Ozone Activated Cool Diffusion Flames of Butane Isomers in a Counterflow Facility

Thesis by

Abdullah Abdulaziz Al Omier

In Partial Fulfillment of the Requirements

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The thesis of Abdullah Abdulaziz Al Omier is approved by the examination committee.

Committee Chairperson: Prof. S. Mani Sarathy
Committee Members: Prof. Ingo Pinna, Prof. Min Suk Cha
ABSTRACT

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Abdullah Abdulaziz Al Omier

Proceeding from the aim to reduce global pollution emissions from the continuous burning of hydrocarbons stimulated by increasing energy demand, more efficient and ultra-low emissions’ combustion concepts such as the homogenous charge compression ignition engines (HCCI) have been developed. These new engines rely on the low temperature chemistry (LTC) combustion concept. A detailed investigation of the properties of cool flames, governed by LTC, is essential for the design of these new engines.

The primary goal of this work was to build a fundamental counterflow experiment for cool flames studies in a diffusive system, to better understand combustion in LTC engines. The project was intended to provide a basic understanding of the low-temperature reactivity and cool flames properties of butane isomers under atmospheric pressure conditions. This was achieved by establishing self-sustaining cool flames through a novel technique of ozone addition to an oxygen stream in a non-premixed counterflow model.

The ignition and extinction limits of butane isomers’ cool flames have been investigated under a variety of strain rates. Results revealed that establishment of cool flames are favored at lower strain rates. Iso-butane was less reactive than n-butane by showing higher ignition and extinction limits. Ozone addition showed a significant influence on cool flame ignition and sustenance; it was found that increasing ozone concentration in the oxidizer stream dramatically increased the reactivity of both fuels. Results showed increased fuel reactivity as the temperature of the fuel stream outlet increased.
A numerical analysis was performed to simulate ignition and extinction of the cool flame in diffusive systems. The results revealed that ignition and extinction limits of cool flames are predominantly governed by LTC. The model qualitatively captured experimental trends for both fuels; however, it overpredicted both ignition and extinction limits under all strain rates and ozone concentrations. The discrepancies were within a factor of eight for the ignition limit and a factor of two for the extinction limit. Finally, sensitivity analyses were conducted to understand the reactions responsible for cool flames ignition. It was found that majority of the sensitive reactions are those that occur at low temperatures.
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<td>UHC</td>
<td>unburned hydrocarbons</td>
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<tr>
<td>IC</td>
<td>internal combustion engine</td>
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<tr>
<td>SI</td>
<td>spark-ignition engine</td>
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<tr>
<td>CI</td>
<td>compression ignition engine</td>
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<tr>
<td>HCCI</td>
<td>homogeneous charge compression ignition engine</td>
</tr>
<tr>
<td>PPCI</td>
<td>partially premixed compression ignition engines</td>
</tr>
<tr>
<td>GDCI</td>
<td>gasoline direct-injection compression-ignition engines</td>
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<td>LTC</td>
<td>low temperature chemistry</td>
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<td>HTC</td>
<td>high temperature chemistry</td>
</tr>
<tr>
<td>NTC</td>
<td>negative temperature coefficient</td>
</tr>
<tr>
<td>KHP</td>
<td>ketohydroperoxide radical</td>
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<tr>
<td>RCM</td>
<td>rapid compression machine reactor</td>
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<tr>
<td>JSR</td>
<td>jet-stirred reactor</td>
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<tr>
<td>DME</td>
<td>dimethyl ether</td>
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<tr>
<td>PMT</td>
<td>photomultiplier</td>
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<tr>
<td>MFC</td>
<td>mass flow controller</td>
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<tr>
<td>LDV</td>
<td>single-point laser doppler velocimetry</td>
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<td>PLIF</td>
<td>planar laser-induced fluorescence</td>
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LIST OF SYMBOLS

\( \tau_r \) 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 the stagnation plane.
\( X_{O2,2} \) oxidizer mole fraction
\( T_2 \) temperature of oxidizer jet
\( \rho_2 \) density of oxidizer jet
\( V_2 \) oxidizer flow velocity normal to the stagnation plane
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Chapter 1: Introduction and Motivations

1.1 Energy Needs and Consequences

Since the onset of civilization, human beings have understood simple types of energy--such as fire--as being critical to their needs; the discovery enhanced quality of life, and human mobility was further improved with the invention of wheels and machines. These now-necessities require secure, economical and environmentally-friendly energy sources to ensure safe and convenient quality of living worldwide. Economic growth and development has caused a significant increase in energy demand, expected to continue throughout the world. The global energy supply increased by nearly 150% between 1971 and 2014 [1]. Despite the variety of alternative energy sources, 85% of any nation’s energy currently relies mainly on chemical energy from hydrocarbons like coal, petroleum, and natural gas [2], which, for their convenience, high-energy amount, and economics, still play the central role in the world’s total energy picture [3]. Fig. 1 shows the increased consumption of energy derived from petroleum in the transportation sector. However, this growth in energy use, caused by the expansion in human activity, has several consequences that extend beyond immediate applications.
Our world faces a significant pollutant emission problem which threatens the environment and the quality of life of the entire planet. Rapid pollution expansion, as a result of unprecedented development in the energy sector, has occurred in recent years as shown in Fig. 2. Most of these emissions are attributed to combustion byproducts caused by burning of hydrocarbons to meet those energy needs. Major combustion-generated pollutants are carbon dioxide (CO₂), carbon monoxide (CO), sulfur oxides (SOₓ), nitrogen oxides (NOₓ), soot and unburned hydrocarbons (UHC); these poison the environment and are considered to be the main contributors to air pollution. For example, emitted SOₓ forms sulfuric acid, precipitated as acidic rain. NOₓ can be formed from high-temperature combustion situations and it is a major contributor to urban smog when it reacts with UHC. NOₓ also defects the ozone layer by removing ozone from the stratosphere, allowing more ultraviolet radiation to enter the earth’s atmosphere [5]. The rising level of anthropogenic atmospheric
CO₂ causes the catastrophic environmental problem which is global warming. Because it works as a trap for heat, effectively changing the balance of heat radiation through the entire atmosphere, it increases the earth's temperature. Soot particles from incomplete combustion of hydrocarbons impact the respiratory organs, resulting in lung diseases such as pulmonary edema and asthma; they can also cause coronary artery disease, heart disease, cancer, and even death.

