching reactions that drive a combustion system to completion in a short period. More knowledge about this phenomenon is required to improve engine performance, reduce NOx and CO₂ emissions, and improve fuel economy. Such knowledge can be gained from the development and application of simulation tools with accurate chemical kinetic models.

The development of reliable chemical kinetic models for autoignition relies on well-defined experiments for validation. These include experiments in homogeneous systems such as shock tubes [7, 52, 53], rapid compression machines [10, 54-58], and jet stirred reactors [59]; however these systems are limited largely to gas phase studies. Heterogeneous combustion facilities, such as ignition quality testers (IQT), offer an alternative to explore the ignition properties of liquid sprays. An IQT is a constant volume combustion chamber with a spray injection system; it is
designed to measure the ignition delay time of various fuels, including low volatility fuels [60]. The temperature, pressure, mass of fuel injected and charge oxygen concentration in an IQT can be well controlled, making it a useful system for experimental data to validate chemical kinetic models--provided that the appropriate simulation tools are available. As reported in [60], the small fuel mass requirement in an IQT makes it an excellent system for study of ignition delay times in fuels not readily available in larger quantities. Another experimental facility used in generating data for development of chemical kinetic models and computational fluid dynamic (CFD) simulations, is a constant volume combustion chamber (CVCC) [61-65]. This is a high-pressure facility which generates data for the Engine Combustion Network (ECN) [23, 24, 66], a library containing diesel spray experiments at various engine-relevant operating conditions.

In practical combustion systems, ignition delay time is the difference between the start of injection (SOI) to the start of combustion (SOC). It consists of a physical ignition delay (atomization, vaporization and mixing of fuel and air) and a chemical ignition delay. The chemical ignition delay period of the overall ignition delay occurs once a gaseous fuel/air mixture with suitable temperature and mixture ratio is obtained, so that fast chemical reactions can be initiated [14, 15]. The ignition delay in an IQT and a CVCC includes both physical and chemical ignition delay periods; therefore, it is required that a modeling code encompass both mixing and chemical kinetics to accurately predict ignition processes in these facilities. The two-stage Lagrangian model (TSL) employed in this study describes mixing as a two-stage process seen in a frame moving downstream with the normal fluid motion. The model can adopt detailed chemical kinetics, and simulating basic mixing processes important in turbulent gaseous-jet diffusion flames [15, 23-28].
To date, only a few studies have reported using the TSL model. These include the works of Pickett et al. [26], Broadwell et al. [27], and Han et al. [28]. Though these studies provided insight into how the TSL works, their focus was on soot and NO\textsubscript{x} emission, with no emphasis on ignition. Using the TSL, Meijer et al. [23] studied the effects of mixing on ignition delay time of a diesel fuel surrogate in a constant volume combustion chamber. They found that, as a result of overmixing, second-stage ignition delay time of diesel fuel increased as the injection pressure increased from 1000 to 2000 bar, while the trend of first-stage ignition showed the opposite result. Cung et al. [67] studied the effect of temperature on ignition delay time of DME in a high-pressure facility using the TSL model. The present study is among the few of its kind to use the TSL model to investigate, in detail, the factors controlling ignition processes. The ignition delay times of iso-octane and n-heptane in an IQT are examined in this study. The model was also used to simulate CVCC ignition delay data of n-dodecan and n-heptane, available in the ECN library [66]. The study of iso-octane and n-heptane ignition delay time is especially important because these are primary reference fuels (PRF) for octane ratings. n-heptane and n-dodecane are used as diesel fuel surrogates [68-70].

The ignition properties of iso-octane were previously investigated in shock tubes and RCMs in [57, 70, 71]. However, little effort was made to study ignition properties of iso-octane in IQTs. Similarly, the ignition characteristics of n-heptane fuel were extensively investigated in RCMs and shock tubes in [7, 58, 68, 71]. n-heptane ignition was investigated experimentally and numerically in an IQT by Bogin et al. [19, 20, 72]. Key to the outcome of their study was the exhibition of negative temperature coefficient (NTC) behavior by alkanes, including C7 isomers. They also observed the two stage behavior of alkanes in the NTC region. Dodecane ignition properties using CVCC facilities were also reported in [73-75]. Most numerical studies on
ignition in IQTs or CVCCs adopted reduced chemical kinetic models. Alternatively, to study the ignition properties of these fuels in an IQT and CVCC, the simpler TSL modeling tool can accommodate high-fidelity detailed kinetic models at a reduced computational cost.

This work tests the ability of the TSL model to reproduce trends in the ignition delay time of iso-octane and $n$-heptane in an IQT, and $n$-heptane, and $n$-dodecane in the CVCCs. The aim of this study is to shed light on the ignition properties of various fuels and conditions under which a TSL model can be applied. An investigation of the physical and chemical processes affecting ignition delay times of iso-octane fuel under IQT conditions is also conducted. Concerning IQT study, simulations were validated using experimental data from the KAUST research ignition quality tester (KR-IQT) [76], while for the CVCC, validations were performed using archived ECN data [66] at various charge temperatures and pressures.

2.2 Methodology

2.2.1 TSL model

The two-stage Lagrangian model was used for a zero-dimensional (0-D) simulation of iso-octane, $n$-heptane and $n$-dodecane spray combustion processes; this is a FORTRAN based code that calculates the species mass fractions, reaction rates, and temperature in a non-premixed turbulent jet. Unlike other 0-D modeling tools, the TSL model was introduced to preserve the ability to use detailed chemical kinetic models, while also simulating basic mixing processes important in turbulent gaseous jet diffusion flames [25]. Unlike multidimensional CFD modeling approaches that rely on reduced reaction mechanisms with fewer reactions and species, the TSL model can utilize a detailed reaction mechanism with little computational cost. Figure 2-1 gives an explanation of the model.
The model is based on the experimental observation that reactions in gaseous jets occur in two sheets; reactions were initiated in the diffusion regions and continued in regions that were nearly homogeneous as a result of turbulent mixing. Entrained hot air from the ambient mixed with the jet fluid in a stoichiometric amount at the flame sheet of the diffusion region, then products from the flame sheet region moved to the homogeneous core reactor where they mixed homogenously with incoming fuel jet. This procedure was continued to the flame tip where the remaining fuel was consumed [25-27].

The TSL model typically incorporates two reactors: the first reactor represents the homogeneous regions while the second reactor represents the diffusion flame sheet. The homogeneous regions are represented by a perfectly stirred reactor (PSR), while the diffusion sheets can be modeled as either a one-dimensional strained diffusion flame or a PSR. Previous studies have shown that the
use of the two-reactor PSR model gives results similar to the reactor-flame version, at reduced computational cost [25, 27]. Therefore, in this study, both the homogeneous and the flame sheet regions were modeled as PSRs.

Equations for the conservation of mass and energy, which describes the flow field for the homogeneous reactor (modeled as a PSR), are as follows [25, 27]:

\[
\frac{dm_h}{dx} = f(x) \quad (1)
\]

\[
\frac{dY_{k,h}}{dx} = \left(1 + B\right) \frac{dm_h}{m_h} \left(Y_{k,f} - Y_{k,h}\right) + \left(\frac{\dot{\omega}_k W_k}{\rho}\right)_h \frac{1}{u} \quad k = 1, \ldots, K \quad (2)
\]

\[
\frac{dT_h}{dx} = \left(1 + B\right) \frac{dm_h}{m_h C_p} \sum_k Y_{k,f} \left(h_{k,f} - h_{k,h}\right) - \frac{1}{\rho_f u C_p} + \sum_k \left(h_k \dot{\omega}_k W_k\right)_h - \frac{q}{u C_p} \quad (2)
\]

\[
B = \frac{(f_{st} - f_{\infty})}{(f_h - f_{st} + \varepsilon)} \quad (3)
\]

\[
f = \sum_{k=1}^{K} \frac{Y_k}{W_k} \sum_{j=C,H} a_{j,k} M_j \quad (4)
\]

The conservation equations for the flame-sheet reactor (modeled as a PSR):

\[
0 = \frac{1}{\tau_f} \left[\left(Y_{k,\infty} - Y_{k,f}\right) + B\left(Y_{k,h} - Y_{k,f}\right)\right] + \left(\frac{\dot{\omega}_k W_k}{\rho}\right)_f \quad k = 1, \ldots, K \quad (5)
\]

\[
0 = \frac{1}{\pi c_p} \left[\sum_k Y_{k,\infty} \left(h_{k,\infty} - h_{k,f}\right) + B \sum_k Y_{k,h} \left(h_{k,h} - h_{k,f}\right)\right] - \frac{1}{\rho_f c_p} \sum_k \left(h_k \dot{\omega}_k W_k\right)_f - \frac{q}{c_p} \quad (6)
\]

Where \(x\) is axial distance from the nozzle; \(m=\rho u A\) is the axial mass flow rate. The first equation for the homogeneous reactor requires a function \(f(x)\), which provides the entrainment rate of a surrounding fluid into the jet.

The benefit of using the TSL model (apart from its ability to use large kinetic mechanisms at less computational expenses), is that preparation of the tool and its input is easier than using CFD codes. Input required by the model includes state variables of the jet (temperature, pressure,
composition, illustration of the jet (nozzle hole diameter, velocity), and parameters that control entrainment. The TSL model uses CHEMKIN, TWOPNT and DASSL subroutines. The CHEMKIN program evaluates chemical production rates and writes a linking file, and then DASSL integrates the first-order differential equations for the reactors while TWOPNT solves the numerical solution to finite differential equations. An executable (TSL.exe) reads the CHEMKIN linking file and the input files, together with the boundary conditions, and writes both text and binary output files [26]. Details of the formulation and description of TSL can be found in previous work [15, 25-28].

2.2.2 Approach

The focus of the present work is on ignition, so the flame-sheet reactor was turned off by maintaining its temperature at 350 K. The homogeneous reactor ignited, allowing the analyses of mixing effects on ignition delay. In running this code, both detailed and reduced chemical kinetic models were employed. For iso-octane and n-heptane, a comprehensive gasoline surrogate mechanism from LLNL [78], with 1858 chemical species and 7809 elementary reactions, was utilized. Additionally, an optimized chemical kinetics model from RWTH Aachen University, for gasoline surrogates [79], consisting 335 chemical species and 1610 elementary reactions, was used for validation of iso-octane in the IQT. For n-dodecane, detailed and reduced kinetics, models by Sarathy et al. [80] and Narayanaswamy et al. [75], were respectively utilized.

As stated earlier, validations of the simulated data were performed against previous experimental results using the IQT [76] and CVCC [66]. The experimental conditions used for this simulation are presented in Table 2-1.
Table 2-1: Details adopted for TSL simulation

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Details adopted for TSL simulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>LLNL Gasoline Surrogates</td>
<td>Mehl et al. (2009)</td>
</tr>
<tr>
<td>RWTH Gasoline Surrogates</td>
<td>Cai et al. (2014)</td>
</tr>
<tr>
<td>C7-C20 2-methylalkanes</td>
<td>Sarathy et al. (2011)</td>
</tr>
<tr>
<td>n-Dodecane Mechanism</td>
<td>Narayanaswamy et al. (2013)</td>
</tr>
<tr>
<td>Ambient gas</td>
<td></td>
</tr>
<tr>
<td>IQT</td>
<td>Air</td>
</tr>
<tr>
<td>CVCC</td>
<td>O₂, CO₂, N₂</td>
</tr>
<tr>
<td>Pressure (bar)</td>
<td></td>
</tr>
<tr>
<td>IQT</td>
<td>21.3, 16.4, 12.9</td>
</tr>
<tr>
<td>CVCC</td>
<td>49.3-50.6(n-heptane), 49.3-79.4(n-dodecane)</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td></td>
</tr>
<tr>
<td>IQT</td>
<td>720-860</td>
</tr>
<tr>
<td>CVCC</td>
<td>850-1200</td>
</tr>
<tr>
<td>Nozzle diameter (mm)</td>
<td></td>
</tr>
<tr>
<td>IQT</td>
<td>0.722</td>
</tr>
<tr>
<td>CVCC</td>
<td>0.084</td>
</tr>
<tr>
<td>Temp. of the liquid fuel (K)</td>
<td></td>
</tr>
<tr>
<td>IQT</td>
<td>326</td>
</tr>
<tr>
<td>CVCC</td>
<td>373</td>
</tr>
<tr>
<td>Injection pressure (bar)</td>
<td></td>
</tr>
<tr>
<td>IQT</td>
<td>179.26</td>
</tr>
<tr>
<td>CVCC</td>
<td>~1500</td>
</tr>
<tr>
<td>Injection duration (ms)</td>
<td></td>
</tr>
<tr>
<td>IQT</td>
<td>2</td>
</tr>
<tr>
<td>CVCC</td>
<td>1.5</td>
</tr>
<tr>
<td>Fuel density (kg/m³)</td>
<td>n-heptane(684), iso-octane(692), n-dodecane(752)</td>
</tr>
</tbody>
</table>

The TSL code is only capable of handling simulations in the gas phase. Therefore, liquid fuel in this study was modified to a gas phase condition; so the fuel temperatures were reduced to 230K and 300K for IQT and CVCC simulations, respectively, ensuring that the adiabatic flame temperature of the gas jet matched the adiabatic flame temperature of the liquid fuel. Again, for
the gas to have the same mass flow and momentum as the liquid fuel, the density of the liquid was reduced, and the diameter of the orifice was enlarged. Details on the calculation methods are available in [26].

The rate of mixing into the two reactors was determined by the stoichiometric requirement of flame-sheet reactor and also by the empirical correlation for jet mixing, as proposed by [26]:

$$\frac{m}{m_o} = C \frac{x}{d_o} \left( \frac{\rho_o}{\rho} \right)^{1/2}$$

(7)

where $C$ is a constant (0.32 is for un-reacting jets. For reacting jets, heat release inhibits the air entrainment rate, reducing $C$ to 0.16 for momentum driven flames). Subsequently, $C$ of 0.16 is used in these simulations. For more details on the simulation method using TSL, refer to [26].

In engines, ignition delay is the time difference between the start of injection (SOI) to the start of combustion (SOC) [14, 15]. The ignition of typical alkane fuels having NTC behavior is governed by three distinct regimes: first-stage ignition, NTC regime and second-stage ignition. It is important to investigate the processes that influence these regimes of ignition. In the current study, overall ignition delay time was taken as the time from the beginning of simulation to the time when the temperature rate change with time was maximum $(dT/dt)_{max}$.

2.3 Results and Discussion

The following section consists of four parts: First, the model is compared against experimental data. Next, concentration time-histories, OH rate of production, and sensitivity analysis of selected species are presented. Finally, the effects of other parameters on first- and second-stage ignition regimes are investigated in detail.
2.3.1 Validation of ignition delay time

Three different ambient pressures were simulated for the IQT experiments; ignition delay time was plotted against various injection temperatures (Fig. 2-2a), using chemical kinetic models from Mehl et al. [78] and Cai et al. [79]. Similarly, a detailed mechanism by Mehl et al. [78] was used for the simulation of \( n \)-heptane in the IQT (Fig. 2-2b).

Results from various chemical kinetic models for \( n \)-heptane and \( n \)-dodecane in the CVCC are presented in Fig. 2-2c. As mentioned previously, \( n \)-dodecane was simulated using detailed kinetic models by Sarathy et al. [80] and Narayanaswamy et al. [75], while \( n \)-heptane was simulated using the model by Mehl et al. [78]. Also, the updated mechanism by Cai et al. [79] was used to simulate the ECN’s \( n \)-heptane data.
Figure 2-2: Simulated ignition delay times using various kinetic models compared against experimental a) iso-octane IQT data (this study), b) n-heptane IQT data (this study), and c) n-heptane [66] and n-dodecane CVCC data [66]

For iso-octane, the trends were well captured by the TSL model, showing that the ignition delay time decreased with increasing ambient pressure and temperature. The quantitative agreement was also acceptable for iso-octane in the IQT and n-heptane and n-dodecane in the CVCC. Iso-octane simulations using the model by Cai et al. [79] showed better agreement with the experiments; however quantitative discrepancies of up to 50% remained. Detailed chemical kinetic models for highly branched hydrocarbons [81-83], such as iso-octane, were not as predictive as those for n-alkanes when attempting to estimate even fundamental combustion data, such as homogenous ignition delay times in shock tubes.

As presented in Fig. 2-2b, the simulated IQT n-heptane ignition delay qualitatively agreed with the experimental trend, however there was a quantitative over-prediction of the experimental data. The discrepancy in n-heptane IQT simulations was partly due to its short ignition delay, which was controlled by physical processes such as droplet formation and eventual fuel-air mixing. As noted by Bogin et al. [19, 20, 60, 72], when ignition delay time is short (< 20 ms), physical processes related to spray breakup and vaporization dominate over chemical kinetics.
However, when the ignition delay period is long, chemical kinetics plays an important role, as is the case for iso-octane. The n-heptane CVCC operating conditions enabled the system to quickly reach conditions controlled by gas-phase chemical kinetics, due to higher injection pressure and smaller nozzle hole diameter. Hence, the time scale between the physical and chemical processes decreased in the CVCC due to enhanced vaporization and mixing, so that the gas-phase chemistry was rate controlling. For this reason the TSL simulations accurately captured the ignition delay times in the CVCC for both n-heptane and n-dodecane, especially at higher temperatures. At the lowest temperatures in the CVCC, the model over-predicted ignition delay time data for n-heptane and n-dodecane.

Detailed chemical kinetic models for n-alkanes were not rigorously tested at high and low temperatures due to lack of experimental data under such conditions. Recent work by Wang and Sarathy [84] showed that an extended low temperature oxidation mechanism, involving third O$_2$ addition reactions, accelerated the reactivity of alkanes at low temperatures and high pressures. Including these reactions in detailed kinetic models for n-heptane and n-dodecane may improve the TSL model’s ability to predict IQT and CVCC data. Additionally, higher fidelity CFD simulations, such as those of Bogin et al., may improve predictions of IQT; but that is beyond the scope of the present work. It can be noted that the present TSL simulations for n-dodecane agreed with experimental data nearly as well as high-fidelity CFD simulations for ECN sprays [24, 85-87].

2.3.2 Mass fraction and rate of production analysis

To gain insight into the chemical kinetics of the two-stage ignition behavior of iso-octane, the rate of production (ROP) of OH and mass fraction analyses of some selected species are presented in sections 2-3 and 2-4 respectively. Species selection was based on reactions with the
highest ROPs at first and second-stage ignition delay times. For the ROP analysis in Fig. 2-3, positive and negative values mean production and consumption of OH radicals, respectively. The temperature profiles in Fig. 2-4 show a well-defined two-stage ignition. The first rise (Fig. 2-4a) occurred at around 39 ms while reactivity was then suppressed due to NTC reactions. After a brief period, at around 50 ms, the temperature rose again sharply, causing the second-stage ignition.