![Global Greenhouse Gas Emissions by Gas, 1990–2010](image)

**Figure 2:** Global greenhouse gas emissions between 1990-2010. Adopted from U.S Environmental Protection Agency [6]

### 1.2 Path Forward

Emission accumulation has become a significant concern requiring immediate action. Climate scientists predict that air pollution due to human activities will soon worsen without significant action [1]. Governments and responsible agencies have initiated decisive steps to limit severe environmental impact. Enormous effort is being made to develop new technologies to direct combustion research toward energy saving, reducing
fuel combustion emissions, attaining sustainability, and enhancing overall energy efficiency. During the 21st century, combustion technologies advanced to achieve environmental acceptability, shaped by political and economic factors. Beginning in the late 1960’s the combustion community became interested in making combustion safer, cleaner and more efficient, since it applied in many universal applications such as transportations, industrial processes, power generations, and chemical engineering [7]. Since the early 1970s, the world has experienced extensive development aimed at more efficient and cleaner burning systems [3].

In modern industrial society and most developed economies, transportation is of central importance. There are over a billion motor vehicles in the world today [8], their numbers constantly increasing. The International Energy Outlook reported in 2016 that total global energy consumption by the transportation sector increases at an annual average rate of 1.4% [9], making the obvious argument for development of unique and advanced engine concepts and non-conventional fuel sources. These two challenges are related: new fuel sources with versatile characteristics must be compatible with emerging high-efficiency engines to provide improved efficiency and cleaner combustion that reduce fuel use and greenhouse gas emissions. For this reason, the research community and engine manufacturers are investing in producing an internal combustion (IC) engine fueled mainly by liquids derived from petroleum. Petroleum-derived liquid fuels have been the main source of transportation power for the past century and they are expected to remain so in the future [10].
1.3 Engines - Efficiency and Emissions

The conventional two types of IC engines are spark-ignition (SI) engines and compression ignition (CI) engines [11]. SI engines--known as gasoline engines--run on highly-refined fuels with narrow specifications, such as gasoline refined from petroleum crude oil. The fuel is initially premixed with air and compressed using compression stroke. After compression, combustion is initiated by spark ignition at the top of the compression stroke. Because they are equipped with catalytic after-treatment, SI engines operate cleanly, with lower emissions; but because of low compression ratios and throttling losses used to control air intake, they are less efficient [12]. On the other hand, CI engines--known as diesel engines--are considered to be the most fuel-efficient because of their high compression ratio and lack of throttling-plate losses [13]. Combustion is initiated by autoignition of vaporized fuel, mixed with compressed oxygen inside the cylinder. However, both of these engines have some drawbacks.

Because they burn a fuel-rich mixture, causing soot formation, in a high-temperature diffusion flame, leading to NOx formation [13]; diesel engines produce more soot and NOx emissions. These NOx and soot emissions must be controlled to meet very stringent global emission standards; to overcome these compromises in efficiency and emission controls, new engine concepts must be developed.

1.4 Knocking in SI Engines

Knocking is produced by the undesired autoignition of unburned gasses (end gasses). Knocking is an abnormal phenomenon causing noise and limiting the efficiency of SI engines; it can cause pressure waves that hit the cylinder walls forcefully and lead to serious
damage in the form of material removal from pistons walls. In highly boosted SI engines it has been observed that super-knocks cause engine destruction [14]. Knocking occurs because of spontaneous combustion of unburned gasses, ahead of the propagation of flame front, created by sparks [15]. The compression of end gasses by the expansion of burned gasses behind the flame front elevates the temperature and pressure, resulting in hot-spots which form because of non-uniformities in temperature and concentrations inside the engine cylinders. If the temperature and pressure of end gasses in these spots are relativity high, ignition will occur before they are consumed by the flame front; it is advance autoignition before flame front propagation that controls knocking.

Autoignition is governed exclusively by chemical kinetics [15]. The decomposition of hydrogen peroxide (H$_2$O$_2$) by three-body reaction could be the main chain branching pathway that explains why knocking occurs at intermediate temperatures (above 850 K and below 1200 K [15] ). However, it has been observed that knocking occurs at a much lower temperature in automotive engines because heat loss of end gasses in real engines is higher than in test engines. In fact, the decomposition of H$_2$O$_2$ is too slow to dominate chain branching reactions in the low-temperature range [15]. Thus, the chain branching mechanism governing this low-temperature range is different and more complicated [16]. To provide a chemical basis for understanding engine knock, additional mechanisms are required for the oxidation chemistry taking place in the low-temperature combustion range.

1.5 Need for New Engines Concepts

To meet emission regulations, and to address the combined need for improved efficiency and lower cost, engine combustion researchers are turning to alternative forms of CI
combustion. There has been significant interest in advanced-technology CI engines recently, such as homogeneous charge compression ignition engines (HCCI), partially premixed compression ignition engines (PPCI), and gasoline direct-injection compression-ignition engines (GDCI) [13], which attempt to combine the best features of both gasoline and diesel engines by using a well-mixed fuel-air charge--like SI engines, and by relying on compression ignition--like CI engines [17]. Their main advantages are high efficiency with very low NO\textsubscript{x} and soot emissions, because they depend on the principle of sufficient diluted premixed, or partially premixed, combustion to reduce emissions [18]. Combustion of lean homogeneous fuel-air mixtures takes place by autoignition caused by high compression. Fig. 3 illustrates the differences between current and future engine concepts. New concepts, such as HCCI engines, show promise for future automobile engines and power generation applications [17]; and they can target 25-40% improvement in fuel economy in light-duty vehicles [17].

Figure 3: Current and future internal combustion engine concepts. Adopted from J.P. Angelos, W.H. Green, and M.A. Singer.
1.6 Main Challenges and Properties of New Engines Concepts

In addition to the advantages of HCCI-like engines, there are some challenges that must be overcome. One of these is the difficulty in controlling heat release during high compression. Heat release is responsible for autoignition and it is determined by the preignition stage and the initial conditions, which makes control of combustion extremely difficult [10]. Heat release rates are not determined by physical processes such as flame propagation speed or vaporization—as in SI engines, or mixing time of fuel—as in diesel engines, but rather by chemical kinetics [19]. Furthermore, the ignition timing is controlled by fuel chemistry, the basis for engine design and determining combustion characteristics [20]. The high dilution fuel-air mixture leads to low autoignition temperature, demonstrating that the ignition process in these engines is controlled by low-temperature chemistry (LTC).