Figure 2-3: OH rate of production analysis for major OH producing and consuming reactions for isooctane fuel in the IQT at 21.27 bar, 740 K; a) at first-stage ignition b) at second-stage ignition.
The first rise (Figs. 2-4a and 2-4b) was a result of the complicated kinetics of low temperature hydrocarbon combustion; this has relevance in practical combustion systems [51]. After the abstraction of H from the fuel—mainly by O₂, the fuel radical reacted with molecular oxygen to form a peroxy radical. The fate of this radical is determined by temperature. At sufficiently high temperatures, the radical falls apart and dissociates back to R and oxygen. At lower temperatures, the equilibrium favored \( \text{RO}_2 \) (alkyl peroxy radical). \( \text{RO}_2 \) isomerized to \( \text{QOOH} \) (hydroperoxy alkyl radical), which later reacted with another \( \text{O}_2 \) molecule to form \( \text{O}_2\text{QOOH} \), and this molecule isomerized and decomposed to ketoxydroperoxide (KHP), plus two OH radicals. The type of KHP species formed varies. In this study, IC8KETAB (see species dictionary), a KHP had the highest rate of production (Fig. 2-3a). Therefore, this species was used in Fig. 2-3a for species mass fraction analysis. The KHP rapidly increased and decomposed soon after attaining its decomposition temperature. After decomposition, the KHP produced two OH radicals (as seen by the small increase in temperature on Figs. 2-4a and 2-4b); this was the branching reaction that gave rise to low temperature heat release. This is a marker of the first-stage ignition, sometimes referred to as the cool flame [51]. As the temperature of the mixture
increased, the equilibrium shifted and RO₂ dissociation was preferred. This decreased the production of KHP while the fuel continued to consume radicals produced by KHP decomposition. The heat release also dropped, and the overall rate of reaction decreased. This produced the NTC region. Though the heat released here was not sufficient to cause second-stage ignition, first-stage ignition is important in combustion systems as it provides early heat release, so that mixtures reach second-stage ignition temperatures sooner than without this low temperature heat release [51].

Immediately after the first-stage ignition, H₂O₂ was formed, primarily from the reaction of iC₈H₁₈ and HO₂. The concentration of H₂O₂ began to build (see NTC area on Fig. 2-4) until it reached its peak at around 1000 K. Below this 1000 K, the decomposition of H₂O₂ was much slower than its buildup. At relatively high temperatures, H₂O₂ dissociation began, according to the reaction H₂O₂ (+M) ⇔ 2OH. This reaction is pressure and temperature dependent [78]. The pool of H₂O₂ disappeared rapidly, producing two OH radicals, as indicated by a sharp rise in temperature (Figs. 2-4a and 2-4b), and corresponding to H₂O₂ decomposition having the highest rate. As noted by Westbrook [51], the increase in these OH radicals consumes all the remaining fuel, followed by an instant rise in temperature and resulting in the second-stage ignition. Therefore, H₂O₂ plays a major role in second-stage ignition; wherein its disappearance is a marker of the second-stage ignition. Also, its rapid or slow accumulation before it reaches its dissociation temperature reveals how long the system will take before it finally ignites. This can be seen by comparing plot 2-2a at 21.27 bar and plot 2-2b at 12.9 bar. At lower pressure (Fig. 2-4b), it takes a long time for H₂O₂ to reach its decomposition temperature; thus, it has a longer ignition delay compared to the higher-pressure case in Fig. 2-4a.
Formaldehyde could be used as a marker of low temperature chemistry. For this reason, the mass fraction of formaldehyde was plotted against temperature on Fig. 2-5. Accumulation of CH$_2$O starts around 700 K. The mass fraction of CH$_2$O decreases as the ambient pressure is lowered. Therefore, as noted by [69], since this specie is easily accessible using LIF-optical diagnostics, it could be used as an indicator of an initially fuel-rich premixed reaction region.

![Figure 2-5: Normalized CH$_2$O mass fractions vs. T (K) at different ambient pressures](image)

The effect of ambient pressure can be seen by fixing the ambient temperature while varying the charge pressure, as shown on Fig. 2-6. It is also interesting that the location at which ignitions occur shifted downstream of the nozzle as the ambient temperature and ambient pressure decreased. Lower pressures and temperatures resulted in longer ignition delay times, allowing for more air entrainment downstream and leaner fuel/air mixtures that also decreased reactivity.
2.3.3 Sensitivity analysis

A temperature sensitivity analysis was carried out at 21.27 bar and 750 K at the time of ignition to determine the reactions controlling the overall oxidation process at the end of NTC (i.e., at second-stage ignition). A rigorous sensitivity analysis is beyond the current capability of the TSL code, so a simple technique was utilized here. Individual reaction rates were doubled, and the ignition delay time was recomputed using the TSL code, producing the results in Fig. 2-7. The percentage sensitivity is defined as. [78]:

\[
\% \text{sensitivity} = \frac{\tau(2ki) - \tau(ki)}{\tau(ki)} \times 100
\]

where \(\tau(2ki)\) corresponds to ignition delay when the rate coefficient is doubled and \(\tau(ki)\) is nominal ignition delay time.

A negative percentage change correlates to longer ignition delay and decrease reactivity while positive percentage change results in shorter ignition delay and increased reactivity. The reaction
with the highest positive sensitivity was most effective in promoting overall oxidation rate. H$_2$O$_2$ decomposition to 2OH radicals is very effective in igniting the system.

The sensitivity of H abstraction from the fuel by OH depends on the site from which H is abstracted. H abstractions from iso-octane yield positive sensitivities, with the exception of abstraction from the c-site carbon atom. The sensitivity analysis showed that H abstraction from a-site (a primary carbon) increased the oxidation process greatly because it could abstract nine H from three different sites. On the contrary, OH abstraction from the c-site had a negative sensitivity. This is because internal hydrogen abstraction from O$_2$QOOH to produce ketohydroperoxide + OH was curtailed by the fact that abstraction was easier from the carbon bonded to OOH. Since there were no more available H atoms to be abstracted at the c-site (see the graph 2-7b), the reaction scheme could not produce ketohydroperoxide and OH. This inhibited or slowed the low temperature chemistry and delayed final ignition. QOOH decomposition into ketohydroperoxide, and OH and subsequent decomposition of ketohydroperoxide into OH, also had positive percentage sensitivities because this reaction produced OH and contributed to early heat release. AC8H18OO-B$\leftrightarrow$IC8ETERAB + OH had negative sensitivity because this reaction was a competing pathway to the low temperature chemistry pathway (i.e. the addition of O$_2$ to QOOH).
2.3.4 Effects of ambient oxygen concentration on ignition of iso-octane

Reduction in oxygen concentration is achieved mainly through exhaust gas recirculation (EGR) in engines, which becomes more relevant with the introduction of new engines, such as the HCCI or LTC engines. EGR inhibits the formation of NO\textsubscript{x} and soot in engines by reducing the flame temperature [5, 15]. Also, it is a common practice in IQT experiments to simulate the EGR effect by decreasing charge oxygen concentrations [19, 72]. This is important for high volatility fuels with short ignition delay times, as it allows the fuel-air mixture to reach pseudo-homogeneous conditions, so that NTC regions become noticeable. To understand the effects of O\textsubscript{2} concentration on ignition delay time, the core temperature was plotted against time in Fig. 2-8a. Different ambient oxygen concentrations were considered.

Decreasing the oxygen concentration from 22% to 10% increased the ignition delay time. At lower oxygen concentrations, the rate of reaction decreased, as indicated by falling combustion temperature. Less heat was also released at the end of the first-stage ignition, which caused an increase in the total ignition delay time at lower oxygen concentration. The graph also shows that an increase in temperature by 50 K significantly decreased the ignition delay period at all O\textsubscript{2} concentrations. This was caused by an increase in the overall rate of reaction due to decreased activation energy.

Also, for insight on the effect of oxygen concentration on ignition location, the core temperature was plotted against a non-dimensional axial distance in Fig. 2-8b. As the concentration of oxygen was reduced, the location at which ignition occurred shifted further downstream; this
downstream shift occurred because longer ignition delay times permitted more air entrainment, further reducing reactivity.

Figure 2-8: Simulated effects of oxygen concentrations on a) second-stage ignition delay time b) ignition location at 850 K

2.3.5 First-stage ignition delay time

First-stage ignition delay time ($\tau_f$) has a substantial impact on the total ignition delay time ($\tau_t$). As noted by Zhao et al. [88], since $\tau_t$ is associated to $\tau_s$ (second-stage ignition delay time) through heat release at the end of the first stage, much of the information required to study chemical kinetics of ignition is contained in $\tau_f$ (first-stage ignition delay time). Therefore, it is equally important to study the first-stage ignition delay time.

2.3.5.1 Effect of ambient pressure on first-stage ignition

To see these effects, the first-stage ignition delays of iso-octane were plotted against ambient pressures for three different temperatures (Fig. 2-9a). The result suggests that there is a small, or negligible, effect of ambient pressure on first-stage ignition delay at these pressure ranges. This suggests that first-stage ignition delay is not sensitive to changes in ambient pressure at these
conditions; therefore, the majority of the effect of ambient pressure is in \( \tau_s \). A similar trend was observed by Zhao and Law [88]; they observed that at low pressure and low temperature, the first stage is not sensitive to change in ambient pressure.

![Figure 2-9: Simulated effect of ambient pressure on a) first-stage ignition delay time b) temperature at the end of the first-stage ignition](image)

### 2.3.5.2 Effect of exothermicity on first-stage ignition delay

The temperature at the end of first-stage ignition is plotted against the ambient temperature in Fig. 2-9b. As the ambient temperature was increased, the temperature at the end of the first-stage ignition also increased, indicating the role of low temperature heat release on the overall ignition delay time. However, the temperature increase was less than the initial temperature difference. Furthermore, \( T_{ef} \) (temperature at the end of the first-stage ignition) was higher at 21.27 bar than at 16.4 and 12.9 bar, implying that the role of pressure on the overall ignition delay time was primarily to raise the temperature at the end of the first-stage ignition (but not actually changing first-stage ignition delay time).

### 2.3.5.3 Effect of ambient oxygen concentration on first-stage ignition
To see the effects of oxygen concentration on first-stage ignition delay time, six different ambient oxygen concentrations were considered. The first-stage ignition delay is plotted as a function of the different ambient oxygen concentrations in Fig. 2-10a.

The graph shows that timing of the first-stage ignition was less affected by the changes in O$_2$ concentration. However, Fig. 2-10b shows that O$_2$ concentration played a greater role in the low temperature heat release. The temperature at the end of the first-stage ignition increased with increasing O$_2$ concentrations, indicating the faster arrival of the second-stage ignition.

Figure 2-10: Simulated effect of ambient oxygen concentration on a) first-stage ignition delay time b) temperature at the end of the first-stage ignition

2.3.5.4 Strain rate on ignition

As described above, ignition processes involve many intermediate species and radicals. The lifetime of these species and radical is significantly influenced by the strain rate. To see how this strain rate affects ignition delay time of iso-octane in the IQT, the second-stage ignition delay time was plotted at various strain rates in Fig. 2-11a. The strain rate is defined as the ratio of the inlet velocity $u_0$ to the orifice diameter $d_0$, which gives the strain rate in terms of (1/s). Therefore,
strain rates here were obtained at various \( u_0/d \) and are representative of various spray injection velocities. As the strain rate was increased, the ignition delay period became longer. This is especially evident at lower charge temperatures. To see the possible reason for this behavior, the homogeneous core reactor equivalence ratio was plotted at different strain rates in Fig. 2-11b. The plot shows that as the strain rate was increased, the core equivalence ratio decreased as a result of overmixing, forming leaner mixtures—especially at high strain rates—and increasing the ignition delay time.

![Figure 2-11: Simulated effect of strain rate on a) second-stage ignition delay time b) equivalence ratio at ignition](image)

2.4 Conclusions

In this research, the TSL model was used to simulate ignition characteristics of iso-octane and \( n \)-heptane in the IQT and \( n \)-heptane, and \( n \)-dodecane in the CVCC. The quantitative agreement between the simulations and the experiments was acceptable, except for \( n \)-heptane in the IQT. The inability of the TSL model to predict IQT ignition \( n \)-heptane was attributed to the model’s inability to accurately capture physical processes when they became rate controlling in the
ignition processes. The model was used to further investigate other properties of *iso*-octane ignition in the IQT.

In summary the results are as follows;

1. The TSL model effectively simulated IQT of long ignition delay time fuels. It was also effective for CVCC experiments with high injection pressures, when physical processes did not contribute much to the ignition delay time.

2. Increasing ambient pressure decreased the overall ignition delay time, but it did not affect the timing of the first-stage ignition. However, the temperature at the end of the first-stage ignition increased with increased ambient pressure; this accelerated the arrival of the second-stage ignition by increasing low temperature heat release.

3. Decreasing ambient oxygen concentration lengthened ignition delay time and shifted the ignition location further downstream. Varying the ambient oxygen concentration did not affect the timing of the first-stage ignition. The final temperature at the end of the first-stage increased with increased oxygen concentration, which advanced the arrival of the second-stage ignition delay time.

4. The OH rate of production analysis and mass fraction analysis of some species for *iso*-octane fuel at the end of the first-stage ignition showed the importance of IC8KETAB, and it decomposed to supply early energy to the system. ROP at the end of the second-stage ignition showed that the decomposition of H$_2$O$_2$ into two OH radicals supplied the much-needed energy to finally ignite the system.

5. Sensitivity analysis showed that abstraction of H by OH from *a*, *b* and *d* sites increased the reactivity of *iso*-octane fuel, while abstraction from the *c*-site slowed reactivity.
6. Ignition delay times increased as the strain rate increased. This is because, at very high strain rates, the equivalence ratio was greatly reduced due to overmixing, thereby forming lean mixtures with longer ignition delay times.
3 Chapter 3: Modelling ignition processes of palm oil biodiesel and diesel fuels using a Two-Stage Lagrangian approach

In this chapter, the ignition characteristics of conventional diesel and palm biodiesel fuels were simulated using the two-stage Lagrangian (TSL) simulation, a zero-dimensional (0-D) modeling technique. For the diesel fuel surrogate, a detailed chemical kinetic model for n-heptane from LLNL (Lawrence Livermore National Laboratory), with 550 chemical species and 2450 elementary reactions was utilized. The palm biodiesel surrogate used a detailed mechanism (4800 species and 2450 elementary reactions) for the five basic biodiesel components: methyl palmitate, methyl stearate, methyl oleate, methyl linoleate and methyl linolenate. Simulations were also performed using a reduced mechanism (115 species and 460 reactions) for surrogates of palm oil biodiesel, comprising mixtures of methyl decanoate, methyl decenoate and n-heptane. The simulated data were validated against published experimental results in a constant volume combustion chamber. Validations were performed at an ambient density of 15kg/m$^3$ and injection pressure conditions of 100, 200, and 300 MPa. For both the diesel and biodiesel, predicted ignition delay agreed with the trend obtained in the experiment at all injection pressures. The TSL model was further employed to investigate the chemical processes responsible for controlling overall ignition under various conditions.

3.1 Introduction

Biodiesel is one of the promising alternative fuel sources, due in part to its ability to reduce CO, soot and unburned hydrocarbon (UHC) emissions. Many countries in Europe, as well as the US, are advocating for the use of alternative fuels. Recently, the top CO$_2$ emitters--China and the US--agreed to cut greenhouse gas (GHG) emissions by 28% and 20%, respectively, by the year
Many of the advantages of using biodiesel as an alternative fuel can be found in [29, 32, 50, 89-93]. It has been reported [91] that modern diesel engines can utilize biodiesel with a significant reduction in emissions and without major change to their design. Biodiesels have a few number of major fatty acid methyl ester (FAME) components, making it possible to include all its components in experimental or kinetic model analysis [91]. The five major components of a palm oil biodiesel include unsaturated methyl oleate (C_{19}H_{36}O_{2}), methyl linoleate (C_{19}H_{34}O_{2}) and methyl linolenate (C_{19}H_{32}O_{2}), as well as saturated methyl palmitate (C_{17}H_{36}O_{2}) and methyl stearate (C_{19}H_{38}O_{2}).

A diesel engine leads other power generating engines in the transportation sector in both reliability and efficiency [26]. Notwithstanding, more studies are required to improve their efficiency. Temporal control of combustion events in an engine is an essential parameter affecting efficiency and exhaust gas emissions [94]; one way to achieve this is by controlling the timing of ignition. Fuel ignition in diesel engines is achieved by compression of the stratified fuel/air charge. Therefore, timing of this event could be influenced by a variety of factors, such as ambient temperature, ambient pressure, injection pressure, and by varying the concentration of O_{2} in the cylinder. Several efforts were made by Cung et al. [68] and Kobori et al. [67, 94] to study ignition processes in diesel engines. They found that an increase in both injection pressure and ambient temperature decreased the ignition delay time (time between injection start to ignition onset).

Because there is a growing interest in the use of biodiesel and diesel fuels in diesel engines, it becomes imperative to study the ignition processes of these fuels. As such, this work seeks to reveal the underlying phenomena affecting both diesel and biodiesel fuel ignition, and to compare the ignition behavior of the two fuels using the two-stage Lagrangian model.
Simulations were validated against a previous experiment conducted by Kuti et al. [95], using a constant volume combustion chamber.

3.2 Research Methodology

Details of the procedure, and the assumption sustained in running this numerical work, are mentioned in chapter 2. In running the TSL code, a detailed reaction mechanism [96] was utilized as the diesel surrogate; n-heptane was chosen because it has a cetane number of 56, comparable to that of a conventional diesel fuel. As reported by Musculus et al. [97], n-heptane has ignition and an apparent heat release rate (AHRR) behavior in engines similar to that of a typical diesel fuel. For palm biodiesel, a detailed mechanism [96] (4800 species and 2450 elementary reactions) for the five basic biodiesel components (methyl palmitate, methyl stearate, methyl oleate, methyl linoleate and methyl linolenate) was used for validation at 100MPa. Parametric studies were also performed using the reduced mechanisms [32] (115 species and 460 reactions) for the palm oil biodiesel, comprising a mixture of methyl decanoate, methyl decenoate and n-heptane as surrogates. Details of their mixture composition can be found in [14, 95]. As stated earlier, validations of the simulated data for both diesel and palm oil biodiesel were performed against previous experimental results using a constant volume combustion chamber, as reported in [95]. The experimental conditions used as a baseline condition for the simulation are presented in Table 3-1. The experimental facility is presented on Fig. 3-1.
Table 3-1: Experimental conditions adopted for TSL simulation

<table>
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<th>Mechanism</th>
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<td>Diesel</td>
<td>nC\textsubscript{16}H\textsubscript{16} LLNL [78]</td>
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<tr>
<td>Biodiesel Reduced</td>
<td>C\textsubscript{11}H\textsubscript{20}O\textsubscript{2}(MD),</td>
</tr>
<tr>
<td></td>
<td>C\textsubscript{11}H\textsubscript{19}O\textsubscript{2}(MD9D),</td>
</tr>
<tr>
<td></td>
<td>nC\textsubscript{7}H\textsubscript{16}. [32]</td>
</tr>
<tr>
<td>Biodiesel Detailed</td>
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</tr>
<tr>
<td></td>
<td>ML(C\textsubscript{19}H\textsubscript{34}O\textsubscript{2}),</td>
</tr>
<tr>
<td></td>
<td>MLN(C\textsubscript{19}H\textsubscript{32}O\textsubscript{2}),</td>
</tr>
<tr>
<td></td>
<td>MP(C\textsubscript{17}H\textsubscript{34}O\textsubscript{2}),</td>
</tr>
<tr>
<td></td>
<td>MS(C\textsubscript{19}H\textsubscript{38}O\textsubscript{2}). [96]</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tbody>
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</tr>
<tr>
<td>Temperature (K)</td>
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</tr>
<tr>
<td>Nozzle diameter (mm)</td>
<td>0.16</td>
</tr>
<tr>
<td>Injection duration (ms)</td>
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</table>
### Results and Discussion

This study consists of four parts. First, the model is validated against experimental data. Next, mass fraction analysis and rate of production analysis of some selected species at these two stages is presented. Finally, the second-stage ignition and the first-stage ignition regimes are investigated in more detail. However, for the purpose of writing this dissertation, only Validation, and few highlights on the effects of injection parameters on ignition delay were reported here. The remaining part of this study can be found in [98].

#### Validation of Ignition delay time

The model was first validated against experiments performed at three different injection pressures, 100, 200 and 300MPa respectively. In Fig. 3-2; there was good agreement with the experiment for both diesel and palm oil biodiesel surrogates, especially in the ignition delay times. The trends were also well predicted, showing that the ignition delay times decreased with increased injection pressure, and those of biodiesel were shorter than diesel. Reasons for these trends are discussed in the next section. The quantitative agreement was also acceptable for both fuels. Simulated ignition delay times of biodiesel with reduced and detailed mechanisms were within 26 % and 73% respectively of experimental values; simulated diesel values for diesel fuel were within 12 % of experiments. The simulations over-predicted ignition delay times under all

<table>
<thead>
<tr>
<th>Injection Pressure(MPa)</th>
<th>100, 200 and 300</th>
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<tr>
<td><strong>Fuel density</strong></td>
<td>diesel (830), palm oil biodiesel (874.4)</td>
</tr>
<tr>
<td><strong>Cetane Number</strong></td>
<td>diesel (56) palm oil biodiesel (64.4)</td>
</tr>
</tbody>
</table>
conditions. Deviation from the experiment, especially by the detailed biodiesel surrogate mechanism, could be a result of the chemical kinetic model. Chemical kinetic models for biodiesel combustion have not been well developed.

![Figure 3-2: Validation of ignition delay time for diesel and biodiesel fuel at three different injection pressures](image)

### 3.3.2 Effects of injection pressure on ignition delay for diesel and biodiesel

Three different injection pressures of 100 MPa, 200 MPa and 300 MPa were used to understand the effects of injection pressure on ignition delay. In Fig. 3-3, the ignition delays at the three different injection pressures were plotted against the time after start of injection. Increased injection pressures shortened the ignition delay period for both diesel and biodiesel surrogates. This decrease could be due to the increase in mixing that was achieved as the injection pressure was increased. Also, the graph shows that the ignition delays of biodiesel surrogate were shorter than that of the diesel surrogate at all injection pressures; similar trends were observed in the experiment. This is because biodiesel has a higher CN (60) than diesel (56). CN gives an indication of the ignitability of fuels. Fuels with high cetane number ignite faster: the higher the
CN number of a fuel, the shorter its ignition delay time. As discussed earlier, the two peaks noted on the plots represent two-stage ignition delay.

Figure 3-3: Simulated diesel surrogates [95]. Ignition delay at different injection pressures, ambient pressure (4MPa) and ambient temperature (885K)

To understand the effect of injection pressure on ignition location, the core temperature was plotted against a non-dimensional axial distance, as shown in Fig. 3-4. As injection pressure was increased from 100 to 300 MPa for fuels, the ignition location shifted further downstream. This is attributed to an increase in injection velocity at higher injection pressures. The time of ignition that occurred at these distances corresponds to the ignition delay time in Fig. 3-3.
3.3.3 Effect of ambient pressure on ignition delay

In order to understand the effect of ambient pressure on ignition delay, three different ambient pressures (4, 5 and 6MPa) respectively were considered at different temperatures (Fig. 3-5). Second-stage ignition delay time was plotted against the ambient temperatures. The plot shows that at a particular ambient temperature, increased ambient pressure decreased the ignition delay time. Ignition delay time was inversely proportional to the ambient gas pressure, suggesting that the ignition of diesel fuel spray was rate controlled by the molar concentration of oxygen. At higher ambient pressure there was an increase in concentration of oxygen, and this increased the reactivity and shortened the ignition delay time. Although not shown here, less heat was released at the end of the first-stage ignition at lower ambient pressures. This also caused the second-stage ignition delay to be longer at lower pressures.
3.4 Conclusion

In this work, the ignition characteristics of diesel and palm oil biodiesel fuel surrogates were studied in a constant volume combustion chamber using a TSL model. The quantitative agreement between the model and the experiment was acceptable. Although not shown here, the model was used to further investigate other properties of diesel and palm oil biodiesel ignition. The results are as follows:

1. The ignition delay time of palm oil biodiesel was shorter than that of the diesel fuel surrogate at all injection pressures. Increased injection pressure shortened the ignition delay time for both palm biodiesel and diesel fuel surrogates; it also shifted the location at which ignition occurred further downstream.

2. Increase ambient pressure decreased the overall ignition delay time, but it appeared not to affect the timing of the first-stage ignition. However, the temperature at the end of the first-stage ignition increased with increased ambient pressure. This accelerated the arrival of the second-stage ignition by increasing the low temperature heat release.
4 Chapter 4: Specification for counterflow hot diffusion flame experiments and numerical modeling

In this chapter, a newly developed counterflow facility for the study of hot diffusion flame properties is presented. The setup was validated using previous experimental data by Humer et al. [49] and velocity profile measurements. The second section of the chapter describes the procedure used to generate skeletal models with fewer species so they can be effectively used for simulation of counterflow diffusion flames.

4.1 Description of the newly developed experimental setup/procedure

The first aim of this experimental study was to build a counterflow diffusion setup for autoignition experimentation. Figure 4-1 shows the burner and a schematic illustration of the counterflow configuration. The burner consists of two opposing ducts. Preheated air was introduced into the upper duct, while the diluted fuel was injected into the lower duct. The upper part of the burner consists of a quartz tube, internal diameter, d= 25.4mm, directing hot air downward. Heating of the air was achieved with an internal helical SiC heater, capable of heating the air to 1400K. The quartz tube is surrounded by an external Thermcraft heater, plus high temperature-resistant insulation to minimize radiant heat loss. Both heaters are electrically controlled using variable transformers to provide constant power. A flow-straightening stainless steel screen was placed at the bottom of the quartz tube. The fuel stream is diluted with nitrogen. A flow-straightening mesh was placed at a distance--about 35mm away from the outlet of the fuel duct. The upper and lower ducts are surrounded by a concentric curtain-flow, d = 52.2mm, to isolate the flow field from ambient surrounding. The two ducts are separated by a distance L.

To validate the newly developed facility, autoignition experiments were carried out at L/D =
0.944, while \( L = 10 \text{ mm} \) was used for extinction experiments. The fuel mass fraction, temperature, density of the fuel stream and the component of the fuel flow velocity normal to the stagnation plane at the exit of the fuel outlet, were \( Y_{f,1}, T_1, \rho_1, \) and \( V_1, \) respectively. The oxygen mass fraction, oxidizer temperature, density and the oxidizer flow velocity normal to the stagnation plane at the exit of the oxidizer outlet, were \( Y_{O_2,2}, T_2, \rho_2, \) and \( V_2, \) accordingly. All experiments were conducted assuming plug flow conditions, maintaining the momenta of the counterflowing streams equal i.e. \( \rho V_i^2, i = 1,2. \) The strain rate, \( a, \) Eq. (1-1), was defined as the normal gradient of the normal component of the flow velocity, and this value changed from the exits of the fuel to the oxidizer ducts, respectively [31]. Assessment of the experimental strain rate in this study was performed in accordance with the procedure outlined by Humer \textit{et al.} [49] and Niemann \textit{et al.} [99], where the explicit derivation of the characteristic strain rate was also provided.

Autoignition experiments were conducted at \( T_1 \approx 300 \text{ K} \) and \( X_{f,1} = 0.15. \) At a particular strain rate \( a_2, \) the temperature of the oxidizer was slowly increased by controlling the voltage to the heating element until autoignition occurred. The temperature of the air, just before autoignition occurred at the exit of the oxidizer duct \( T_2, \) was measured using an Omega Engineering K-type precision thermocouple with a bead diameter of 0.025 mm. All oxidizer temperatures, \( T_{2,i}, \) were corrected to account for the heat lost due to radiation, using the procedure described by Brady \textit{et al.} [16, 100]. The flow rates of the two counterflowing streams were continuously adjusted based on their temperature, to ensure a balanced momentum.
Figure 4-1: schematic diagram of the counterflow setup

4.2 Validation of Experimental facility

The next goal of this chapter is to perform a complete validation and characterization of the newly developed counterflow facility to enable better comparison with similar fundamental experiment. The counterflow diffusion setup was previously employed by several other researchers to clarify the ignition and extinction characteristics of various liquid and gaseous
fuels. Fotache et al. [101] developed a variable pressure counterflow ignition system to study autoignition temperature of H₂/air at various strain rates. Brady et al. [16] also developed a variable pressure counterflow to examine the effects of structural isomerism and strain rate on ignition temperature of butanol isomers. As an illustration of common practice in the experimental community, both Fotache and Brady et al. performed a comprehensive validation of their experimental setups. For example, Brady et al. [16] provided a validation of their experimental system which included velocity profiles of the flow field, ignition location and temperature gradient information. More importantly, Brady et al. reproduced the ethylene ignition temperature data from Hummer et al. [49]. They noted that a detailed validation and characterization of a counterflow system would ensure good adherence to the one-dimensional assumption made in numerical modeling of ignition data. For this reason, validation and illustration of this setup was performed. The procedure is described in the previous section.

4.2.1 Burner flow field

A non-intrusive 2D particle image velocimetry examination was conducted to identify the airside velocity flow field between the two opposing ports of the burner. A 10KHz maximum frequency LDY.300PIV Litron laser and an Imager Pro HS LaVision camera were used. The interrogation window was defined as 12x12 pixels (pixel size~0.13 mm) and the two acquired images had a delay time of 300 μs, while a cross correlation was used for the determination of the velocity components. A fluidized bed seeder was used to inject the seeding particles into the flow field of the air side. The seeding particles are TiO₂, with a nominal diameter of 0.5 μm.

Figure 4-2 shows cold flow axial velocity profiles along the radial distance at different axial locations, measured from the airside. The flow conditions were set at a strain rate of 150 l/s. The results show that the nominal velocity decreased along the axial distance as the stagnation plane
was approached. In addition, a flat core—where the axial velocity fluctuations are minimal—was determined and found to be nearly 60% of the radial distance. The airside outlet diameter was 25.4 mm.

![Radial distribution of airside axial velocity at different axial locations “Y” from the outlet. X-axis represents radial distance in mm, Y-axis represents axial velocity in m/s](image)

Figure 4-2: Radial distribution of airside axial velocity at different axial locations “Y” from the outlet. X-axis represents radial distance in mm, Y-axis represents axial velocity in m/s

### 4.2.2 Comparison with previous ignition temperature data

For the purpose of validation, comparisons were made between ignition temperatures of ethane, and ethylene from the newly developed setup, with that of a similar experimental system by Humer et al. [49]; see Fig. 4-2. Experiments were conducted at fuel mole fraction $X_f = 0.15$, and fuel stream temperature $T_1 = 300$ K. Ignition temperatures presented here are corrected for radiation, according to procedures outlined by Brady et al. [16, 100, 102]. Despite the uncertainties in measurements and the complexities of radiation correction, the ignition temperature obtained from the present setup compares reasonably well with the data by Humer et
al., with a difference of 30-35 K. This difference is within the range of the error bars and could be attributed to a different type of thermocouple, positioning of the thermocouple, or flow controllers.

Figure 4-3: Comparison of ignition temperature data from the newly developed counterflow facility and data from Humer et al. [49]

4.2.3 Comparison with previous extinction data

For this validation, extinction experiments were also carried out strictly in accordance with the procedure outlined by Humer et al. [49]. These were performed by adjusting the location of the flame sheet, allowing small changes in the flame position. The flame sheet is a region where the flux of the fuel and oxygen are in stoichiometric proportion; it can be expressed as: \( \xi = \left(1 + \frac{v_{O2}Y_{F1}W_{O_2}}{Y_{O2}W_F}\right)^{-1} \). Therefore, these experiments were carried out at constant \( \xi = 0.1 \).

Temperature of the fuel stream \( T_1 \approx 300 \) K and \( T_2 = 298 \) K. At a given fuel strain rate, a stable flame was formed. The strain rate was gradually increased, while a balanced momentum of the
two counterflowing streams was maintained until the flame was extinguished. The corresponding strain rate at extinction, $a_{2,E}$, given by Eq. (1-1), is recorded.

A comparison was made between extinction results from the present experimental facility and the extinction data from Humer et al.\textsuperscript{16}. Three fuels were tested for this study and the oxygen mass fraction $Y_{O_2}$ was plotted against the extinction strain rate $a_{2,E}$, Fig. 4-3. The newly developed facility captures the extinction data of Humer et al., showing that the extinction limit of the tested fuels increased in the following order: $C_3H_8 > C_2H_6 > C_3H_6$.

![Figure 4-4: Comparison of extinction data from the newly developed counterflow facility and data from Humer et al. \cite{49}](image)

4.2.4 Ignition location

The location of the flame at the onset of ignition is crucial to the assumption of a quasi-one-dimensionality of the counterflow experiment. It is desirable that ignition be initiated at the center of the flow field. However, in some cases ignition may occur prematurely at some locations away from the center of the flow field, due to uneven distribution of curtain flow or
velocity gradients. In such situations, where ignition occurs away from the ignition kernel, it also possible that ignitable conditions have been reached outside the ignition zone before an ignitable state was reached within the core flow field. This can result in underestimation of ignition temperatures data. Figure 4-4 shows images of flames from the counterflow burner. The right image shows the initial location of the flame at the onset of autoignition while the right side image shows a stable 1-D flame for methane/air mixtures 350 s\(^{-1}\).

![Figure 4-5: Images from this counterflow burner a) showing stable 1-D flame and b) initial location of auto-ignited flame](image)

4.3 **Reduction of detailed kinetic models**

Advancement in computational chemistry and chemical kinetics leads to the development of comprehensive oxidation models of higher molecular weight fuels, such as the gasoline and biodiesel surrogates [78, 96]. These models consist of detailed representations of intermediate reactions and species, adding size and complexity to the kinetic mechanisms. For example, Wang *et al.* [82, 84] recently discovered an alternative pathway to the low temperature chain branching reaction of alkanes, thereby increasing the size of the existing models. Although detailed representation of reactions and species improves the prediction capability of kinetic models, these models must be reduced to be used effectively for CFD and flame simulations. Previous studies have shown that computational time is directly proportional to the square of the number
of reactions in the kinetic mechanism [32]. Several methods of mechanism reduction have been reported in the literature, including methods of sensitivity and path flux analyses by Turanyi, [103] and Sun et al. [104] respectively, which identify the most important reactions and pathways in fuel oxidation. Depending on the intended purpose for reduction, heat release is the most important parameter for flame initiation and extinction. In all the previously reported reduction tools, Direct Relation Graph (DRG) based methods offer greater efficiency because the time it take to reduce a detailed model is proportional to the size of the model [105]. DRG-X in particular offers better flexibility and accuracy, as the method is fully automated and allows a controlled reduction error for heat release and other species of interest. The DRG-X method is based on the premise that during combustion processes, some species are weakly coupled to others, and therefore could be eliminated from the mechanism without altering with the chemical fidelity of the model [106].

\[
\delta_{Bi} = \begin{cases} 
1, & \text{if reaction } i \text{ involves specie } B \\
0, & \text{otherwise}
\end{cases}
\]

Equation (4-1) [106]

Equation 4-1 is an expression that indicates the error in the rate of production of A when specie B is removed. If B is in the reaction, then \(\delta_{B} \) is one and \( r_{AB} \) is large. On the other hand, if B is not important to the rate of A production, \( \delta_{B} = 0 \), \( r_{AB} \) is small and it can be removed. In general, a small threshold \( \varepsilon \) was set here so if \( r_{AB} \) was less than the value (\( r_{AB} < \varepsilon \)), then the dependence of A on B was negligible and could be removed. If \( r_{AB} \geq \varepsilon \), then A strongly depends on B and it could be retained in the mechanism. Figure 4-5 shows a schematic diagram of the working principle of DRG-X. The DRG-X method requires an input of one or few major species, A, as the search-initiating species, and user-specified default error tolerance for species with large uncertainties, e.g. 0.3. By default, B and C would be retained since they are directly coupled to
A. Additionally, if D, E and F and their associated reactions are desired, with accuracy, small x-values could be assigned to such species [106-108]. These species could be H or CH\textsubscript{3} radicals or pollution such as NO\textsubscript{x} or CO\textsubscript{2}.