The second challenge is the partial mixing and inhomogeneity of the combustion, which makes autoignition is further controlled by fuel diffusion. In spite of attempts to achieve homogenous well-mixed fuel-air inside the engine’s cylinders, there is always some thermal or mixture inhomogeneity in real HCCI engines [13], for this reason current research and development efforts are directed toward overcoming these difficulties and implementing the HCCI concept in practical engines.

1.7 Research Motivations

The primary motivation is to reduce pollutant emissions and satisfy stringent global standards, which simultaneously requires the design of more efficient engines. To achieve any significant progress in overcoming the limitations of operation range, ignition timing
and reduced knocking, a thorough understanding of the oxidation processes governing in-
cylinder ignition for these advanced combustion modes is necessary. In addition, combustion of hydrocarbons fuels in such systems exhibits complex thermochemical behavior in which ignition consists of two-stage processes [15]: First-stage ignition is controlled by LTC in which heat released during the first-stage greatly affects the timing of the second-stage [20]. Ignition timing and engine knock are influenced by LTC. This implies that the new engine concept must be governed by low-temperature combustion, which is responsible for ultra-low emissions, and which explains the importance of the low-temperature chemistry.

HCCI-like engines and real combustors are characterized by non-premixed combustion, which could be represented by non-premixed diffusion flames. Diffusion flames usually have high fuel rich zones which are responsible for soot production, and high-temperature zones which are responsible for NOx production. Irregularities in temperature or concentrations cause autoignition; so transport is also significant because of the inherent interdependence between the physical and chemical time scale [21], in addition to the importance of LTC in the ignition process. Thermal and mixture inhomogeneity requires development of basic experiments to investigate the fundamental reactions underlying autoignition in the inhomogenous environment. Studying LTC in a system with strong coupling among chemistry, heat release, and transport would impact all aspects of performance and emissions of emerging high-efficiency, clean, and low-temperature combustion engine.
Chapter 2: Background

2.1 Low-temperature Chemistry (LTC)

The ignition process is the main factor influencing performance, emissions, and other characteristics of many combustion systems [15]. Ignition depends on system features such as physical, chemical mixing and transport properties [15]. In practical combustion systems, chemical kinetics is the main mechanism that controls ignition and fuel burning rate [15].

Ignition of different hydrocarbons fuels and intermediate species follows several reaction pathways, developed through several elementary steps; these pathways are divided into different categories which depend greatly on temperature ranges. Fuels behave differently in different temperature ranges [22], consequently, kinetic mechanisms change continuously with temperature [22]. In HCCI-like engines, the autoignition process is dominated by LTC kinetics, which can explain the performance of an entire system [17]. Fig. 4 shows that HCCI engines operate in the LTC region, where the formation of soot and NOx is avoided. Therefore, understanding basic low-temperature hydrocarbons oxidation is crucial to developing kinetic models that can analyze ignition in real systems.
Basically, LTC is the prevailing kinetic mechanism governing the oxidative reactions of hydrocarbons under a low-temperature regime (500-800 K) [21]. The temperature range of cool flame depends mainly on the nature of the fuel and local conditions (i.e. pressure). The chemistry in this regime is relevant to ignition in practical combustors, which is responsible for the knocking phenomena [3]. Usually, LTC is described by the term *cool flame*. Cool flame is a special flame appears at low-temperature regime and sustained almost solely by LTC, which occurs during the combustion of heavy hydrocarbons [21]. It has unique chemical reaction rates and mechanisms, different from conventional high-temperature flames (*hot flame*); and its reaction rates are much lower than those of high-temperature oxidation chemistry (HTC). The unique feature of cool flame is that its chemical reaction rates increase first, and after achieving a temperature range, they decrease with the increasing temperature. This means that the flame gets weaker, rather
than stronger, as the released heat decreases. As the temperature increases further, cool flame eventually transitions to hot ignition.

Cool flame is considered to be the precursor of hot flame ignition since it eventually transits to hot flame as the temperature increases [3]. Cool flame is usually characterized by the appearance of pale blue light, due to the chemiluminescence of excited formaldehyde (CH$_2$O$^+$) and peroxides. This bright light makes cool flame difficult to observe experimentally. Because of the small amount of chemical energy released from the fuel, heat released from the exothermic chemical reactions in cool flame is relatively small, causing a small rise in temperature--less than 200 K [21]. The reactions consume only small amounts of hydrocarbon--around 5-10 percent of fuel [3]. Since cool flames exhibit partial or intermediate oxidation reactions, they result in the formation of various amount of radicals and ionized chemical intermediate species (e.g. peroxides, aldehydes, acids, and alcohols) [23]. These precursors accelerate overall reaction rates by favoring chain-branching reactions. Because of its direct relevance to many practical combustion applications, LTC is considered to be the future of combustion systems.

### 2.2 Negative Temperature Coefficient (NTC) Phenomena

The combustion of hydrocarbons in terms of the explosion p-T diagram, can vary in complexity, depending on their molecular size and on the energy needed to break down the C-H bond, which is the difference in the activation energy of reactions [3]. Because of the higher energy of C-H bond dissociation, smaller hydrocarbons (methane, ethane, propane), are harder to ignite than those molecules with many carbon atoms. The reactivity of oxidation reactions increases with rising temperature, demonstrating the increasing
homogenous oxidation rates which lead to enhancing radical propagation rates and chain-branching reactions. After temperatures have sufficiently increased however, the cool flame exhibits a unique phenomenon called *negative temperature coefficient* (NTC). The NTC phenomena is an interesting LTC feature of large hydrocarbons. This increase in temperature could be due to an unbalance between heat loss in the system and heat release from chemical reactions. NTC is a phenomenon associated with cool flame behavior, which appears as a result of the competition between chain-branching and chain-termination reactions. In this temperature dependence, the increase in temperature rapidly decreases oxidation reactivity by slowing the reactions. Characteristic behavior of NTC is depicted in Fig. 5, which illustrates that as temperature rises in a range (800-1000 K), it causes an increase in ignition delay time as a reflection of the decrease in reactivity. This occurs because of decomposing chain-branching precursors and the beginning of chain-termination reactions, as their activation energy is lowered with temperature. Therefore NTC is considered as the transition region between low- to intermediate-temperature oxidation mechanisms.
Figure 5: NTC phenomena represented by ignition delay times for n-alkanes from C8 to C16 at 20 atm, equivalence ratio = 3, in the air [24].