![Diagram](image.png)

**Figure 4-6: A schematic illustration of DRG-X**

The DRG-X method was used in this study to reduce detailed chemical kinetic models to skeletal models so they could be effectively used for flame simulation. The ability of this reduction tool to generate skeletal models with chemical fidelity similar to the detailed models were first tested. In this study, various skeletal models for iso-octane, dimethyl ether and cyclo-pentane were generated. The models were reduced and tested against ignition delay time simulations in zero-dimensional models, heat release and products formation in engines and IQTs using CFD codes, as well as against flame speed simulations. Overall, the DRG-X reduction method retained the fidelity of the respective detailed models in simulating the above parameters. The DRG-X method was subsequently used for the reduction of C1-C5 alcohols, FACE gasoline surrogates used for simulation of flames in this dissertation. The sections below describe the procedure for generating and validating the skeletal models mentioned above.
4.3.1 Skeletal model for iso-octane combustion

A skeletal model was generated from the recently updated iso-octane model, using the DRGX method [109]. The newly reduced model was tested against laminar flame speed data available in the literature, at atmospheric pressure [110-115] and high pressure [116]. The detailed model has 2768 species and over 9200 reactions. To reduce simulation requirement and time, the model was reduced to less number of species and reactions, and only high the temperature pathways were taken.

Reduction was carried out using the DRG-X according to the procedure already described above. Here, the error tolerance for heat was set as release as 0.01, for OH, H and iso-octane was set as 0.1 and 0.5 and the default error for other species as set as 0.4. Target pressure and temperatures for the reduction are 1-10 atm and 1000-2300 K, respectively. A skeletal mechanism with 189 species and 1136 was generated from the detailed mechanism. The transport parameters for some species which are not available in the literature were estimated by analogy. Lennard-Jones collision parameters, were estimated using critical pressure and temperature, and acentric factor properties, based on the method proposed by Tee et al. [117].

4.3.1.1 Laminar flame speed

Validation of the new model against flame speed simulations was carried out on Cloud Flame [118-120], a Cantera-based cyber-infrastructure on CCRC-KAUST [121]. Figure 4-7 shows the experimental and predicted results using the reduced model for flame speeds at 1 atm. In general, the model matches well with the experimental data at 355 K and across various equivalence ratios. Similarly, simulations were also carried out at higher pressures. Figure 4-8 shows that the
reduced model predicted experimental data within the uncertainty reported by the experiment [116].

Figure 4-7: Iso-octane/air premixed laminar flame speeds at one atm and (a) 298 K and (b) 355 K. Experimental data (symbols) are given for open squares [110], closed triangles [112], crosses [115], open triangles [111], open circles [113], and closed squares [114]. Solid lines represent simulations using the updated model.

Figure 4-8: Iso-octane/air premixed laminar flame speeds at ten atm initial pressure and different initial temperatures. Experiments (symbols) are from [116]. Solid lines represent simulations using the updated model.
4.3.1.2 Counterflow diffusion flame

Simulations were also carried out to compare predictions from the generated skeletal model against ignition temperature measurements by [44] at different strain rates. Counterflow flame ignition simulations were performed using the OPPDIF solver in CHEMKIN-PRO [122] according to the procedure described in the next chapter. Overall, the newly reduced model captured the experiment with a maximum 10 K difference, as shown in Fig. 4-8.

![Graph showing ignition temperature vs. strain rate and fuel mass fraction.](image)

Figure 4-9: Iso-octane/air counterflow diffusion flame ignition temperature; experiments (symbols) are from [116]. Solid lines represent simulations using the updated model.

4.3.2 Skeletal model for cyclopentane combustion

The results from this work are published in [123]. A skeletal model for cyclopentane combustion was generated using the DRG-X method. The detailed model has over 1600 species and 6800 reactions; its large size made the detailed model unsuitable for flame speed calculation. To reduce simulation requirement and time, the model was reduced to less number of species and reactions, and only high the temperature pathways were taken. The reduction was performed by
specifying the error tolerance for heat release as 0.01, for cyclopentane was 0.3, while for H and OH radicals were 0.1. The error tolerance for other species was 0.4.

The reduced mechanism consisted of 173 species. Analogies to molecules of similar structure were made to determine polarizability and dipolar moment transport properties of species in the cyclopentane sub-mechanism. Figure 4-9 shows that the reduced model predicted cyclopentane flame speeds well, particularly at lean conditions. For stoichiometric and rich conditions, the model under-predicted flame speed by up to 43% at $\phi = 1.7$. Under the conditions investigated, maximum speed was observed at $\phi = 1.1$, where the deviation between model and experiment was only 4%.

![Graph showing flame speed vs equivalence ratio](image)

Figure 4-10: Experimental [124] and simulated flame speed data of cyclopentane at atmospheric temperature and pressure

4.3.3 **Skeletal model for combustion of C1-C5 alcohols**
In this work, a reduced model was generated to simulate new flame speed data from experimental data by the Indian Institute of Technology Bombay. Results from this work have been submitted to fuel and energy and fuel journals for publication. The detailed high temperature alcohol mechanism by Sarathy et al. [50] was used; the model has 354 species and 2462 reactions. To minimize computational time, this model was reduced using the method of direct relation graph with expert knowledge (DRG-X); reduction was carried out for high temperatures with an error tolerance for heat release set at 0.01. The error tolerance for H and OH radicals was 0.3 and 0.1 respectively, while the default error tolerance for other species was 0.4. A resulting skeletal mechanism with 199 species and 1427 reactions was generated. The skeletal model was used to simulate a new flame speed experimental data. Simulations were performed with CHEMKIN-PRO, using the PREMIX solver, with thermal diffusion and mixture-averaged transport. Many grid points were used to completely resolve various temperature and species gradients within the flame (~1700), employing convergence parameters of GRADIENT = 0.01 and CURVATURE = 0.03. GRADIENT and CURVATURE are adaptive grid control parameters that control the extent to which the solution gradient and curvature was resolved. Figure 4-10 shows the comparison of the predicted flame speed of n-pentanol from the newly reduced model, and previous models from the literature. Figs. 4-11a and 4-11b show the performance of the newly reduced model against the new experimental data from IIT. Overall, this reduced model compared very well with the experimental result.
Figure 4-11: Comparison of laminar burning velocities of n-pentanol-air mixtures across temperature ranges with a) mechanisms b) literature data
Figure 4-12: Comparison of predicted laminar burning velocity with experimental data a) methanol b) ethanol c) propanol

4.3.4 **Skeletal model for di-ethyl ether (DEE) combustion**

In this work, a reduced model was generated from a detailed model of DEE combustion to simulate a new experimental data from a CI engine. (Results from this work are published in [125]). A detailed description of the development of the detailed chemical kinetic model for DEE mixtures follows. First, the model was built in a hierarchical manner [126], starting with Aramco Mech 1.3 C_0-C_4 base chemistry from Metcalfe et al. [127]. When Aramco Mech was combined with ethanol and DEE, the predictions were highly inaccurate. Significant improvements were required to develop a comprehensive DEE sub-mechanism, as discussed below.

Yasunaga et al. [128] presented a DEE chemical kinetic model for high temperature pyrolysis and oxidation conditions. The experimental studies on DEE focused primarily on high temperature conditions (above 1000 K); but the DEE model was not validated under lower temperature conditions of relevance to CI engine ignition. Therefore, a decision was made to begin with the high temperature kinetic model from Yasunaga et al. [128]. The low temperature
reaction classes and related rate constants were added by analogy to the comprehensive di-butyl ether (DBE) kinetic model developed by Cai et al. [129].

The newly developed chemical reaction mechanism for DEE and ethanol encompassed 1916 reactions and 348 species. To lower the computational time, the developed mechanism was reduced using the method of direct relation graph with expert knowledge (DRG-X), described above. Here, the detailed mechanism was reduced by specifying the error tolerance for heat release as 0.2. The error tolerance for H, OH, and HO₂ radicals was 0.5, 0.3 and 0.5 respectively, while the default error tolerance for other species was 0.9. A skeletal mechanism with 88 species and 470 reactions was generated. The model was then employed for the studies of various physical properties and autoignition characteristics of DEE sprays using converge (CFD) code.

4.3.4.1 Validation of the reduced model

Numerical simulations were performed and compared with experimental results to determine the accuracy of the developed model. Figure 4-12 shows a comparison of the in-cylinder pressure trace from the engine experiment and numerical simulation for DE mixtures. The peak pressure, ignition delay and SOC of all DE mixtures matched well with the experimental data. The inclusion of low temperature chemistry for DEE captured the combustion phenomenon in the CI engine, validating the numerical model. Conceptually, the hydrogen attached to oxygen in DEE was loosely bonded, enabling effective H abstraction and forming peroxide radicals. However, when the proportion of ethanol in DE mixture was higher, the scavenging effect suppressed radical formation; this has been well reflected in the simulation results. Even in the numerical study, auto ignition of DE25 could not be achieved. This complies exactly with the outcome of the experimental study, proving the accuracy of developed model.
4.3.5 **Skeletal model for alcohols, naphtha and FACE gasoline surrogates**

The above studies, using the DRGx method, provided information and a good platform for generation of skeletal models for use in multi-dimensional flows. Skeletal models were subsequently generated and used for the simulation of counterflow flames in this dissertation. Descriptions and procedures for the reduction of these models are presented in the corresponding sections.
5 Chapter 5: Effects of substitution on counterflow ignition and extinction of C3 and C4 alcohols

Dwindling reserves and inherent uncertainty in the price of conventional fuels necessitates a search for alternative fuels. Alcohols represent a potential source of energy for the future. The structural features of an alcohol fuel have a direct impact on its combustion properties. Substitution in alcohols in particular can alter global combustion reactivity. In this study, experiments and numerical simulations were conducted to investigate the critical conditions of extinction and autoignition of \( n \)-propanol, \( l \)-butanol, \( iso \)-propanol and \( iso \)-butanol in non-premixed diffusion flames. Experiments were carried out in the counterflow configuration, while simulations were conducted using a skeletal chemical kinetic model for the C3 and C4 alcohols. The fuel stream consists of the pre-vaporized fuel diluted with nitrogen, while the oxidizer stream is air. The experimental results show that autoignition temperatures of the tested alcohols increase in the following order: \( iso \)-propanol > \( iso \)-butanol > \( l \)-butanol ≈ \( n \)-propanol. The simulated results for the branched alcohols agreed with the experiments, while the autoignition temperature of \( l \)-butanol was slightly higher than that of \( n \)-propanol. For extinction, the experiments showed that the extinction limits of the tested fuels increased in the following order: \( n \)-propanol ≈ \( l \)-butanol > \( iso \)-butanol > \( iso \)-propanol. The model suggests that the extinction limits of \( l \)-butanol was slightly higher than \( n \)-propanol, with extinction strain rate of \( iso \)-butanol and \( iso \)-propanol maintaining the experimentally observed trend. Transport weighted enthalpy (TWE) and radical index (Ri) concepts were utilized to rationalize the observed reactivity trends for these fuels.
5.1 Introduction

The increased use of automobiles has made harmful soot and NOx emissions a serious global issue. To circumvent the issues of pollution and carbon emissions, there is a need to explore the use of alternative fuels, such as alcohols [50]. Alcohols are oxygen-rich fuels, and when derived from biomass they are considered to be carbon neutral [130]. With their high octane rating and low ignition propensity [50], C1-C4 alcohols increase the performance of spark ignition (SI) engines and reduce CO and particulate matter emissions when used as additives. Previous studies by Agarwal et al., [131] showed that blending ethanol or 1-butanol with gasoline can reduce knocking tendency in the SI engine, while a blend of diesel fuel with some percentage of these alcohols can reduce CO and NOx emission.

Moss et al. [132] investigated the high temperature reactivity of four butanol isomers in a shock tube, and found that 1-butanol is the most reactive while tert-butanol is the least reactive. Veloo et al. [133] performed a flame propagation study of all four butanol isomers using the counterflow premixed twin-flame technique. They observed a similar reactivity for 1-butanol, iso-butanol and sec-butanol. A comparative study on alcohol ignition delay times by Noorani et al.[134] concluded that the high temperature ignition delay time of all normal alcohols (with the exception of methanol) is similar for a given stoichiometry. In separate studies, Beeckmann et al.[135] and Sarathy et al.[50]--noted a similarity in the burning velocities of n-propanol, 1-butanol and ethanol at equivalence ratios between 0.8 and 1.1. A similar observation was made by Veloo et al.[136] when measuring laminar flame speeds of methanol, ethanol and 1-butanol at a range of equivalence ratios.

Many studies have reported the combustion properties of these important alcohols. However, studies about their autoignition and extinction behavior in counterflow diffusion flames remain
scarce (as reviewed in detail by Sarathy et al., [50]), although they are important for validating high temperature ignition and flame chemistry in kinetic models. Counterflow diffusion flame studies are more representative of combustion modes in practical non-premixed combustors, while also enabling validation of both transport and kinetics in reacting flows.

To our knowledge, no study exists on the ignition temperatures of \textit{n}-propanol and \textit{iso}-propanol in the counterflow diffusion flame. The only extinction data of \textit{n}-propanol and \textit{iso}-propanol in counterflow diffusion flame was presented by Veloo et al.[136]. They conducted an experiment using oxygen as the oxidizer and noted a lower reactivity for \textit{iso}-propanol compared to \textit{n}-propanol. Through sensitivity analysis, they found that the difference in reactivity between \textit{n}-propanol and \textit{iso}-propanol occurs mainly because the former produces higher concentrations of formaldehyde, producing formyl radicals whose subsequent reactions promote reactivity. Their numerical simulation were carried out using two models, the Curran et al.[137] model and a combination of Curran and a USC model II [138]. Overall, the combined mechanism showed a better agreement with the experiment than the single model of Curran et al.

Similarly, the only \textit{1}-butanol and \textit{iso}-butanol ignition data in the counterflow diffusion flame came from Brady et al. [16]. Extinction data for \textit{1}-butanol was previously provided by Veloo et al. [136] and Hashimoto et al. [139]; while data for the three butanol isomers was provided by D. Kyritsis et al. [140]. Brady et al. [16] employed a high pressure counterflow burner to study the effects of molecular structure on ignition temperatures of four butanol isomers at fuel mole fraction, \(X_f = 0.15\) and pressure-weighted strain rate range of (200-400) 1/s. They noted higher ignition temperatures for \textit{iso}-butanol compared to \textit{1}-butanol. Their result were simulated using butanol models by Sarathy et al. [33] and Merchant et al. [141]. In general, both models predicted the trends observed in the experiment, but slightly over-predicted the ignition
temperatures. Kyritsis et al. [140] compared the extinction limits of three butanol isomers at different equivalence ratios and explained the observed reactivity of the fuels in terms of their bond dissociation energies. They noted higher extinction limits for 1-butanol than iso-butanol, mainly because 1-butanol has more inner carbon atoms with smaller bond dissociation energies. So, few extinction studies of these fuels have been performed, and no autoignition studies are available.

Comparison of ignition and extinction data on these important classes of fuels in the counterflow remain scarce over a wide range of strain rates. For this reason, an experimental and kinetic modelling study was carried out on 1-butanol (nc4h9oh), iso-butanol (ic4h9oh), n-propanol (nc3h7oh) and iso-propanol (ic3h7oh) fuels in the counterflow flame configuration at fuel mole fraction, $X_f = 0.4$ and various strain rates. This study aims at providing additional experimental data and numerical simulations for further insight into the ignition/extinction behavior of C3 and C4 alcohols in a non-uniform flow field. These properties were selected because they are sensitive to both chemical kinetics and transport, and therefore could be used to validate chemical kinetic models. Another goal is to provide an understanding of the effects of substitution (e.g., CH$_3$ and OH) on alcohol fuel reactivity in flames, as previously performed on hydrocarbon fuels [142, 143]. To this end, the critical conditions of autoignition and extinction of 1-butanol, n-propanol, iso-butanol and iso-propanol were studied in the counterflow configuration.

5.2 **Description of Experimental and Numerical procedures**

5.2.1 **Experimental Procedure**

The experimental measurements were carried out using the counterflow diffusion flame facility at the University of California San Diego. The general schematic of the counterflow facility is
described in Fig. 4-1; a more detailed explanation of the facility has been given in [49, 144]. In summary, the burner consists of two-opposing ducts. Preheated air is introduced into the upper duct, while the diluted fuel is injected into the lower duct. The fuel stream consists of the fuel diluted with nitrogen. The two ducts are separated by a distance L. Autoignition experiments were carried out at L = 14 mm, while L = 12 mm was used for extinction experiments. The fuel mass fraction, temperature, density of the fuel stream, and the component of the fuel flow velocity normal to the stagnation plane at the exit of the fuel outlet were \( Y_{f,1}, T_1, \rho_1, \) and \( V_{1,1} \), respectively. The oxygen mass fraction, oxidizer temperature, density and the oxidizer flow velocity normal to the stagnation plane at the exit of the oxidizer outlet were \( Y_{O_2,2}, T_2, \rho_2, \) and \( V_{2,2} \), accordingly. The diameters \( d, \) of the oxidizer and the fuel ducts were both 23 mm. All experiments were conducted assuming plug flow conditions, and keeping the momenta of the counterflowing streams equal \( (\rho V_i^2), i = 1,2 \). The strain rate, \( a_2, \) Eq. (1), is defined as the gradient of the normal component of the flow velocity. This value changes from the exits of the fuel to oxidizer ducts respectively \[31\].

Assessment of the experimental strain rate in this study was performed in accordance with the procedure outlined by Niemann et al. [99], where the explicit derivation of the characteristic strain rate was also provided.

Autoignition experiments were conducted at \( T_1 \approx 400 \text{ K (±15 K)} \) and \( Y_{f,1} = 0.4 \). At a certain strain rate \( a_2, \) the temperature of the oxidizer was slowly raised by controlling the voltage to the heating element, until autoignition occurred. The temperature of the air at the exit of the oxidizer duct just before autoignition occurred \( T_2, \) was measured using a Pt-Pt 13% Rh-type thermocouple with a bead diameter of 0.015 mm. All oxidizer temperatures \( T_{2,i}, \) were corrected to account for the heat lost due to radiation using Nusselt number \( Nu = 2, \) and a constant
emissivity, \( e = 0.1 \). The flow rates of the two counterflowing streams were continuously adjusted based on their temperature, to ensure a balanced momentum.

Extinction experiments were also carried out at \( T_1 \approx 400 \text{ K} \) (±10 K) and \( T_2 = 298 \text{ K} \). At a given fuel mass fraction \( Y_{f,1} \), a stable flame is formed. The velocities of the two flowing streams \( V_1 \) and \( V_2 \) were gradually increased by increasing the flow rates while maintaining a balanced momentum between the two counterflowing streams until the flame was extinguished. The corresponding strain rate at extinction, \( a_{2,E} \), given in Eq. (1-1), was recorded.

The accuracy of the measurement of the oxidizer temperature was determined to be ±20 K. The experimental repeatability of the recorded temperature of air at auto-ignition was ±5 K. The accuracies of the strain rate and fuel mass fraction were 5\% and 3\% of the recorded values, respectively. The experimental repeatability of the reported strain rate at extinction was 3\% of the recorded value.

5.2.2 Numerical procedure

Numerical simulations were carried out with CHEMKIN PRO [145]. For ignition simulations, a detailed high temperature alcohol combustion mechanism by Sarathy et al. [50] was used. The model was comprised of 354 species and over 2400 chemical reactions and it included a complete C1-C5 alcohol sub-mechanism. For extinction simulations, a skeletal mechanism derived from this mechanism was utilized. The skeletal model consists of 205 species plus 1539 chemical reactions. It was generated manually by adding high temperature sub-mechanisms for C1-C5 alcohols to the skeletal mechanism from the iso-pentanol study of Sarathy et al. [146].

Flame ignition simulations were conducted using the OPPDIF solver available in CHEMKIN PRO [145]. First a temperature profile was established with cold mixtures at fuel and oxidizer
inlets, then the temperature of the oxidizer inlet was raised gradually until ignition occurred. The composition of the reactants and the temperature of the fuel stream, $T_1$, were kept constant while this process was performed. The calculations were carried out with thermal diffusion, mixture-averaged transport and convergence parameters of \( \text{GRAD} = 0.1 \) and \( \text{CURVATURE} = 0.1 \). \( \text{GRAD} \) and \( \text{CURVATURE} \) are adaptive grid control parameters that control the extent to which the solution gradient and curvature is resolved.

For extinction simulations, the extinction solver in CHEMKIN-PRO was employed. The solver uses an arc length continuation method to generate the S-curve. First, a stable flame was established, using the OPPDIF code at conditions near extinction, this solution was then restarted in the extinction solver. A two-point extinction method with 1000 steps was used. Large convergence factors (\( \text{GRAD} 0.1 \) and \( \text{CURVATURE} 0.5 \)) controlled the maximum gradients and curvatures allowed between grid points. Thermal diffusion and a mixture-average transport were used to determine the species diffusion coefficients and fluxes.

5.3 Results and discussion
5.3.1 Autoignition results
Counterflow diffusion flame autoignition experiments were conducted using the procedure described in the preceding section. Figure 5-1 shows the temperature of the air at autoignition as a function of strain rate. The experimental results show that a higher oxidizer temperature was required to achieve autoignition when the strain rate increased. The temperature required for fuel autoignition increased in the following order: iso-propanol > iso-butanol > 1-butanol \( \approx \) n-propanol. This trend clearly demonstrates the effect of chain substitution in decreasing the reactivity of the branched alcohols. Similar observations were also made of normal and branched hydrocarbons by [38, 142, 147, 148]. Those studies noted that increased methyl substitutions...
leads to the formation of less reactive intermediates, some of which are resonantly stable, thereby decreasing general reactivity. Overall, the model was able to predict the trends observed in the experiment, except for \( n \)-propanol. The simulated results on Fig. 5-1 under-predicted the ignition temperatures for \( n \)-propanol, and contrary to the experiments, refuted the theory that \( n \)-propanol ignites faster than \( 1 \)-butanol.

![Figure 5-1: Air temperature at autoignition, \( T_{2,1} \) as a function of strain rate, \( a_2 \). Symbols are experimental data; lines represent modelling predictions. Error bars represent uncertainties in ignition temperature measurements.](image)

5.3.2 Extinction results

The procedures described in previous section were used in counterflow extinction experiments. Figure 5-2 shows the mass fraction of fuel as a function of strain rate for both experiments and simulations. The experimental result shows that extinction limits for these tested alcohols are in the following order: \( n \)-propanol \( \approx \) \( 1 \)-butanol > \( iso \)-butanol > \( iso \)-propanol. In other words, \( n \)-propanol and \( 1 \)-butanol flames are the most difficult to extinguish while \( iso \)-propanol flame is
easiest to extinguish, demonstrating the effect of substitution on lower extinction limits in the iso-alcohols.

Experimental results in Figs. 5-1 and 5-2 show that 1-butanol and n-propanol have similar autoignition temperatures and extinction limits. Similar trends were previously observed by Veloo et al.[133], Beeckmann et al.[135] and Sarathy et al.[50], in which all normal C3-C5 alcohols were shown to have similar laminar flame speeds. The agreement between the experimental data and the model prediction is acceptable, except for n-propanol. The simulation over-predicted the reactivity of n-propanol and suggests that n-propanol is slightly more reactive than 1-butanol. The reason for this behavior by the model is investigated in next section.

Figure 5-2: The mass fraction of fuel as a function of strain rate at extinction, $a_{2,E}$ in the counterflow diffusion flame. Symbols represent experimental data, lines are modelling predictions. Error bars represents expected uncertainty in fuels mass fraction and extinction strain rates.
To understand the kinetic contribution towards diffusion flame extinction, Won et al. introduced the *transport weighted enthalpy* (TWE) and *fuel radical index* (Ri) concepts. The TWE is defined as a product of fuel concentration [149], heat of combustion ($\Delta H_c$), and inverse of the square root of the ratio of fuel molecular weight to nitrogen molecular weight ($MW_{\text{fuel}}/MW_{N2}$)$^{-1/2}$. The use of this expression enables normalization of the molecular transport and thermal contribution towards diffusion flame extinction. Therefore, the difference in reactivity of fuels can be determined by plotting extinction strain rates against the transport weighted enthalpy [150, 151]. Figure 5-3 is a graph of extinction strain rate versus TWE. The order in reactivity using the TWE is as follows: $n$-propanol > $1$-butanol > *iso*-butanol > *iso*-propanol, rationalizing the use of the extinction strain rate to explain reactivity of fuels based on their ability to form radicals.

The *fuel radical index* (Ri), can be used to quantitatively describe the kinetic role of fuel chemistry, based on the ability of a particular fuel to produce H or OH radical concentrations in a flame relative to a normal alkane [107, 150]. The TWE and Ri are based on the premise that the rates of heat release in the reaction zones are highly sensitive to diffusivities of fuel, OH and H radicals. Thus, flame quenching is less likely in fuels that produce more of these radicals. For this reason, simulations were carried out at fixed TWE $\sim$ (2.46), strain rate $\sim$ (250 s$^{-1}$), and initial fuel temperature, $T_1 = 125$ C, to calculate $Ri_H$ and $Ri_{OH}$. Propanol was used as a base fuel and the result is shown in Table (5-1). $n$-propanol was chosen as the base fuel because previous findings [50, 133, 152] showed that normal alcohols have comparable laminar flame speeds as normal alkanes. The order of these fuels, in terms of their ability to produce OH and H radicals, is: $n$-propanol > $1$-butanol > *iso*-butanol > *iso*-propanol, which clearly explains the reason for the observed differences in extinction limits of these fuels by the model. Figure 5-4 shows that the
extinction strain rate of all fuels would be almost the same when plotted as a function of TWE*Ri. Note that the correlations from the present study agree with the data by Won et al. This agreement illustrates the suitability of the radical index concept for various fuels.

Table 5-1: Summary of radical indexes RiH and RiOH of the candidate fuels

<table>
<thead>
<tr>
<th>Fuel</th>
<th>RiOH</th>
<th>RiH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-butanol</td>
<td>0.94</td>
<td>0.93</td>
</tr>
<tr>
<td>n-propanol</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>iso-butanol</td>
<td>0.89</td>
<td>0.85</td>
</tr>
<tr>
<td>iso-propanol</td>
<td>0.68</td>
<td>0.58</td>
</tr>
</tbody>
</table>

Figure 5-3: Extinction limits at different TWE. TWE = ([F]*ΔHc*(MW_{fuel}/MW_{N2})^{1/2} cal/cm³)
Figure 5-4: General correlations of extinction strain rates as a function of the product of transport weighted enthalpy and radical index. Open symbols are data from Won et al. [150], closed symbols represent current study.

To further understand why according to the model \( n \)-propanol produced more \( \text{Ri}_\text{H} \) and \( \text{Ri}_{\text{OH}} \), and consequently higher reactivity than \( 1 \)-butanol, computational analyses of the concentration profiles were carried out at a fixed TWE = 2.0 and initial fuel temperature \( T_f = 398 \text{ K} \). Additionally, integrated flux analyses were performed on these fuels to understand the controlling kinetic mechanisms of their oxidation. Figures 5-5a and 5-5c reveal that a high amount of propene and propargyl intermediates exist in \( 1 \)-butanol as compared to \( n \)-propanol. On the contrary however, the amount of propanol and formaldehyde produced by \( n \)-propanol is higher (21 and 1.5 times respectively) than the amount produced by \( 1 \)-butanol. Previous studies have shown that the presence of higher concentrations of propene in the reaction pool decreases reactivity[133]. Likewise, the comparison of the flux analyses in Figs. 5-6a and 5-6c prove that, while several pathways produce propene and propargyl radical in \( 1 \)-butanol, only a small percent
of the pathways yield propene from \( n \)-propanal flames. Most of the intermediates from \( n \)-propanol oxidation favor the formation of formaldehyde and propanal, which decompose into formyl radicals and eventually lead to the production of more active radicals. Almost 78% of propene in \( l \)-butanol flames are produced through the reaction of \( \text{C}_4\text{H}_8\text{OH}-3 \Leftrightarrow \text{C}_3\text{H}_6 + \text{CH}_2\text{OH} \), which subsequently consumes active radicals to form a resonantly stable allyl species \( \text{C}_3\text{H}_5-\text{a} \). The preferred pathway for the reaction of propargyl radical is the consumption of atomic hydrogen to form \( \text{C}_3\text{H}_4-\text{p} \). Subsequently, the high concentration of propene and propargyl in the \( l \)-butanol flame consumes the fewer OH and H produced by \( l \)-butanol, lowering its reactivity as compared to \( n \)-propanol.

Similar analysis was made in an effort to understand the effects of substitution on the observed reactivities of the tested alcohols. Figure 5-5 shows that the OH/CH\(_3\)-substituted alcohols produced almost twice the amount of propene and propargyl as \( n \)-alcohols, consequently, they produce a less reactive pool of intermediates. A comparison of \( n \)-propanol and \( iso \)-propanol fluxes in Figs. 5-6a and 5-6b respectively reveals that a greater percentage of the latter results in the formation of propene and propargyl intermediates than in \( n \)-propanol. In addition, while a large percentage of less reactive acetone is formed in \( iso \)-propanol flames, most of the intermediates produced in \( n \)-propanol would subsequently yield active radicals. As for C4-alcohols, a similar comparison can be made between the flux analyses in Figs. 5-6c and 5-6d. These comparisons show that \( iso \)-butanol produces a high percentage of \( iso \)-butene intermediates, whose succeeding reactions consume active radicals to form propene and allyl radical. Fewer such pathways are observed in \( l \)-butanol compared to \( iso \)-butanol flames. Hence, the formation of a higher amount of less reactive intermediate in \( iso \)-propanol and \( iso \)-butanol flames suggests their role in decreasing the overall reactivities of these fuels.
Figure 5-5: Comparison of concentration profiles from the oxidation of: (a) n-propanol (b) iso-propanol (c) 1-butanol (d) iso-butanol
Figure 5-6: Flux analysis showing the major pathways for all tested fuels and intermediates consumption at fixed TWE; numbers indicate consumption percentage (a) n-propanol (b) iso-propanol (c) 1-butanol (d) iso-butanol

5.4 Conclusions

In the present study, experiments were conducted using the counterflow flame apparatus. Experimental data was obtained for autoignition temperatures and extinction strain rates of four alcohol fuels. Numerical simulations were performed, and predicted results were compared to the experiments. Overall, the quantitative agreement between the model and the experiments was acceptable. The experimental results showed that ignition temperatures of 1-butanol were comparable to that of n-propanol, while the simulation over-predicted the reactivity for n-propanol. Furthermore, experiments indicated that n-propanol and 1-butanol flames had similar
extinction limits, whereas simulated results suggests that \( n \)-propanol flame was more resistant to extinction. The inability of the model to accurately predict the trend in reactivity between \( l \)-butanol and \( n \)-propanol was investigated further in numerical simulations. The result revealed that \( l \)-butanol produced higher concentrations of propene and propargyl radicals, slowing its overall reactivity. On the other hand, \( n \)-propanol produced more formaldehyde and propanal, whose subsequent reactions produced more active radicals, enhancing further reactions. Radical index analysis also showed that \( n \)-propanol produced more OH and H radicals, thereby increasing the ability to sustain a diffusion flame when compared to \( l \)-butanol.

Similarly, the amount of propene and propargyl produced by the substituted alcohols was significantly higher than the amount produced by normal alcohols, consuming the active radicals produced to form relatively stable intermediates, and probably rationalizing lower reactivity in the former.
6 Chapter 6: Counterflow ignition and extinction of FACE gasoline fuels

The demand for petroleum-derived gasoline in the transportation sector is on the rise. For better knowledge of gasoline combustion in practical combustion systems, this chapter presents experimental measurements and numerical prediction of autoignition temperatures and extinction limits of FACE A, C, F, I, J and G gasoline fuels in counterflow flames. The fuel stream consists of the pre-vaporized fuel diluted with nitrogen, while the oxidizer stream is air. The results revealed that the ignition temperatures of the tested fuels are nearly the same. A slight difference exists in the extinction limits of the fuels. An assessment of the contribution of RON and fuel molecular weight on the extinction limits of the FACE gasoline fuel was performed. The analysis revealed that both properties contributed to the reactivity of FACE gasoline fuels in diffusion flames.

6.1 Introduction

As the demand for petroleum powered cars increases, there is a need for greater knowledge about the high temperature kinetics of this fuel in transport-affected environments, as well as combustion events in practical combustors like gasoline direct injection (GDI) engines. Gasoline fuel consists of hundreds of different hydrocarbons; their composition varies significantly with location, making it difficult to model and understand its autoignition behavior from the first principle. Therefore, molecules with similar structures are often grouped together, and surrogate fuels are formulated to match the important target properties. Because the chemical and physical properties of these surrogate fuels are similar to those of the real fuel, it is easier to develop simpler models that are computationally less expensive [153].
Many target properties have been proposed for the development of surrogate fuel compositions. For example, PRF based on research octane number (RON) has been widely used as a surrogate for gasolines to match its autoignition behavior. The early work of Ranzi et al. (2) suggested a number of target properties which a surrogate fuel should possess. These properties include viscosity, octane number, thermal stability among other physical and chemical properties. Dooley et al. [154] proposed H/C ratio as one of the important target properties that a surrogate should match. Their reason was that H/C determines the enthalpy of reaction, and therefore, the adiabatic flame temperature of a fuel. For gasoline fuels, Ahmed et al. [155], recommended H/C ratio, research octane number (RON), distillation curve and density as the target properties a surrogate should have in order replicate the ignition behavior of gasolines.

The development of surrogate models that can be used to understand the autoignition properties of gasoline fuels relies on experimental data in idealized systems for validation. Such experimental data include ignition delay time data, species distribution, ignition temperatures, flame propagation and extinction, among others. However, such data about FACE gasoline fuels remain scarce. Sarathy et al. [156] compared the ignition delay time of PRF 84 and two alkane-rich FACE A and FACE C (~84, s=0) gasoline fuels in the ST and RCM. Their results showed that multicomponent surrogate blends could replicate the experimental ignition delay time of FACE A and FACE C better than the PRF 84. Javed et al. [153] used a laser-based method to measure the ignition delay time and species profiles of FACE A and FACE C fuels. They noted a similarity in reactivity and species profiles between the FACE fuels and the PRF and suggested that octane number can be used as a target property for surrogate formulation. Their simulated results using the kinetic model developed by Mehl et al. [78] were unable to capture the trend of species distribution observed in the experiment, and they suggested further improvement in the
kinetic model. In a separate study, Sarathy et al. [37] studied the effects of molecular structure on reactivity of FACE gasoline fuels. Their results indicated that FACE gasolines show similar reactivity at high temperature, irrespective of their octane rating. Their results also suggested that TPRF mixtures are only useful in reproducing the ignition properties of lower sensitivity fuels, while multicomponent surrogate mixtures are required for high sensitivity fuels.

However, all the experiments mentioned above were performed in homogeneous systems where transport occurs rapidly and contributes little to ignition events. And in practical combustion systems, ignition takes place in the presence of temperature and concentration gradients, so that species and radical diffusion can affect the progress of ignition kinetics and contribute much to ignition and extinction events. For example, Egolfopoulos et al. (9) pointed out that in non-premixed systems, ignition temperatures of multi-component surrogates are sensitive to both diffusion and kinetics in almost equal form.

In the past, the counterflow facility was utilized to study ignition temperatures and extinction limits of gaseous [43, 49] and liquid [157] fuels. The ignition temperatures of all n-alkanes and alcohols (with the exception methane) were found to increase with an increase in the fuel molecular size [38, 49, 158]. Bieleveld et al. [44] conducted a study in the counterflow on two commercial gasoline fuels (ON 87 and 91). They found that ignition temperatures and extinction limits of these fuels were nearly the same. Their numerical work also showed that PRF mixtures based on octane number was not sufficient criteria to reproduce ignition and extinction limits of gasoline fuels, and they suggested the need for multicomponent compounds for surrogate fuel formulation.
Experimental data on ignition and extinction limits of FACE fuels in the counterflow is lacking. Therefore this study is aimed at employing the counterflow configuration to investigate in details the ignition temperatures and extinction limits of FACE gasoline fuels. Also, there is a need to see if the previously developed surrogate mixtures for gasoline fuel will work under non-homogeneous environment.

6.2 Methods/experimental facility

The schematics of the counterflow burner are shown in Fig. 4-1. The burner consists of two-opposing ducts: preheated air is introduced into the upper duct, while the diluted fuel is injected into the lower duct. The upper part of the burner consists of a quartz tube directing hot air downward. The air is heated with an internal helical SiC heater, capable of heating the air to 1400K. It is electrically controlled, using variable transformers to provide constant power. The quartz tube is surrounded by high temperature-resistant insulation to minimize radiant heat loss. The fuel stream includes the fuel, diluted with nitrogen. At a distance from the outlet of the fuel duct and the oxidizer duct is a flow-straightening mesh. The upper and lower ducts are surrounded by concentric curtain-flow to isolate the flow field from ambient surrounding. The two ducts are separated by a distance L.

Autoignition experiments were carried out at L = 14.5; L = 12.5 mm was used for extinction experiments. The fuel temperature, density of the fuel stream, and the component of the fuel flow velocity normal to the stagnation plane at the exit of the fuel outlet are T1, ρ1, and V1, respectively. The oxidizer temperature, density and the oxidizer flow velocity normal to the stagnation plane at the exit of the oxidizer outlet are T2, ρ2, and V2, accordingly. All experiments were conducted assuming plug flow conditions, maintaining the momenta of the
counterflowing streams equal i.e. $\rho V_{i,2,i} = I,2$. The strain rate, $a$, Eq. (1-1), is described in chapter 1.