2.3 History of Cool Flame

Cool flames have been a topic of discussion for more than a century and their discovery in the late 20th century [25] still elicits controversy. H. Pearlman et al. reported that Sir Humphry Davy first observed cool flames in 1817 [26]. A cool flame captured his attention when he noticed that it did not burn his fingers nor ignite a match. It was at first a matter of curiosity; and Davy thought it could be spontaneously developed into a hot conventional flame. Despite Davy’s discovery, it was believed that cool flames were first noticed accidentally by Perkin in 1882 [25]. He observed that a pale bluish flame was floating on a hot sand bath that was evaporating. Because the flame has a faint luminescence, which occurs during incomplete combustion of phosphorous, it was consequently known as a phosphorescent flame. Later, Perkin tested several fuels--alkanes, alkenes, aldehydes, alcohols, and fatty acids [27]; and he observed that most of these fuels produced cool
flames, while being combusted in air. The term *cool flame*, used to describe a faintly luminous flame, was first given by Emelius in 1929 [28]. He showed that cool flames of a variety of hydrocarbons exhibit the same spectrum regardless of the type of fuels used to produce the flame. However, cool flames have a completely different spectra than conventional hot flames, as recorded by Emelius [22]. The cool flame spectrum was characterized by a series of bands of caused by the excited CH\(_2\)O, demonstrated by Kondratiev and Ubbelhode [22]. In the 1960s, research focused on the experimental observation of cool flame phenomenology [21]; and in the 1980s, the basic principles of cool flame and low-temperature oxidative reactions were presented, after stating the importance of free radicals and establishing the principles of chain-branching reactions [29]. Even though cool flames have been studied for a long time, their behavior requires greater understanding, especially under different conditions.

### 2.4 LTC Chemical Oxidation Mechanism

The reactions of alkylperoxy (ROO\(^-\)) and hydroperoxyalkyl (QOOH) radicals are the most important in combustion chemistry, taking place in the low-temperature region (less than around 800 K) [23]. Fig. 6 shows a brief schematic mechanism for LTC. The initial step begins with slow H-abstraction reactions from fuel molecules (RH) by molecular oxygen (abundant at this early stage of the combustion process), to form an alkyl radical (R\(^-\)). This is followed by a molecular oxygen addition to the R\(^-\) radicals, leading to the formation of ROO\(^-\). This reaction is strongly temperature dependent where it is favored at low temperatures [15]; however, at elevated temperatures, the formed ROO\(^-\) are unstable and dissociate to form R\(^-\) radicals and O\(_2\) through the backward reaction. They then undergo a
\(\beta\)-scission reaction that presents the main combustion pathway at high temperatures. At low temperatures, the ROO\(^{\cdot}\) can either undergo concerted hydroperoxyl radical (HO\(_2\)) elimination reaction to form olefin, or isomerization to make QOOH. The joint elimination pathway is considered to be a chain-termination at low temperature due to the formation of HO\(_2\), which are less reactive radicals [23].

**Figure 6:** Schematic mechanism for low-temperature oxidation chemistry [23].

RO\(_2\) isomerization takes place when an internal H-atom migrates to form QOOH, which can have several alternative reaction pathways. It can produce HO\(_2\) and olefin through strenuous elimination, form OH (in addition to the cyclic ether), or follow the second addition to O\(_2\), forming hydroperoxyalkylperoxy radicals (O\(_2\)QOOH). The formation of
olefins, or cyclic ethers, is considered a chain propagation pathway. \( \text{O}_2\text{QOOH} \) isomerizes further via internal H-atom migration, followed by OH release and the formation of ketohydroperoxide (KHP or \( \text{HOOQ}_\text{H} \)). KHP species decompose further, releasing another OH radical, which provides the chain-branching pathway at low temperatures. The OH radicals produced then attack the fuel molecules through H-abstraction, producing more R· radicals, which undergo the same LTC scheme. The rate of H-abstraction by OH is higher than by \( \text{O}_2 \) and O·; consequently, the more OH in the mixture, the higher the rate of fuel consumption, leading eventually to fuel autoignition.

Normally, reactivity increases with increasing temperature; however, competition between the chain propagation of \( \text{QOOH} \) and the chain-branching pathways results in NTC of the alkanes, in which fuel reactivity decreases with increasing temperature. The decomposition of KHP occurs around 800 K, which is lower than the decomposition of hydrogen peroxide (\( \text{H}_2\text{O}_2 \)), at about 900 K. This presents the main chain-branching step at an intermediate temperature [15]. The decomposition of both KHP at low temperatures, and \( \text{H}_2\text{O}_2 \) at an intermediate temperature--in addition to their heat release--causes the autoignition of reactive mixtures in the engine cylinder during compression stroke, an indication of the influence of LTC on engine performance.

2.5 Fundamenta\( 1 \) Experimental Experiments for Cool Flame Studies

The main goal of the study of chemical kinetics is to provide comprehensive kinetic models that can be used to describe the combustion of hydrocarbons. These developed models must be validated by various results from fundamental experimental systems, such as a static reactor, rapid compression machine (RCM), shock tube, flow reactor, jet stirred reactor
(JSR), counterflow diffusion flame, engine, and any experiments available to test the reaction mechanism. LTC combustion and the study of its elementary reactions have been examined extensively over decades in several of these fundamental experimental systems [30]. The concept of LTC and NTC is well documented for various fuels in homogeneous systems such as RCM [31][32][33], shock tubes [34][35][36], flow reactors [37][38], and JSR [39][40]. Many attempts have been made to understand cool flame behavior and LTC in these systems. These efforts influenced the advancement in building chemical mechanisms used to model the homogeneous systems. One key process used to study the LTC and NTC to build these chemical mechanisms is the ignition phenomena. A thorough understanding of this phenomena can enhance safety considerations and the combustion process in practical combustors and engines [41]. Due to the complexity of LTC, most of the experimental data are collected by well-mixed homogeneous systems because they are easily represented with a simple physical model that can aid in the understanding of autoignition [14]. Some of these idealized laboratory experiments will be highlighted briefly.

2.5.1 Homogenous Systems

Historically, the heated static reactor has been used to study cool flame and autoignition [30]; it consists of a closed glass or quartz bulb with external thermal insulation, and it is usually housed inside the oven to maintain a temperature from 300 to 500 °C [14]. Before being analyzed, a reactive mixture is enclosed inside the reactor for a few minutes during the experiment. This is a simple experiment; its model still not so obvious [14]. RCM is a common apparatus used to study LTC in a non-isothermal environment [15]. It is
composed of a combustion chamber with a single stroke, as shown in Fig.7a, operated by rapid compression of the reactive mixture to temperatures and pressures representative of engine conditions, such as the simulation of a single internal combustion engine cycle. This apparatus is mainly used to measure autoignition delay time of cool flame at the end of compression. It can also be used to the study reaction process in a range of pressures and temperatures.