Autoignition experiments were conducted at $X_{f,1} = 0.4$ and $T_1$ kept close to the boiling point of each fuel. At a particular strain rate, $a_{2}$, the temperature of the oxidizer was slowly increased by controlling the voltage to the heating element, until autoignition occurred. The temperature of the air at the exit of the oxidizer duct just before autoignition occurred, $T_2$, was measured using an Omega Engineering R-type precision thermocouple with a bead diameter of 0.025 mm. The flow rates of the two counterflowing streams were continuously adjusted, based on their temperature to ensure a balanced momentum. Extinction experiments were also carried out at $T_2 = 298$ K, and $T_1$ kept close to the fuel’s boiling point. At a given fuel mass fraction $Y_{f,1}$, a stable flame was formed. The velocities of the two flowing streams $V_1$ and $V_2$ were gradually increased by increasing the flow rates while maintaining a balanced momentum of the two counterflowing streams until the flame was extinguished. The corresponding strain rate at extinction, $a_{2,E}$, given by Eq. (1-1), was recorded.

6.3 Numerical procedure

6.3.1 Mechanism reduction

For the simulation, the FACE gasoline surrogate model by Sarathy et al. [37] was utilized. However, due to its large size, the detailed model was unsuitable for ignition and extinction simulation; therefore, the detailed mechanism was reduced to remove the low temperature oxidation of FACE fuels surrogate components. The model was reduced using the direct relation graph with expert knowledge [108] (DRG-X). Details about the reduction method have been explained in the previous chapter. In this study, the detailed mechanism was reduced by specifying the error tolerance for heat release as 0.01; for H and OH radicals, tolerance was 0.1,
remaining surrogate components were at 0.3 error tolerance. The default tolerance error for other species was 0.4. A skeletal mechanism with 343 species was generated from the detailed mechanism. The transport parameters for some of the species in the skeletal model were calculated according to the method described by Sarathy et al. [159].

6.3.2 **Ignition and extinction simulation**

Table 6-1 shows the multicomponent surrogate mixtures used for these numerical modellings. Ignition simulations were carried out using the OPPDIF solver in CHEMKIN PRO. A temperature profile was first established with cold mixtures at both fuel and oxidizer sides; the temperature of the oxidizer, $T_2$ was then slowly raised until ignition was observed. The composition of the reactants and the temperature of the fuel stream, $T_1$, were kept constant while this process was performed. The simulations were performed with thermal diffusion (Soret effect), mixture-averaged transport and convergence parameters of GRAD and CURV = 0.1. For extinction simulations, the extinction solver in CHEMKIN-PRO was employed. The solver uses an arc length continuation method to generate the S-curve. At first, a stable flame was established using the OPPDIF code at conditions close to extinction, then the solution was restarted in the extinction solver. A two-point extinction method with 1000 steps was used. Convergence factors GRAD and CURV = 0.2 controlled the maximum gradients and curvatures allowed between the grid points.

<table>
<thead>
<tr>
<th></th>
<th>FACE A</th>
<th>FACE C</th>
<th>FACE G</th>
<th>FACE F</th>
<th>FACE I</th>
<th>FACE J</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>2-Methyl butane</strong></td>
<td>12</td>
<td>5</td>
<td>9.5</td>
<td>9.8</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td><strong>2-Methyl hexane</strong></td>
<td>10.3</td>
<td>4.7</td>
<td>9.8</td>
<td>7</td>
<td>28</td>
<td>23</td>
</tr>
<tr>
<td><strong>Cyclopentane</strong></td>
<td>0</td>
<td>0</td>
<td>15.3</td>
<td>15.8</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td><strong>1,2,4-Trimethylbenzene</strong></td>
<td>0</td>
<td>0</td>
<td>21.1</td>
<td>8.4</td>
<td>0</td>
<td>30</td>
</tr>
<tr>
<td><strong>1-Hexene</strong></td>
<td>0</td>
<td>0</td>
<td>8.1</td>
<td>8.4</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td><strong>2,2,4-Trimethylpentane</strong></td>
<td>60</td>
<td>54.6</td>
<td>18</td>
<td>43.7</td>
<td>35</td>
<td>12</td>
</tr>
</tbody>
</table>

Table 6-1: Mole percentages compositions of the surrogate for each fuel [37, 155, 156]
### 6.4 Results and discussions

#### 6.4.1 Autoignition results

Figure 6-1 presents the oxidizer temperature at autoignition as a function of strain rate. First, the experimental results showed that a higher oxidizer temperature was required to achieve autoignition when the strain rate increased. This was because, at the higher flow rates, the ignition kernel experienced a loss of heat and radicals, making higher temperatures necessary for autoignition. Like what was observed in ST, the graph suggests little difference in the ignition temperatures of the tested fuels at high temperatures.

![Figure 6-1](image)

Figure 6-1: Air temperature at autoignition, $T_{2,1}$ as a function of strain rate, $a_2$. 

<table>
<thead>
<tr>
<th></th>
<th>0</th>
<th>4.8</th>
<th>10.6</th>
<th>0</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Toluene</strong></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td><strong>n-butane</strong></td>
<td>7.7</td>
<td>18.4</td>
<td>7.6</td>
<td>6.9</td>
<td>0</td>
</tr>
<tr>
<td><strong>n-heptane</strong></td>
<td>10</td>
<td>12.5</td>
<td>0</td>
<td>0</td>
<td>12</td>
</tr>
<tr>
<td><strong>Cyclohexane</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5</td>
</tr>
</tbody>
</table>
6.4.2 Extinction results

Figure 6-2 shows the extinction strain rate at different fuel concentrations. The extinction limits of FACE-G are consistently lower at all fuel concentrations. Because FACE-G has the lowest H/C, % n-paraffins, and high % olefins and average molecular weight, it produces fewer active radicals and is less diffusive. FACE I has the highest extinction limits. As seen in Fig. 6-3, FACE I has low RON value and low average molecular weight, meaning that the fuel can populate radicals that sustain the flame and diffuse across the stagnation plane at a faster rate. The extinction limits of the remaining fuels are nearly the same and reflect a combined influence of both RON and average molecular weight.

![Graph showing extinction strain rate and fuel mass fraction](image-url)

Figure 6-2: The mass fraction of fuel as a function of strain rate at extinction, $a_{2,E}$, in the counterflow diffusion flame.
6.4.3 Numerical results

Extinction results presented in Fig. 6-2 were simulated using the extinction solver on Chemkin Pro. As described in the previous section, the FACE gasoline surrogate model by Sarathy et al. [37] was reduced with DRG-X and used for simulations. The simulated extinction limits of the six FACE gasoline fuels are presented in Fig. 6-4. Overall, the model agreed well with experimental data, except for FACE G; many reactions involving tri-methyl benzene were manually removed from the reduced model to reduce its stiffness. This could be the source of disagreement between the model and the experiment for FACE G.
Figure 6-4: The mass fraction of fuel as a function of strain rate at extinction, $a_{2,E}$ in the counterflow diffusion flame. Symbols represent experimental data, lines represent modelling predictions.
Results from the experiments for autoignition are simulated using the OPPDFIF solver on Chemkin Pro. The simulated autoignition temperatures of the six FACE gasoline fuels are presented in Fig. 6-5. Overall, the model agreed well with experimental data, including FACE G fuel. However, the model over-predicted the ignition temperatures of FACE J at low strain rate.
Figure 6-5: Oxidizer temperatures at autoignition as a function of strain rate, $a_2$ in the counterflow diffusion flame. Symbols represent experimental data, lines represent modelling predictions.

6.5 Conclusion

Experiments were conducted to investigate the autoignition temperatures and extinction strain rates of six FACE fuels. It is apparent from the present study that several competing mechanisms contributed to the reactivity of FACE gasoline fuels in diffusion flames. Previous studies in homogeneous systems showed that the higher the RON of fuel, the less reactive it is, this study showed that other factors, such as fuel diffusivity, also play a major role. Also, like the results from previous studies in ST, the ignition temperatures of the tested FACE fuels in transport-
affected environment were nearly the same. Unlike the ignition temperatures, a more visible difference existed in the extinction limits of these fuels. Numerical simulations were also carried out using a reduced version of the Sarathy et al. model [37], to determine the ability of multi-component surrogate mixtures to reproduce the ignition temperatures and extinction limits of FACE gasoline fuels in diffusive systems. The model agreed with all the experimental data, except for the extinction limits of FACE G and autoignition temperature of FACE J at low strain rate.
Chapter 7. Cool diffusion flames of butane isomers activated by ozone in the counterflow

Ignition in low temperature combustion engines is governed by couplings between low temperature oxidation kinetics and diffusive transport; therefore, full understanding of the coupled effects of heat release, low temperature oxidation chemistry and molecular transport in cool flames is imperative to the advancement of new combustion concepts. This study investigates the low temperature cool flame behavior of butane isomers in the counterflow configuration through the addition of ozone. The initiation and extinction limits of butane isomers’ cool flames have been investigated under a variety of strain rates. Results revealed that with the addition of ozone, butane cool diffusion flames were successfully established at low and moderate strain rates. Iso-butane has lower reactivity than n-butane, as shown by the higher fuel mole fractions required for cool flame initiation and lower extinction strain rate limits. The addition of ozone significantly influenced the initiation and sustenance of cool diffusion flames, as the ozone-less cool diffusion flame of butane isomers could not be established, even at high fuel mole fractions. The structure of a stable n-butane cool diffusion flame was qualitatively examined using a time-of-flight mass spectrometer. Numerical simulations were performed using a detailed chemical kinetic model and molecular transport to simulate the extinction limits of the cool diffusion flames of the tested fuels. The model qualitatively captured experimental trends for both fuels and ozone levels; but it over-predicted the extinction limits of the flames. Reactions involving low temperature species predominantly govern the extinction limits of cool flames. The simulations were used to understand the effects of methyl branching on the behavior of n-butane and iso-butane cool diffusion flames.
7.1 Introduction

In their efforts to comply with stringent emission regulations, auto manufacturers are investigating various combustion strategies to produce lower combustion temperatures. Such low temperature combustion (LTC) strategies (e.g. the partially premixed combustion, PPCI [3]) are increasingly attractive, as they produce fewer emissions and improve overall engine efficiency.

One of the challenges of these engines, however, is controlling heat release during the compression stroke--and thus--ignition timing. Ignition in LTC engines often occurs in two stages: the first-stage which occurs at low temperature, and the second-stage ignition, respectively. Low temperature cool flames, and associated heat release during the first-stage, affect the timing of the second-stage ignition. Engine studies [97, 125] have shown that stratified combustion concepts display ignition phenomenon governed by both molecular transport and chemical kinetic processes.

The concept of LTC and controlling oxidation chemistry is well documented for different fuels in homogeneous systems such as jet stirred reactors (JSR), rapid compression machines (RCM) and shock tubes (ST) [9, 37, 98, 109, 123, 156, 160]. Many studies were carried out to understand low temperature fuel oxidation and intermediate species produced in these systems. These have influenced understanding and advancement in building chemical mechanisms used in modeling LTC in homogeneous systems. However, transport processes are negligible in these homogeneous systems, and do not contribute to the evolution of cool flames and low temperature heat release. In counterflow diffusion systems, where the fuel is initially separated from the oxidizer, the transport, or mixing, timescale is comparable to the reaction time scales. Therefore, both transport and kinetics contribute to the morphology and sustenance of cool flames using the
opposed flow configuration [48]. These systems are canonical representations of transport-kinetic couplings present in PPCI combustion engines.

Because most previous studies focused on testing high strain rates, which require high temperature to achieve ignition [40, 107, 150, 161, 162], cool flame ignition in the counterflow configuration has received little attention. Nevertheless, initial evidence from studies by Zheng et al. [163] and Grana et al. [157], involving hot diffusion flame, suggest the existence of low temperature reactivity in the counterflow flame. Later, Law et al. [13] computationally investigated the exhibition of LTC in the counterflow using n-heptane as the fuel. They noticed the occurrence of a secondary s-curve which is controlled by low temperature species.

Few experimental studies on low temperature combustion have been carried out using the counterflow configuration. Deng et al. [48] examined the low temperature ignition of dimethyl ether (DME) and measured the intensities of formaldehyde species (HCHO) with the aid of infrared imaging. They provided experimental evidence of the occurrence of such flame by applying optical detection and measurement in the counterflow of a heated air stream against a diluted N₂/DME mixture. They used a photomultiplier (PMT) to detect the CH₂O* chemiluminescence, which characterized the low temperature reaction; while sensitive infrared imaging was used to observe the ignition temperature. They revealed that low temperature ignition is favored at low strain rates. In a separate study by Deng et al. [164], the extinction strain rates and ignition limit of DME/air were studied at high pressures. They observed and quantified the existence of a hysteresis between cool flame ignition and extinction and noted that heat release from LTC and hysteresis are promoted largely at high ambient pressure and oxygen concentrations.
The major challenge in establishing stabilized cool flames in a non-premixed counterflow is the slow initiation chemistry at low temperatures, which stops the fuel from breaking down into small radicals and formaldehyde, thus preventing low temperature branching reactions and self-initiation of the flame. Won et al. [165] developed an innovative experimental technique to initiate self-sustaining cool diffusion flames using n-heptane fuel. They demonstrated that by adding ozone to the oxidizer stream in opposed flow systems, atomic oxygen, produced as a result of ozone decomposition, significantly reduces the initiation time scales of low temperature chemistry, lengthening the flammable region of cool diffusion flames. Their numerical simulations showed that n-heptane cool diffusion flames are controlled by transport of species and low temperature chemistry triggered by ozone breakdown. In a separate study, Reuter et al. [45] used a similar procedure to compare the extinction limits of cool diffusion flames of large saturated alkanes from n-heptane to n-tetradecane. They found that fuels with longer hydrocarbon chain lengths produce stronger cool diffusion flames, but at low strain rates, the addition of ozone greatly improved low temperature chemistry and made the cool flame reactivity independent of carbon chain length. In the same study, they observed that cool diffusion flames can be sustained for large alkanes at high fuel mole fractions without ozone; however, it was doubtful that ozone-less cool flames could be sustained for n-alkanes less than n-hexane.

Clearly, the experimental method proposed by Won et al. [165] facilitates the establishment of sustaining cool diffusion flames in the counterflow facility in conditions at which cool flames may not be sustained. It also provides a platform to simultaneously study the combined effect chemical kinetics, heat release and transport on low temperature cool diffusion flames. One of the major revelations from the above studies is that existing numerical models over-predict the
measured cool flame ignition and extinction limits [45, 165-167]; implying that the LTC is still not well developed and current chemical kinetic models cannot accurately describe cool flame behavior, despite their ability to reproduce many homogeneous experiments at low temperatures.

With this in mind, this study employs the counterflow diffusion configuration, assisted by ozone addition, to determine whether butane isomers exhibit low temperature behavior in transport affected systems. As previously performed for hot flames [107, 143, 158], the present work clarifies the influence of methyl branching on extinction limits and initiation of cool diffusion flames at various strain rates, and examines the influence of both temperature and ozone concentration on the extinction limits of the tested fuels. Qualitative measurements of characteristic low temperature species--as well as other species--were obtained using a mass spectrometer containing a sampling system, ion source, mass analyser and a detector--all maintained under high vacuum conditions. Finally, with the aid of molecular transport and detailed chemistry, an analysis is carried out to understand the detailed structure and reactions responsible for the extinction of cool diffusion flames of butane isomers.

The choice of butane isomers as fuels cannot be over emphasized. Butane is a constituent of commercial gasoline and the simplest alkane exhibiting structural isomerism. n-Butane (RON-94) and iso-butane (RON 102) exhibit different knocking properties in spark ignition engines. Furthermore, n-butane is a simple gaseous hydrocarbon that shows a broad range of combustion properties such as negative temperature coefficient (NTC), low temperature chain branching, cool and hot flame [162]. Moreover, accurate kinetic models of butane are necessary to build oxidation mechanisms of higher hydrocarbons. Several studies have been carried out to understand the combustion characteristics of butane isomers, leading to the development of many comprehensive kinetic models for butane oxidation [168-174]. Nevertheless, a detailed
low temperature study of butane isomers in a non-premixed diffusive system is still not available. This study provides additional data for validation of the existing butane models.

7.2 Experimental and Numerical procedures

Figure 7-1 illustrates the counterflow configuration used in this work. The burner had two opposing duct nozzles. A preheated fuel/N₂ mixture was introduced into the upper nozzle while the oxidizer was injected into the lower nozzle. The upper part of the burner consists of an alumina tube, with an internal diameter d = 25 mm, directing preheated fuel stream downward. A preheater and an external Thermcraft heater (1-1/4ID, X8L, 365W, 115V, 12” braided leads) heats the fuel stream. A high temperature-resistant insulation surrounds the alumina tube to minimize radiation heat loss. The heaters were electrically controlled with variable transformers to provide constant power.

The oxidizer stream consists of oxygen and ozone. An ozone generator from Ozone Solutions (TG40) generates ozone from pure oxygen (>99.9% purity). A calibrated ozone monitor (2B Technology Model 106-H) is connected to the outlet of the ozone generator before the lower duct of the burner, to enable constant and accurate measurement of ozone concentration in the oxidizer stream. This analyzer measures ozone concentration using UV light absorption with accuracy greater than 0.02wt% O₂ or 2% of measurement. Production of ozone from the ozone generator is inversely proportional to the oxygen flow rate; therefore, feed oxygen is maintained throughout all measurements to keep the concentration of ozone constant [165]. To ensure constant O₃ concentration, the O₂ flow rate must be held constant, at the same time, momentum balance must be achieved. The counterflow flame momentum was balanced by changing the fuel side flow rate (both nitrogen and fuel), accounting for oxidizer momentum and fuel dilution. The variation in total fuel stream flow rate was compensated by a change in the total fuel stream
velocity and this was achieved by controlling both pure fuel and nitrogen volumetric flow rate, achieving a momentum balance. Since ozone concentration in the oxidizer stream is influenced by the volumetric flow rate of oxygen to the ozone generator, three different oxygen flow rates were tested in this experiment. To change the strain rates, the nozzles separation distance was varied.