The shock tube is in the same family of RCM’s with a similar concept: The propagation of plane shock (caused by the sudden expansion of gas under high pressure into a gas in a low-pressure compartment) produces the rapid increase in temperature and pressure of the reactive mixture. This technique is used for ignition delay time and chemical kinetics’ measurements, particularly in the study of elementary reaction steps and pyrolysis in high-temperature autoignition. However, it could also be used to study LTC autoignition and to observe the NTC in which cool flame transits to hot flame. The flow reactor is a simple concept in which a heated quartz tube is used to flow a reactive mixture with a laminar or turbulent flow. A sample of reacted gasses can be taken at the end of the tube for analysis. Finally, JSR is another common experimental apparatus with which to study cool flames. It consists of a heated quartz sphere with four turbulent injection jets located at its center, as shown in Fig. 7b. The reactive mixture is preheated in an annular preheating zone to bring the gasses to the desired temperature of the reaction. After combustion, a sample of reacted gasses can be analyzed using different diagnostics. This experiment operates at a pressure range from 1 to 10 bar and temperatures from 250 to 800 °C [14].
2.5.2 Inhomogeneous Diffusive-Conductive Systems

The only relevant aspect of ignition in homogeneous systems is the spatial growth of radical concentration as a result of chain reaction and thermal feedback of exothermic reactions [42]. However, the working principle of homogeneous systems does not consider the main effects of transport. Since transport occurs so quickly, it does not contribute to the evolution of cool flame and low temperature heat release. Therefore, current understanding of homogeneous ignition is not a fully realistic reflection of its practical applications. Practical combustors exhibit local spatial inhomogeneity in their ignition, which appears as variations of concentrations, temperatures, and flow velocities. The transport process plays a major role in the ignition of inhomogeneous systems; it significantly influences the ignition by convective-diffusive mixing of fuel and oxygen, as well as heat conduction caused by the spatial temperature gradient [41]. Characteristic diffusion time usually becomes comparable with chemical reaction time, which contributes to the evolution of cool flame and low-temperature heat release. In this regard,
inhomogeneous experimental systems more realistically simulate the actual combustion environment. This inhomogeneity can be found in some basic flame types, such as non-premixed flames, also called *diffusion flame*. Non-premixed flame is a diffusion flame in which the fuel and oxidizer are not mixed in advance of combustion, but rather they mix in the reaction zone as the reaction takes place.

In general, the most common research configurations used to study diffusion flames are non-premixed counterflow and coflow combustion systems [12]. Non-premixed counterflow configuration is more commonly employed in diffusion flame studies [43]. In counterflow diffusion flame, the transport—or mixing timescale—is comparable to the reaction time scales. Therefore, the two processes will be firmly coupled, and the combined effect of chemistry and transport on the morphology and sustenance of cool flames can be well understood [44]. Additionally, counterflow diffusion flames studies are more representative of practical combustors, such as the diesel and gasoline engines, because, in these types of engines, both chemistry and transport are very important.

### 2.5.3 Non-premixed Counterflow System

Because of its symmetry and simplicity, the most favored plan for the counterflow system is the opposed nozzle configuration, usually simulated as quasi-one-dimensional [3]. Uniform fuel and oxidizer jets are first injected and transported against each other from an opposing nozzle (Fig. 8). At the nozzle exits, the separated fuel and oxidizer is brought to a common position by diffusion, where mixing and reacting occur simultaneously. The position at which the distance between the two opposed nozzles is equally separate is known as *the stagnation plane*. Forced convection dominates the flow, with the buoyancy
effect neglected, making the resulting flame quite steady [3]. The chemistry is complex because it covers the entire range of equivalence ratios.

![Diagram of counterflow flame generated by opposing nozzles](image)

**Figure 8:** Schematics of counterflow flame generated by opposing nozzles [3].

In this configuration, the structure of non-premixed flame consists of three main zones, as shown in Fig. 9. These zones are the rich combustion zone, occurring on the fuel side; the lean combustion zone occurs on the oxidizer side, and the reaction zone appears somewhere in between [12]. Since chemical reaction time ($\tau_r$) is much shorter than diffusion time ($\tau_d$), and the reaction rate is much faster than diffusion velocity, the implication is that the combustion event is controlled by transport, which makes mixing in the molecular level essential before burning [43]. In the counterflow diffusion system, the combustion reaction occurs rapidly and a small amount of fuel and oxidizer leak through the reaction zone (Fig. 9). As shown, fuel, and oxidizer diffuse to the flame front where they undergo sustained temperature, concentration, and velocity gradients by
chemical reaction [12]. The flame front is fixed at a location where the stoichiometric composition is achieved. Thus, stoichiometry controls the position of the reaction zone. Usually, this position is near the stagnation plane, where the temperature is known to be highest. After the combustion of fuel in the reaction zone, the product species and liberated heat diffuse away from the flame zone in all directions.

![Figure 9: Structure of non-premixed flame: Physical configuration of one-dimensional flame; temperature and concentration profiles within flame thickness [3].](image)

### 2.5.4 Strain rate

Due to the symmetry of the system, the flame is planar, and it is assumed to be one-dimensional by holding the boundary condition approximation, where the flame is believed to be uniform in the radial direction [3]. Detailed experimental measurements and computational calculations can be performed along the axial separation distance between the two nozzles and normal to the flame structure. For example, temperature, velocity, and species profiles can be measured along the separation distance between two nozzles. One desirable variable of a counterflow is the flow velocity along the centerline near the
stagnation plane. This velocity varies linearly with distance, and is characterized by a single parameter named the *velocity gradient or global strain rate* \( (a) \) \[3\]. It represents the physical effect of transport and diffusion on the flame and thickness of mixing layer. The strain rate increase shows the flame stretching due to the increase in jet velocities. Strain rate is governed by flow jet velocity and the gap distance between two nozzles; it increases with increasing flow velocity, or decreasing separation distance between two nozzles. This is illustrated in Eq. 1, which is used to calculate approximate global strain rate \[3\]:

\[
a = \frac{(U_O+U_F)}{L}
\]  

(1)

where \( U_O \) and \( U_F \) are the uniform velocities from the oxidizer and fuel nozzles respectively, and \( L \) is the separation distance between the nozzles. The inverse of strain rate \((1/a)\) represents the characteristic flow time, which is an important parameter, comparable to the characteristic reaction time--the Damköhler number. Strain rate specifications of the flow are still a major uncertainty in such studies however \[3\].
Chapter 3: Literature Review

3.1 Counterflow Diffusion Flames

For decades counterflow diffusion flames have been a topic of interest in research, receiving considerable attention in the field of combustion science [45]. This interest has spread to extensive systematic computational and experimental works for the investigation of laminar counterflow diffusion flames, for example: (1) laminar diffusion flame structures, including flame geometries, flame stretching, major species concentrations structure, and temperature and velocity profiles; (2) flame chemistry and kinetics, such as overall reaction rates for the fuel-oxidant mixture; (3) combustion characteristics like flame ignition/extinction phenomena, and flammability limits; (4) flame properties in an electric field. This research has covered several fuels under different operating conditions, including various pressures, strain rates and temperatures. In recognition of the outstanding efforts in detailed chemistry and transport investigations of counterflow diffusion flames, some important work in extinction and autoignition will be briefly highlighted.

3.2 High-Temperature Oxidation in Counterflow Diffusive Flames

Numerous computational and experimental studies have been conducted to investigate HTC of diffusive flame ignition [46], commonly known as hot flame ignition. These studies tested the autoignition of several hydrocarbons against heated air, in which the system was brought to ignition by gradually preheating the air stream. Recent studies by Darabish and Candel [47], Balakrishnan et al. [48], Kreutz and Law [49][50], and Kreutz et al. [51] examined hydrogen ignition computationally in non-premixed counterflow systems. Fotache et al. experimentally studied ignition temperatures of hydrogen and methane at
variable pressures [52][53][54]; and they extended their investigation to cover ignition of ethane, propane, n-butane, and iso-butane under variable pressures [41]. Jomaas et al. studied the ignition temperatures of ethylene and propylene for various strain rates [55]. Liu et al. measured ignition temperatures of alcohols such as n-butanol, isobutanol, and methyl butanoate for system pressures of 1 and 3 atm [56]. As a primary reference for fuel octane, n-heptane has been the subject of numerous studies regarding autoignition such as those reported by Seiser et al. [57]. Additionally, Zheng et al. experimentally and computationally examined the ignition of dimethyl ether (DME) at different pressures and strain rates [58]. Seshadri et al. studied both the extinction and ignition of methyl decanoate experimentally and computationally [59]. However, all these researchers demonstrated that--under their particular experimental conditions--ignition was governed by HTC, especially at high strain rates, instead of LTC, and without exhibiting NTC behavior.

3.3 Transition from High- to Low-Temperature Investigations

Because most studies focused on testing high strain rates, which require high temperature to achieve ignition, cool flame ignition in the counterflow configuration has received little attention. Higher temperatures, exceeding those of LTC and NTC regimes, are required to provide the necessary heating and mixing to overcome the diffusive loss for ignition kernels, which result in obviating the essential influence of LTC and NTC chemistry. It has recently been discovered that the influence of LTC ignition increases in lower strain rates [57]. However, the initial evidence began with little computational observation of the existence of LTC ignition at moderate strain rates in non-premixed counterflow. In 2005, Zheng et al. computationally observed the occurrence of two ignition turning points in a
moderately strained non-premixed counterflow of DME versus heated air, where the lower turning point occurred in the low-temperature regime [58]. In separate studies, Liu et al. numerically examined the effects of steady and unsteady strain on the transient ignition of n-heptane at elevated pressures, with detailed chemistry and transport in non-premixed counterflow configuration [60] [61]. They found that both low- and intermediate-temperature chemistries evolved for low to moderate strain rates, like that in homogenous systems. Moreover, Grana et al. numerically predicted the critical conditions of extinction and autoignition of condensed hydrocarbon fuels in non-premixed flows [62]. Using a detailed chemical kinetic mechanism, they found that at low strain rates, autoignition is promoted by LTC for straight-chain hydrocarbon fuels.

In further explorations, Law and Zhao recently demonstrated the first distinctive NTC-affected chemistry reactivity computationally, and weakly burning flame at low strain rates, using hot air and n-heptane as model fuels [42]. Their results showed that ignition occurs in two stages within lower temperature regimes; and they identified the presence of NTC phenomena for non-premixed counterflow by observing the existence of a secondary S-curve, grafted onto the lower branch of the primary conventional S-curve. They also discovered that the occurrence of LTC and NTC affected ignition/extinction, presented by a secondary S-curve, becomes more pronounced at reduced strain rates or higher pressures; so ignition at this lower region is controlled by LTC. In 2013, Law and Zhao continued their work by performing a comprehensive computational and mechanism study [63]. They developed a global and detailed reaction kinetics in first stage ignition and concluded that the same chemistry controls the ignition of the non-premixed counterflow as that of the homogeneous mixture, with the same global kinetic parameters.
Few experimental studies on LTC combustion have been carried out using the counterflow configuration. Deng et al. investigated low temperature ignition of DME and quantified CH\textsubscript{2}O species with the aid of infrared imaging [44]. They provided experimental evidence of the existence of such flame by applying optical detection and measurement in counterflow of a heated air stream against a diluted nitrogen/DME mixture. A photomultiplier (PMT) was used to detect the CH\textsubscript{2}O\textsuperscript{*} chemiluminescence which characterizes the low temperature reaction, while sensitive infrared imaging was used to determined corresponding ignition temperature. In their study, ignition temperatures of the air were observed under various strain rates; they also demonstrated that low temperature ignition is favored at low strain rates. In a separate study, Deng et al. examined ignition and extinction strain rates of DME/air at high pressure [64]. They observed and quantified the existence of hysteretic behavior between cool flame ignition and extinction for the first time experimentally. They noted that heat release from LTC and hysteretic behavior are promoted largely at high ambient pressure and oxygen concentrations.