A flow-straightening mesh was placed at the bottom of the oxidizer and the fuel ducts. The upper and lower nozzles are surrounded by concentric curtain-flows to shield the flow field from its surroundings. The two nozzles were separated by a distance, L. The strain rate, a (given by Eq. (1), a), is defined as the density-weighted gradient of the axial flow velocity [31]. The fuel flow velocity normal to the stagnation plane at the exit of the fuel nozzle, and the density of the fuel stream are \( V_1 \) and \( \rho_1 \) respectively. The oxidizer flow velocity normal to the stagnation plane at the exit of the oxidizer nozzle and the density of the oxidizer stream were \( V_2 \) and \( \rho_2 \), respectively. The accuracy of the measurement of the fuel stream temperature was determined to be ±5 K. Accuracies of the fuel mole fraction and strain rate were 3% and 5% of the recorded values, respectively. The experimental repeatability of the reported strain rate at extinction was 3% of the recorded values.

\[
a = \frac{2|V_2|}{L} \left(1 + \frac{|V_1|\sqrt{\rho_1}}{|V_2|\sqrt{\rho_2}}\right)
\]

Numerical extinction simulations were performed using the OPPDIF application in CHEMKIN-PRO [145]. The solver uses an arc length continuation method to generate an S-CURV [175]. A detailed chemical kinetic model for n- and iso-butane by Healy et al. [176-178] was used for simulation. Although not completely shown here, two other models (Aramco Mech. 1.3 [127] and 2.0 [179] were tested). The ozone chemistry subset developed by Ombrello et al. [180] with
an update from [45, 181] was incorporated into the above models for simulation. Seven hundred uniform number of grid points were also used, with 1500 maximum number of grids allowed. The adaptive gradient and curvature limits were set at 0.05 and 0.1, respectively. All simulation results were tested for grid-independence.

![Diagram of the counterflow facility](image)

**Figure 7-1: Illustration of the counterflow facility**

### 7.2.1 The mass spectrometer

Figure 7-2a shows a schematic diagram of the mass spectrometer, comprised of a sampling system, ion source, mass analyser and a detector, all maintained under high vacuum conditions between $10^{-5}$ and $10^{-8}$ torr [182]. A modified Hiden HPR-60 MBMS, connected to a Kore time-of-flight (TOF) mass spectrometer (200 m/z range), was used to measure species profiles as a function of distance from the fuel nozzle. A 200 mm long quartz sampling probe with an orifice diameter of 0.1 mm was used to collect the sample between the two nozzles. The sampling system of the MBMS consists of three stages held at different pressures. The skimmer cones for the first and second-stages are made of nickel with 0.3mm and 2mm orifices respectively, and an
external angle of 34 degrees. The first stage was held at a pressure near $10^{-3}$ Torr by a turbo-molecular pump (Edwards iXR2206, 2200 l/s), while the pressure in the second and third stage was maintained near $10^{-7}$-$10^{-8}$ and $10^{-8}$ Torr, respectively, using a turbo-molecular pump (Edwards nEXT240DX) with a pumping speed of 240 l/s in both pumps [183, 184]. Ionization of the sample was achieved using the method of electron impact (EI) which consists of a beam of electrons hitting the gaseous sample and removing an electron from the molecule [185]. The source for this type of ionization is a heated filament which emits electrons, after which they are accelerated towards an anode to impact the sample. The charged particles were accelerated by means of an electric field with energy $E = qV$ (q: charge of the particle, V: applied voltage).

The time-of-flight mass analyser functions by measuring the time taken for the ions to fly through a field-free region of known length. Thus, the ions can be distinguished by their mass over a charge ($m/z$) ratio [182]. The time-of-flight, shown in Fig. 7-2b, is a tube, 1m long, within which the ions will first be accelerated by a defined voltage, then will travel through a field-free region, after which, each ion will be slowed down inside a reflectron, made by several rings of increasing potential, and sent back to the detector, situated on the same side of the ion source. The detector is a secondary electron multiplier (SEM) which considers the electrons emitted after the impact of ions against its surface. The ionization energy is 20eV and the mass resolution is 3500 $m/\Delta m$. The output consists of a spectrum $m/z$ vs. intensity.
7.3 Results and discussion

Self-sustained cool diffusion flames were established for the tested fuels. Figure 7-3a shows direct photography of a cool diffusion flame, using a digital camera, Nikon D750. The flame was established at 5.02wt% ozone in the oxidizer stream and strain rate of $51 \text{ s}^{-1}$. To further distinguish the cool flame from a hot flame, Fig. 7-3b shows a hot flame initiated from the pre-existing cool diffusion flame, using an external ignition source. The hot flame is characterized by a bright yellow radiation of soot particles from the flame. Initiation of cool flames of both fuels was attempted in the absence of ozone; however, as anticipated by Reuter et al. [45], for these fuels, no cool flame could be observed experimentally without the addition of ozone.
Figure 7-3: Direct photography of n-butane a) cool flame initiated by ozone addition b) hot diffusion flame from the pre-existing cool diffusion flame at 5.02wt% ozone. Strain rate 51 s⁻¹

7.3.1 **Initiation and extinction limits of n-butane and iso-butane**

The initiation limits of cool flames were experimentally determined at various strain rates. Tests were carried out to investigate the influence of changing strain rate on the minimum fuel mole fraction required for cool flame initiation. The tests were performed while the temperature of the fuel stream was maintained at 570K (±5K). Figure 7-4 shows the initiation boundaries of n-butane and iso-butane cool flames. Two borders are visible from the graph, an unstable cool flame and a cool flame, which becomes stable with increasing fuel mole fraction. Typically, an unstable flame is weak and barely remains sustained for more than three seconds. The graph shows that cool flame initiation is favored at low to moderate strain rates. Lower fuel mole fraction is required to initiate the flame at lower strain rates. This is in agreement with previous cool flame studies in counterflow diffusion systems by Won *et al.* [165], Deng *et al.* [48] and Reuter *et al.* [45]. The thickness of the mixing layer and flow residence time decreases as the strain rate increases, and this decreases radical diffusion and reacting time scales. Thus, higher fuel mole fraction is required to initiate the cool flame. It is also evident from Fig. 7-4 that n-butane is more reactive than iso-butane at low temperatures, which is attributed to the differences in their molecular structure.
Figure 7-4: Initiation limits of cool diffusion flame. Fuel mole fractions required for establishment of cool diffusion flames at various strain rates and 5.02 wt% ozone on the oxidizer stream. Fuel side temperature $T_F=570K$. Oxidizer temperature $T_{O2}=300K$. Opened and closed symbols represent n-butane (nC4H10) and iso-butane (iC4H10) initiation limits, respectively. Cool diffusion flame initiation was found to be sensitive to the temperature at the outlet of the fuel duct. For this reason, the mole fraction required to establish a cool flame for n-butane was measured at different fuel outlet temperatures. Figure 7-5 shows that the mole fraction of fuel needed to establish a stable cool diffusion flame decreases with an increase in fuel stream temperature, which can be attributed to increasing cool flame chemical reaction rates with increasing temperature.
7.3.2 Extinction limits of n-butane and iso-butane cool diffusion flames

The extinction limits of butane cool diffusion flames (represented by fuel extinction mole fraction) were measured as a function of strain rate at a constant temperature and various ozone concentrations. Cool flames were extinguished by decreasing fuel mole fraction after a fully developed flame was established. To extinguish a flame at a particular strain rate and separation distance, the fuel mole fraction is gradually decreased while simultaneously increasing the nitrogen mole fraction. Therefore, the total mass flow rate will change, requiring a change in velocity to maintain balanced momentum. The fuel mole fraction at extinction was recorded at various strain rates. Figure 7-6 shows the extinction limits of n-butane and iso-butane cool flames. The results show that at low strain rates, less fuel is required to sustain the cool diffusion flames. However, at higher strain rates, higher fuel mole fraction was required to sustain the flame because it is highly stretched at high strain rates, due to the high velocity gradient. Highly strained flame caused most of the generated radicals to escape from the reaction zone, requiring that fuel mole fraction be increased to sustain the flame. Iso-butane showed a lower extinction
limit than n-butane, which is also associated with the influence of molecular structure on the low temperature reactivity of the tested fuels.

Figure 7-6: Cool diffusion flame extinction limits at various strain rates and ozone concentrations. Fuel side temperature, $T_F = 570K$.

7.4 Numerical results and discussion

As mentioned above, numerical simulations were performed using CHEMKIN-PRO. Although not all are shown here, three chemical kinetic models were initially tested to determine their ability to predict the extinction limits of n-butane: Healy et al. [176], Aramco Mech. v1.3 [127] and Aramco Mech. v2.0 [179]. However, the latter model did not produce a converging solution and the Healy model compared better with the experimental data than Aramco Mech. v1.3 (see Fig. A1, Appendix). For this reason, the Healy et al. model was chosen for subsequent simulations and kinetic analysis. Two ozone sub-models were initially tested: Ombrello et al. [180], with updates by [181], and the Princeton high-pressure ozone mechanism, also used by [186]. The Ombrello et al. sub-model was also used for cool diffusion flame simulations by Won et al. [165], Reuter et al. [45] and Masurier et al. [187]; because it was shown to perform better (Fig. A2, Appendix), it was adopted here for simulation.
Figures 7-7a and 7-7b, respectively, show comparison of the predicted extinction limits for n-butane and iso-butane, by the model, against the experimental data. The model captured the experimental trend but over-predicted the extinction limits by up to a factor of two for n-butane and a factor of three for iso-butane. This is not surprising, as all previous studies of cool flames in diffusion flames showed a similar outcome [45, 165, 166], indicating that the existing chemical kinetic models (the base chemistry or the ozone sub chemistry) cannot accurately describe the cool flame behavior in a diffusive system, despite their ability to reproduce many homogeneous experiments at low temperatures [176]. As pointed out by Reuter et al. [45], a possible reason for the inability of these models to accurately predict cool diffusion flame behavior is that the models are usually validated against ignition delay time and speciation data from established 0-D experiments, such as ST, RCM, and JSR. Because of the long ignition delay time of fuels (especially butane) at low temperature, there is a high possibility of deviation from adiabatic and/or homogenous conditions, an important assumption in modeling these systems. Experiments in jet stirred reactors are carried out at high fuel dilution, which means that heat release and fuel oxidation could be decoupled, making it possible for kinetic models derived from JSR, ST, and RCM to reproduce species data from 0-D homogeneous reactors, but unable to predict flame properties such as extinction, autoignition and flame speeds in a transport affected environment. The Healy et al. [176] model was developed for C1-C4-based hydrocarbon and oxygenated fuels, but has not yet been validated for butane isomers in counterflow diffusion flames.
Brute force sensitivity analyses were performed on both fuels to determine which reactions contribute most to the extinction limits of the cool diffusion flames. These analyses were performed by perturbation of the rate constant coefficients at 5.02wt% ozone addition. The result is presented in Fig. 7-8. Similar to the previous analysis of large hydrocarbons [165], the present sensitivity analysis reveals that cool diffusion flames are largely sensitive to low temperature reactions and reactions involving ozone. Dominant reactions include the reactions of alkylperoxy (ROO) and hydroperoxyalkyl (QOOH) radicals. Fuel abstraction reactions by OH and O have positive sensitivities on both fuels because they produce alkyl radicals that initiate low temperature reactivity. Also, reactions producing ketohydroperoxide; C4H8OOH1-3O2⇌NC4KET13+OH and C4H8OOH-I02⇌IC4KETII+OH have positive sensitivities, as their subsequent decomposition produces most of the low temperature heat release. Similarly, reactions involving ozone O3+N2=\rightarrow O2+O+N2 and O3+O2=\rightarrow 2O2+O both have positive sensitivities, as they produce O radicals which initiate the abstraction of fuel. On the other hand, O3+O⇌2O2 shows negative sensitivity, as it presents a chain termination pathway by
consuming an active O radical. Most of the reactions contributing to the bulk of heat produced include ozone and other low temperature chemistry reactions involving the fuel radicals (Fig. A3, Appendix). This also explains why cool diffusion flames in butane isomers could not be established without adding ozone, because the flame relies on heat release from ozone reactions for stabilization.
Figure 7-8: Rate constant sensitivity analyses for extinction strain rate of a) n-butane b) iso-butane cool diffusion flame at 5.68 wt% ozone. T_F = 570K.

It is apparent from the above sensitivity analysis that fuel abstraction by OH and O contributed to the reactivity of the models. Motivated by this, the rates of fuel abstraction by O atom were divided by a factor of three, and the extinction strain rate was simulated at 5.02 wt% ozone (Fig. A4, Appendix). It follows that just by decreasing this rate, better comparison with the experimental data was achieved. Although the above sensitivity analysis showed that low
temperature reactivity is spread over many species, experimental measurement of the rate of ozone decomposition to atomic O, and subsequent fuel abstraction by O radicals, might improve the ability of this model to predict the properties of cool diffusion flames.

Figure 7-6 proves that n-butane produced stronger cool diffusion flames than iso-butane; for this reason, a reaction path flux analysis was performed to define the observed trend. Based on results of the sensitivity and path flux analyses, mole fraction profiles of some important species were also compared to further explain why the two isomers had different cool flame extinction limits.

Figures 7-9a and 7-9b show the path flux analyses of n-butane and iso-butane, respectively, both at 50% fuel consumption. The analyses show that nearly 65% of n-butane fuel experienced abstraction on the secondary carbon, to subsequently produce an alkylperoxy (ROO\(^-\)) radical through the reaction of SC\(_4\)H\(_9\)+O\(_2\)\(\rightleftharpoons\)SC\(_4\)H\(_8\)O\(_2\). Most of these species isomerize directly to produce various hydroperoxyalkyl (QOOH) radicals. A majority of the remaining 35% of the fuel undergoes hydrogen abstraction on the primary carbon, also producing ROO\(^-\) radicals, through the reaction of PC\(_4\)H\(_9\)+O\(_2\)\(\rightleftharpoons\)PC\(_4\)H\(_9\)O\(_2\). Similarly, over 65% of these species isomerize directly to produce various QOOH radicals. As seen in Fig. 7-9a, the fate of most of the hydroperoxyalkyl radicals is either to directly produce formaldehyde (CH\(_2\)O), acetaldehydes (CH\(_3\)CHO), propionaldehydes (C\(_2\)H\(_5\)CHO), or to yield OH through reactions involving ketohydroperoxides (KHP).

In iso-butane, ~35% of the fuel receives hydrogen abstraction on the tertiary carbon atom to produce alkylperoxy radical. Most of this (ROO\(^-\)) undergoes concerted elimination to yield iso-butene through the reaction of TC\(_4\)H\(_9\)O\(_2\)\(\rightleftharpoons\)IC\(_4\)H\(_8\)+HO\(_2\). According to the analysis in Fig. 7-8b, this reaction has negative sensitivity, so it slows the overall reactivity of the fuel. Although not
shown here, iso-butene reacts with atomic oxygen to produce an iso-propyl radical. The reaction is written in the addition direction, which produces beta scission products without forming an intermediate radical [159]. The iso-propyl radical subsequently reacts to produce propene through another reaction with negative sensitivity; IC3H7O2 ⇄ C3H6 + HO2. In addition, ~57% of iso-butane fuel is then abstracted to produce an iso-butyl radical, which subsequently produces an alkylperoxy (ROO) radical through the reaction of IC4H9 + O2 ⇄ IC4H9O2. Some of this IC4H9O2 also experiences concerted elimination to produce iso-butene through the reaction IC4H9O2 ⇄ IC4H8 + HO2; in contrast to n-butane, in which most of the alkylperoxy radicals isomerize to QOOH radicals. Previous studies [107, 133, 158, 188] have shown that, because they produce resonantly stable radical intermediates, iso-butene and propene lead to dead-end pathways.

A comparison of the species mole fraction profiles for both fuels appears in Fig. 7-10. Figure 7-10a shows that n-butane produces higher CH2O, CH3CHO, C2H5CHO and OH. Previous studies [48, 158, 165, 189] have shown the importance of these radicals to low temperature heat release; therefore, it is not surprising that n-butane produces a stronger cool diffusion flame. However, Fig. 7-10b shows that iso-butane produces higher mole fractions of the resonantly stable C3H5-S, C3H5-T, C3H6 and HO2 species. Although not all shown here, most of the reactions involving these species have negative sensitivity.

The importance of ozone to the initiation of a cool diffusion flame could also be explained by the reaction path flux analysis in Fig. 7-10. It can be seen that most of the fuel abstraction were from OH radicals and O atoms. Figures 7-11a and 7-11b show that almost all O radicals were produced directly from ozone reactions, while the majority of OH radicals were produced either from reaction directly involving ozone or reactions with O atoms, which are themselves
generated from ozone reactions. These analyses were performed at respective positions of the highest mole fractions of O and OH.
Figure 7-9: Reaction path flux analysis at 50% fuel consumption showing major pathways for decomposition of a) n-butane b) iso-butane fuels at 5.02wt% ozone addition and 51 s\(^{-1}\). Numbers indicate consumption percentage.

Figure 7-10: Comparison of species profiles from oxidation of n-butane (dash lines) and iso-butane (solid lines) fuels at 5.02wt% ozone addition and 51 s\(^{-1}\). Arrows indicate corresponding right axis readings.
Figure 7-11: Reaction path flux analysis showing main reaction pathways for production of O and OH radicals at 5.02wt% ozone addition and 51 s\(^{-1}\). Analyses performed at locations of maximum O and OH mole fractions.

7.5 **Structure of n-butane cool diffusion flame**

Previous studies by Won *et al.* [165], Reuter *et al.* [166] and Deng *et al.* [48] used the Gas Chromatography (GC), Laser Induced Fluorescence (LIF), and Photo Multiplier tube (PMT) respectively, to measure concentration as well as intensity of the species produced from low temperature cool diffusion flames. In this present study, the structure of n-butane cool diffusion flame was measured using a time-of-flight (TOF) mass spectrometer. Sampling was carried out at strain rate 61 s\(^{-1}\) and 5.02wt% ozone addition. Intensities of C\(_4\)H\(_{10}\), N\(_2\), O\(_2\) and O\(_3\), CH\(_2\)O,
CH₃CHO, H₂O, and CO₂ are presented on Figs. 7-12a and 7-12b. To compare intensities to model prediction, numerical simulations were carried out at conditions identical to the experiment. The predicted mole fractions of these species are presented in Figs. 7-12c and 7-12d. As indicated by the peak of CH₂O profiles, experimental measurement showed that n-butane cool diffusion flame was located on the oxidizer side, while the model predicted that the flame was located near the stagnation plane in the middle of the two outlets. The observed discrepancy could be due to disturbances introduced by the sampling probe, or the inability of the kinetic model to accurately predict the flame location. It is well known that intrusive sampling of flames using a probe causes significant flame distortion[12, 190-193]; it can act as a heat sink to distort temperature and species profiles. The surface of the probe may also cause radical recombination and can result in significant loss of radicals such as H, O and OH, whose lifetimes are very short. As recently reviewed by Egolfopoulos et al. [12], the quantitative effect of a sampling probe on flow field is not known precisely, but according to J. K. Lefkowitz et al. [194] the effect on speciation is approximately equal to the outer diameter of the sampling probe, in this case ± 0.8 mm. As a consequence of these challenges, only species intensities are reported here. Nevertheless, even without the sampling probe, direct visualization of the flame, as well as the study by Won et al. [165], indicated that cool diffusion flames are located on the oxidizer side of the stagnation plane, most likely due to the strong dependence of the flame on heat release from reactions involving ozone. Both the experiment and the model showed that the fuel and oxidizer streams diffuse into each other at the flame location, indicating slow reaction at low temperature. The trends of species profiles on Fig. 7-12d agree with the experiments, except for CO₂. As seen in Fig. 7-12b, experiments indicated that slower fuel consumption produced broader species profiles and a wider reaction zone, compared to the model, as shown in Fig. 7-12a.
Figure 7-12: Structure of n-butane cool diffusion flame at strain rate 61 s\(^{-1}\) and 5.02wt% ozone addition. Symbols in (a) and (b) represent experimental measurements and lines in (c) and (d) are model predictions.