3.4 Self-Sustaining Cool Flames in Non-Premixed Counterflow

The major challenge of establishing stabilized cool flames in non-premixed counterflow is slow induction chemistry at low temperature, which prevents the fuel from breaking down into small radicals and formaldehyde, also preventing low temperature branching reactions and self-initiation of the flame. Won et al. developed a novel method to establish self-sustaining cool diffusion flames [65]. They recently demonstrated that the addition of ozone to the oxidizer stream in opposed flow systems intensely reduced the induction time scales of low temperature chemistry, thereby extending the flammable region of the cool
flame. In their experimental methodology, diluted nitrogen/fuel stream was preheated and injected to heated counterflow burner while ozone was added to the cold oxygen stream. They measured the extinction limits of n-heptane/oxygen cool diffusion flame over various strain rates experimentally, and determined the flammability diagram of cool diffusion flame. They observed the existence of three different flame regimes, depending on fuel mole fraction and strain rate: hot diffusion flames, cool diffusion flames, and unstable cool diffusion flames. In their work, numerical simulation proved that n-heptane cool diffusion flames are strongly governed by species transport and low-temperature chemistry is activated by ozone decomposition.

Reuter et al. applied the same methodology to investigate the low temperature reactivity of large n-alkanes, ranging from n-heptane to n-tetradecane through cool diffusion flame extinction [66]. They found that the chain length of the n-alkane plays a significant role in determining cool flame reactivity in terms of cool flame extinction limit. A larger chain length produces substantially stronger cool diffusion flames. At low strain rates particularly, it was observed that adding ozone to assist the flame--by dramatically enhancing the low temperature reactivity--made the cool flame reactivity essentially independent of the size n-alkane size. However, the main revelation in these studies was that numerical models over-predict the measured cool flame extinction limit by showing a large scatter in the models. This implies that the LTC is still not well developed and the current chemical kinetic models cannot accurately describe cool flame behavior, despite their ability to reproduce many homogeneous experiments at low temperatures.
This new experimental method enables the establishment of self-sustaining cool flames in conditions at which normal cool flames may not be observable. It also provides a platform to simultaneously study chemical kinetics and the flame dynamics associated with the complex low temperature chemistry in well-known flame geometry. Recent progress promises that using plasma-assisted combustion in counterflow flames could accelerate the induction time of cool flame chemistry by producing active radicals generated from plasma discharge to stabilize diffusion flames [67]. However, due to the complexity of direct plasma discharge on combustion chemistry, ozone is still preferred as an atomic oxygen carrier which reduces the time scale of induction chemistry and activates LTC.
Chapter 4: Research Objectives

Proceeding from the question of whether all fuels exhibiting low-temperature behavior in homogeneously premixed systems show similar tendencies for flows with low levels of nonuniformity, the broader aim of this investigation is to further explore the possible manifestation of cool flame behavior—particularly through ignition and extinction in counterflow diffusive configuration. This inquiry will provide fundamental experimental results to validate low temperature reaction mechanisms and to establish rigorous mechanisms of hydrocarbons oxidations by investigating many more key complex reactions. This study will also clarify the action of chemical kinetics occurring under engine similar conditions to better achieve higher thermal efficiency and low pollutant emissions in both conventional and future engines.

The primary objective of this work is to construct a counterflow-opposed nozzle facility to establish self-sustaining cool diffusion flame with well-defined boundary conditions. The additional goal is to utilize the counterflow diffusion configuration (assisted by ozone addition), to understand the ignition of critical cool flames and the extinction properties of butane isomers. Therefore, this work will demonstrate experimental methodology to establish n-butane and iso-butane cool diffusion flames by ozone addition in an oxidizer stream under atmospheric pressure. The ignition and extinction limits will be specified, and the influence of the strain rate on both the ignition and extinction of cool flame will be investigated. An investigation of the influence of both temperature and ozone concentration on the ignition limits will also be carried out. Finally, with the aid of molecular transport and detailed chemistry, a numerical simulation will be performed to study the accuracy of the chemical kinetics’ model to describe the cool flame in diffusive systems. Also, a
sensitivity analysis will be made to understand the dominant reactions responsible for cool flames ignition of butane isomers.

The preferred choice of butane as a fuel cannot be over-emphasized. Butane is a constituent of commercial types of gasoline and the simplest alkane exhibiting structural isomerism. n-butane (RON-94) and iso-butane (RON 102) present different knocking properties in spark ignition engines [41]. Furthermore, butane is a simple gaseous hydrocarbon with a broad range of combustion properties such as NTC, low temperature chain-branching, cool and hot flame. Since it is a gaseous fuel, it does not require pre-vaporization in the experimentation. Finally, it is not surprising that the kinetics mechanisms of butane would be necessary to build an oxidation mechanism of higher hydrocarbons; extensive studies have been conducted to understand its combustion characteristics. However, comprehensive kinetics’ models have only been proposed for homogeneous C₄ combustion in the several temperature ranges [41][15]. Despite this, a detailed study of ignition and extinction characteristics of butane and its isomer in the non-premixed diffusive system has not yet been conducted.

iso-butane

H₃C

CH₃

CH₃

n-butane

H₃C

H₃C
Chapter 5: Methodology

The methodology of this research is discussed in detail in Chapter 4, which includes the comprehensive experimental goals of the study of butane isomers’ cool flame, activated by ozone addition, and especially the parameters requiring investigation and the experimental data to be collected. The chapter is followed by an overall description of the experimental facility used in this study, detailed experimental and simulation procedure.

5.1 Detailed Objectives and Studying Parameters

The main scope of this study is to provide a basic understanding of the low temperature reactivity of butane isomers under atmospheric pressure conditions. The goal of the experimental work is to investigate the critical points of butane isomers’ cool flames, activated by ozone addition to oxygen, in a counterflow setup. This work has been divided into several sub-experimental deliverables to provide necessary experimental data required for any model and mechanism validation of n-butane and iso-butane in a diffusive system. This work includes experimental investigation of the following parameters:

- Establishing self-sustaining n-butane and iso-butane cool flames at atmospheric pressure.
- Cool flame ignition limits; minimum fuel ignition concentrations with respect to different strain rates and under constant conditions (temperature and ozone wt%).
- Cool flame extinction limits; minimum fuel extinction concentrations with respect to different strain rates and under constant conditions (temperature and ozone wt%).
- The effect of changing ozone concentration on fuel ignition concentration under constant temperatures.
- Cool flame ignition temperature limits; minimum ignition temperature of various fuel concentrations at a particular strain rate.