To further clarify the structure of n-butane cool diffusion flame, the temperature and mole fractions of some important LT species are plotted on Fig. 7-13. As seen, the reaction zone is located close to the stagnation plane, in the middle of the two outlets. The location of the flame is marked by a peak in temperature and CH2O mole fraction. Just before the flame, the fuel undergoes the low temperature branching pathway where O2QOOH and NC4KET13 are formed and consumed to produce the bulk of CH2O. At the flame location, the temperature is slightly higher, and QOOH beta scission forms CH2O, OH to favor C3H6. As the temperature decreases...
away from the flame, the remaining fuel diffusing across the stagnation plane reacts again through the LT pathway to form QOOH and O2QOOH, which subsequently react to produce KHP.

Figure 7-13: Simulated structure of n-butane cool diffusion flame at conditions identical to Fig. 7-12

7.6 Conclusion

An experiment was performed to study the cool diffusion flame behavior of two butane isomers in the counterflow system. With the addition of ozone, self-sustained cool diffusion flames of both butane isomers were affirmed. Ozone-less cool diffusion flames were not observed, even at high fuel mole fraction. Initiation boundaries and extinction limits of butane isomer cool flames were investigated. First, an unstable cool flame formed at a lower fuel mole fraction and a stable cool flame was sustained as the fuel mole fraction was increased. Like previous cool flame studies of high molecular weight hydrocarbons, these results showed that establishment and sustenance of cool diffusion flames of butane isomers is favored at low and moderate strain rates with ozone sensitization. Cool flame initiation was also found to be sensitive to fuel stream temperature. Results showed that the fuel mole fraction necessary to establish a cool diffusion flame decreased at higher fuel stream temperatures. The results also showed that the extinction
limits of n-butane cool diffusion flames are higher than n-butane, reflecting the differences in their low temperature reactivities. The effect of increased ozone loading on the extinction limit of cool diffusion flames was also tested. Adding more ozone to the oxidizer stream strengthened the cool flame and increased the extinction limits of both fuels.

Numerical simulations were conducted using a detailed model by Healy et al. [176-178], to examine the ability of the model to predict cool flame behavior of butane isomers in counterflow diffusion flames. Overall, the model captured the trend in the experiments at all strain rates and ozone concentrations, but it over-predicted experiment results by a factor of two and three for n-butane and iso-butane, respectively. Rate constant sensitivity analysis was carried out to discover the reactions controlling the cool flame extinction limits of both fuels. It was observed that the dominant reactions were those involving low temperature species. Although the sensitivity spread over many low temperature reactions, a measurement of the rates of fuel abstraction by oxygen radical might improve the ability of the model to predict the extinction limits of ozone-assisted cool diffusion flames. The effects of methyl branching on the behavior of n-butane and iso-butane cool diffusion flames were investigated. It has been observed that while most n-butane reacts through the pathways of hydroperoxyalkyl radicals to produce aldehydes, ketohydroperoxide and hydroxyl radicals, iso-butane favors a pathway leading to the formation of iso-butene and propene radicals. Finally, the structure of n-butane cool diffusion flame was examined using a time-of-flight mass spectrometer. The intensities of formaldehyde, acetaldehyde and other species were measured and compared to model predictions. The model captured the trend in fuel decomposition and species evolution, but it could not accurately predict the flame location.
CHAPTER 8: COOL DIFFUSION FLAMES OF PRACTICAL LIQUID FUELS THE COUNTERFLOW

8.1 Introduction

The need for greater engine efficiency has pushed the development of new combustion strategies that produce low flame temperatures. Such low temperature combustion (LTC) strategies are increasingly attractive because they produce less NOx emission and improve overall fuel efficiency. One of the challenges of these engines, however, is controlling heat release during the compression stroke--and thus--ignition timing. Ignition in LTC engines often occurs in two stages: the first stage occurs at low temperature; second-stage ignition occurs at high temperatures. The heat released during the first stage affects events at the negative temperature regime (NTC), the total energy release that drives the system, the timing of the second-stage ignition, and even knocking [195, 196].

Due to its complications, low temperature combustion chemistry would be better understood through chemical kinetic modeling. The development of such chemical kinetic models relies on experimental data from fundamental facilities for validation; however, as outlined in the previous report by this group, little data on LTC are available from systems with strong couplings between chemistry, heat release and molecular transport. Engine studies [195] have shown that stratified combustion concepts display ignition phenomenon governed by both molecular transport and chemical kinetic processes.

In the previous report by this group, and in [166], it was demonstrated that cool diffusion flames could be stabilized in the counterflow facility through the addition of ozone to the oxidizer side. The structure, initiation and extinction limits of butane isomers cool diffusion flames were
successfully investigated using the KAUST counterflow setup. It was shown that by adding ozone to the oxidizer stream in opposing flow systems, atomic oxygen produced as a result of ozone decomposition in the preheating zone significantly reduced the initiation time scales of low temperature chemistry, extending the flammable region of cool diffusion flames to higher stretch rates.

In the present study, the low temperature reactivity of practical liquid fuels was investigated. Gasoline, naphtha, and their surrogates were studied. These fuels were chosen because of their overwhelming importance. First, global demand for liquid fuels in the transport sector is rising, due partly to their ease in handling, and their high growth rate in OECD countries. In 2017, the demand for gasoline fuel reached nine million bpd and, according to reuters.com, global demand is expected to increase to 25 million barrels per day. Gasoline compression ignition (GCI) reduces NO\textsubscript{X} and soot emissions from diesel engines. In GCI strategy, low octane gasoline fuels like naphtha, run in an engine at compression ignition mode and allow more time for the fuel and oxidizer to be premixed before combustion occurs.

Gasoline and naphtha fuel consists of hundreds of different hydrocarbons, and their compositions vary significantly with location. This makes it difficult to model and understand their low temperature combustion behavior from an ordinary first principle. Therefore, molecules with similar structures are often grouped together, and surrogate fuels are formulated to match the important target properties. When the chemical and physical properties of these surrogate fuels are similar to those of the real fuel, it becomes easier to develop simpler models that are computationally less expensive. As noted, development of chemical kinetic models that can be used to understand the low temperature combustion properties of these candidate fuels relies on
well-defined experimental data for validation. Such experimental data for low temperature flame extinction on FACE gasoline fuels and naphtha fuel is not available in the literature.

Previous studies in homogeneous systems at low temperatures have shown that the ignition delay time of gasolines and naphtha fuels correlates with their octane ratings. The higher their RON, the less reactive they are at low temperatures. In the previous chapter on hot diffusion flame ignition and extinction limits of FACE gasoline fuels indicated that ignition limits of these fuels are nearly the same, but slight differences exist in their extinction limits. Also, the numerical using the gasoline surrogate model by Sarathy et al. agreed with all the experimental data, except for the extinction limits of FACE G. Necessitated by their significance in the transport sector and the need to understand their low temperature reactivity, this study will employ the counterflow facility at KAUST to determine whether gasolines, naphtha and their surrogate fuels exhibit low temperature reactivity in diffusive systems. The extinction limits of the cool diffusion flames of these fuels will be measured.

The primary aim of this study is to experimentally determine whether cool diffusion flames of gasoline, naphtha and their surrogate mixtures can be stabilized in the counterflow facility through ozone addition. If affirmed, the extinction limits of light naphtha, Halterman straight run naphtha, PRF 64.8, KAUST naphtha surrogate, Corryton gasoline, Halterman gasoline, FACE A, C, F, I, J, and G gasoline fuels, at various strain rates and fuel loading will be determined. This study would provide clarification of the contributions of RON and fuel molecular weight to the extinction limits of the tested fuels. The ultimate goal of this study is to use the data generated for the validation of the gasoline surrogates model [37] in reacting flows.
8.2 Methods/Experimental facility

The burner is identical to the one shown in Fig. 7-1, detailed description of the burner will not be given in this chapter. Briefly, the burner has two opposing duct nozzles. The fuels were pre-vaporized and diluted with nitrogen. Flow rate of the liquid fuel was controlled by a syringe pump; the fuel supply line was heated with electrical rope heaters to maintain the temperature at the junction of the fuel supply line, as well as the preheated dilution nitrogen at temperatures close to the respective boiling points of the fuels. The vaporized mixture passed through a 280 ml reservoir to minimize fluctuations in the flow rate and mixture concentration. The temperature at reservoir was also maintained close to the boiling point of the tested fuels. Preheated fuel/N\textsubscript{2} mixture was introduced into the upper nozzle, while the oxidizer was injected into the lower nozzle.

The oxidizer stream consisted of oxygen and ozone. An ozone generator was used to generate ozone. A calibrated ozone monitor was connected to the outlet of the ozone generator before the lower duct of the burner to enable constant and accurate measurement of ozone concentration in the oxidizer stream. Once the generator was on, the concentration of ozone to the lower burner varies with respect to the oxygen feed to the ozone generator. After establishing the cool flame, its extinction limit was measured by simultaneously increasing the flow rates of O\textsubscript{2} and N\textsubscript{2} in to the burners until flame extinction was observed. This ensured that the momentum balance of the two streams would be achieved as the strain rate was increased for a given fuel flow rate. The two nozzles were separated by a distance, L. The strain rate, a, given by Eq. (1-1), a, is defined as the density-weighted gradient of the axial flow velocity [49]. The fuel flow velocity normal to the stagnation plane at the exit of the fuel nozzle and the density of the fuel stream are V\textsubscript{1} and \rho\textsubscript{1}
respectively. The oxidizer flow velocity normal to the stagnation plane at the exit of the oxidizer nozzle and the density of the oxidizer stream are $V_2$ and $\rho_2$, accordingly.

8.3 Results

Figure 8-1 present extinction strain limits on cool diffusion flames of naphtha fuels and PRF 64.5. Fuel mass fraction, $Y_F$ refers to the fuel/N$_2$ mixture exiting the upper burner. The cool flame extinction limits of the tested fuels increased slightly in the following order: LN $\approx$ KNS $>$ HSRN $\geq$ PRF 64.5. This order was similar to the results from Javed et al. [197], suggesting that PRF is slightly less reactive at low temperature, possibly due to its lower paraffinic content. Figure 8-2 shows the cool diffusion flame extinction limits of FACE gasoline fuels as a function of fuel mass fraction. FACE I had a high cool flame extinction limit while FACE G had the lowest cool flame extinction limit. The cool diffusion flame of FACE I was more resistant to extinction, possibly due to its low RON (70) value, while FACE G with RON (95) was more prone to extinction. The low temperature reactivity of the remaining fuels reflects the combined influence of their octane numbers and molecular weights.
Figure 8-1: Cool diffusion flame extinction limits of light naphtha (LN), Halterman straight run naphtha (HSRN), KAUST naphtha surrogate (KNS) and PRF 64.5 as a function of fuel mass fraction.

Figure 8-2: Cool diffusion flame extinction limits of Halterman gasoline (HG), Corryton gasoline (CG), FACE C, FACE A, FACE I, FACE J, FACE F and FACE G gasoline fuels as a function of fuel mass fraction.
8.4 Conclusion and Future work

Experiments were conducted on the counterflow system to study low temperature reactivity of practical liquid fuels. Self-sustained cool diffusion flames of the tested fuels, through the addition of ozone, were affirmed. Like previous cool flame studies of butane isomers and studies on high molecular weight hydrocarbons by this group, the present results showed that establishment and sustenance of cool diffusion flames of gasoline and naphtha was favored at low and moderate strain rates with ozone sensitization. For gasoline fuels, the results showed that FACE I had strongest cool diffusion flame while FACE G had the weakest cool flame; reflecting the role of their octane numbers on their reactivity at low temperature. For naphtha fuels, results indicated that PRF 64.5 showed slower reactivity at low temperature. Numerical calculation is underway to investigate the reason for the observed trends.
9 Chapter 9 CONCLUSION AND FUTURE WORK

This project used non-premixed systems to better understand the complex couplings between low/high temperature oxidation kinetics in non-homogeneous environments. The dissertation was divided into two parts; the first part, which employs the TSL to compare model prediction with experimental data from the KAUST IQT and other constant volume combustion chambers, while the second part involves the use a well-characterized counterflow diffusion burner to measure critical conditions of cool and hot flame ignition/extinction. The data generated from the second part was used to validate available chemical kinetic models in transport affected environments.

9.1 Two Stage Lagrangian modelling

In the first section, the TSL model was used to simulate ignition delay time of iso-octane and n-heptane in the IQT, n-heptane and n-dodecane in the ECN’s CVCC and also diesel and biodiesel surrogates in a constant volume chamber from Hiroshima University. The goal of this section was to determine the capability of TSL in reproducing ignition events in the IQT and high pressure CVCC, using detailed kinetic models and comparing the way physical and chemical processes affect ignition events of fuels in these systems. The TSL model was found to be efficient in simulating IQT of long ignition delay time fuels (iso-octane) but was unable to capture the ignition delay time of n-heptane in the IQT. The inability of the TSL model to predict IQT ignition n-heptane was attributed to the model’s inability to accurately capture physical processes when they become rate controlling during ignition processes.
The TSL model is also good for CVCC experiments with high injection pressures, where physical processes contribute little to the ignition delay time. The model was able to reproduce ignition events of biodiesel, diesel and dodecane in the CVCC. Although not shown in this thesis, the TSL also captured trends in ignition location of both diesel and biodiesel with respect to increasing injection pressures. Overall, the TSL modeling approach demonstrated the suitability of using detailed chemical kinetic models to clarify spray combustion processes.

The ability of the TSL simulations to replicate observable trends in ignition delay times regarding changes in ambient/injection conditions (temperature and pressure) allowed the model to provide insights into the reactions contributing towards ignition. Thus, the TSL model was further used to understand the effects of physical and chemical parameters (exothermicity, ambient oxygen enrichment, ambient pressure and injection pressure) on the reactivity of the fuels.

If properly utilized, TSL can be a useful resource for simulating various combustion processes such as ignition delay time, soot and even flame lift off length. There is a need to adapt the code to handle the reactants in liquid phase without converting them to gas phase and also to enhance its physical aspects.

9.2 Counterflow diffusion flames

In the second part of this work, a well-characterized atmospheric pressure counterflow burner was developed and validated against previous experimental data by Humer et al. (2002) and by measuring the velocity profile of the flow field. The counterflow burner was employed to investigate the effects of molecular structure on the low and high temperature reactivity of classical and alternative fuels in transport affected systems. These effects were investigated through measurements of various conditions of extinction and ignition of various fuel/oxidizer
mixtures in hot and cool diffusion flames. The data generated were used to validate various chemical kinetic models in diffusion flames. Where applicable, suggestions were made for improving these models. Initially, the detailed models were too large for simulations, and were reduced to skeletal models with fewer numbers of species. Models reductions were performed using direct relation graph with expert knowledge (DRGX).

For hot flame studies, the tested fuels included C3-C4 alcohols and six FACE gasoline fuels. The results for C3-C4 alcohols indicated that the substituted alcohols were less reactive than normal alcohols. The ignition temperature of FACE gasoline was found to be nearly the same while slight difference existed at their extinction limits. This difference was a result of the combined influence of molecular weights of the tested fuels and their octane ratings. Predictions by the alcohol combustion models of Sarathy et al. (2014) and the gasoline surrogate model of Sarathy et al. (2015) agreed with the experimental data.

For cool diffusion flames studies, tested fuels included butane isomers, light, heavy and Halterman naphtha, six FACE gasolines, Corryton and Halterman gasolines, and their surrogates. Results revealed that with the addition of ozone, establishing cool diffusion flames in the tested fuels was successful at low and moderate strain rates. Ozone addition also showed a significant influence on the initiation and sustenance of cool diffusion flames; as ozone-less cool diffusion flames could not be established even at high fuel mole fractions. Iso-butane fuel has lower reactivity than n-butane, as shown by the higher fuel mole fractions required for cool flame initiation and lower extinction strain rate limits. Numerical simulations were performed to simulate the extinction limits of the cool diffusion flames of the butane isomers. The model qualitatively captured experimental trends for both fuels and ozone levels, but over-predicted extinction limits of the flames. For gasoline fuels, the results showed that FACE I had a stronger
cool diffusion flame while FACE G had the weakest cool flame, reflecting the role of their octane numbers on their reactivity at low temperature. For naphtha fuels, results indicated that PRF 64.5 displayed slower reactivity at low temperature. Simulations are underway to understand the detailed chemistry and the reasons for such trends.

There is a need to better understand why the existing chemical kinetic models do not agree with the experiments for cool diffusion flames. Flame sampling, using non-intrusive techniques, would also minimize the uncertainty in flame sampling.
Figure A1: Comparison of measured and computed extinction limits of n-butane cool diffusion flames as a function of strain rates using two different base chemistry models. Fuel side temperature $T_F=570$K.

Figure A2: Comparison of measured and computed extinction limits of n-butane cool flames as a function of strain rates using two ozone sub models. Dashed red line represents simulation with Princeton HP ozone sub model, solid red line represents simulation using Ombrello et al. ozone sub model. Fuel side temperature $T_F=570$K.
Figure A3: Integrated rate of heat production analysis for: a) n-butane and b) iso-butane. Fuel side temperature $T_F=570$K.

Figure A4: Rate of heat production analysis at 20% and 60% fuel consumption for: a) n-butane and b) iso-butane. Fuel side temperature $T_F=570$K.
Figure A5: Re-examining Fig. 7 with a modified rate of fuel + O. Symbols represents experimental measurement; thick lines are simulations with original rates; dashed lines are simulations with modified rate.

Table A1: Species Dictionary: Structural formula of species and intermediate classes appearing in rate of production (ROP) and sensitivity analyses

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