5.2 Experimental Apparatus Specification

The experimental measurements were performed using a newly-developed counterflow diffusion flame platform established at the Clean Combustion Research Center (CCRC), KAUST. Fig. 10 shows a schematic illustration of the counterflow configuration model. The burner was designed for ignition experiments in atmospheric pressure; it consists of two opposing concentric metal nozzles. N-butane, 99.95% purity, and iso-butane, 99.5% were used as fuel in this experiment. Fuel and nitrogen streams were mixed to achieve the desired dilation, followed by mixture preheating. Preheated fuel/nitrogen mixture was introduced into the upper nozzle while the oxidizer stream was injected directly into the lower nozzle. The upper part of the burner consists of an alumina ceramic tube, 311mm length and 32 mm internal diameter, directing preheated fuel diluted well-mixed stream downward. The alumina tube is fixed between two metal bases sealed with high-temperature silicon glue and ceramic clay to prevent gas leakage. Heating the fuel/nitrogen mixture was achieved with a preheater and an external Thermcraft heater, 1-1/4ID X8L 365W 115V 12” braided leads. The heater is 203mm high. The ceramic tube and heaters are surrounded by a high temperature-resistant insulation to minimize radiant heat loss. Both heaters are electrically controlled using variable transformers to provide constant power.
Figure 10: Schematic diagram of the counterflow system.

The oxidizer stream consists of pure oxygen mixed with ozone. An ozone generator from ozone solution (TG 40) was used to generate ozone via microplasma dielectric barrier discharge, corona cell, from pure oxygen (>99.9% purity). This process uses an electrical spark to split the molecular bond of natural diatomic oxygen to form ozone. The flow of oxygen feed gas through the corona cell directly influences ozone concentration. As the flow increases, ozone concentration decreases, and vice versa. This occurs because more contact time allows for a greater amount of oxygen to be converted into ozone. While flow and pressure of oxygen feed gas to the ozone generator affects the ozone output, the outlet ozone concentration is controlled by regulating the oxygen upstream volumetric flow rate. (Oxygen upstream pressure is maintained at ten psi, as recommended by the manufacturer.) Proper ozone concentration is achieved using the TG Series performance chart. A well-
calibrated ozone monitor, 2B Technology Model 106-H, is used at the ozone generator output and just before the lower duct of the burner, to enable constant, accurate measurement of ozone concentration in the oxidizer stream. This analyzer measures ozone concentration (wt %) in oxygen stream precisely, using a UV light absorption method with an accuracy greater than 0.02 wt % O₂ or 2% of measurement. Fig. 11 shows the ozone generator and analyzer used.

![Ozone Monitor and Sensor](image)

**Figure 11**: TG 40 ozone generator, 106-H ozone monitor, and ozone sensor.

A flow-straightening mesh is placed at the bottom of the fuel and the oxidizer nozzles. Both the upper and lower burner ducts are 25.4 mm inner diameter at the exit; they are surrounded by a concentric curtain flow of nitrogen, 52.2 mm diameter, to isolate the flow field from the ambient surrounding, reduce flame stagnation curvature, and minimize the radial temperature gradient [52]. The two nozzles are separated by a distance L, which could be less than or equal to the inner tube diameter to minimize the effect of the nozzle rim on the main flow [3]. The separation distance is adjustable according to the desired strain rate. Gas flow to the main nozzles is regulated by well-calibrated mass flow controllers (MFCs), MKS-type, with a multi-gas controlling box. Nitrogen co-flow is
regulated with pressure gauges. Gas temperature feedback is measured with a Chromel-Alumel thermocouple (K-type class 2 NCF 600, Cnino), with a highly sensitive, vibration resistance and quick response. Its average outer diameter is 0.5mm; and it is capable of measuring temperatures up to 600°C. The thermocouple tip is placed along the flow centerline, directly under the upper nozzle exit and close to the surface of inner mesh; it measures the axial centerline temperature of the hot fuel stream immediately after the upper nozzle exit. A digital camera (Nikon, D70) was used to capture the flame photos. Fig. 12 shows the actual photo of the counterflow setup.

Figure 12: Counterflow diffusion flame model designed at KAUST, CCRC.
5.3 Experimental Procedure

The experimental procedure was developed to achieve the greatest potential from each experiment. Several testing experiments were performed to validate the setup and to specify suitable working conditions within the cool flame flammability limit. A schematic of the experimental model is shown in Fig. 13. Initially, the setup is heated gradually to the desired temperature. Heating the fuel/nitrogen stream usually takes a couple of hours until a stabilized temperature is reached. For safety reasons, and to reduce unnecessary fuel consumption, initial heating should be done by flowing either nitrogen or air. Fuel flow, and the experiment, can begin after the desired temperature range for cool flame is reached.

Figure 13: Schematic illustration of the experimental facility.
As shown in Fig. 13, gaseous n-butane, or iso-butane fuel, was delivered directly from highly pressurized cylinders via MFCs. Before heating, the fuel flow was diluted by mixing with nitrogen. The diluted fuel stream was then heated and directed to the upper burner. A thermocouple was placed exactly at the center, below the upper burner duct, to measure the fuel stream temperature at the flow centerline. The oxygen stream flow rate was controlled by another MFC before entering the ozone generator. The ozone generator enriched the oxygen stream with ozone. A well-calibrated ozone analyzer was connected in series with the ozone generator to monitor the concentration of ozone generated while the experiment was running. The outlet oxygen/ozone stream was directed to the lower burner. The curtain nitrogen flow from both nozzles was adjusted to stabilize the flame and reduce flame curvature. Usually, guard flow of inert gas (e.g. nitrogen), is added to surround the flow because of its ability to maintain stability and adjust flow velocity by isolating the reactant jets from the environment. To maintain the position of the stagnation plane, the fuel/nitrogen flow must be adjusted to keep the momentum balance between jets, since the oxidizer stream remains unchanged.

5.3.1 Operation Conditions

The focus of this experiment was the temperature range where the cool flame was expected to occur. The investigation tested the temperature range (roughly around 400-590 K). All experiments were performed under atmospheric pressure. Since the counterflow facility was built mainly for the purpose of atmospheric studies, the influence of pressure on cool flame ignition was not a point of interest and outside the scope of this work. After testing the operating conditions, experiments were performed at 570 K fuel stream temperature,
which was used as a reference for calculating fuel and nitrogen flow rates. Because there were several systems involved for heating the fuel stream and controlling four heating sources simultaneously—including a variable transformer, preheater, and heating tapes—maintaining the fuel stream temperature at an exact value presented a challenge. Furthermore, fuel stream temperature is very sensitive to any change of fuel concentration, posing another challenge because the fuel has lower heat capacity compared to nitrogen, causing an increase in temperature with fuel concentration. The procedure also required continuous changing of fuel dilution to obtain ignition; this entailed continuous monitoring of the temperature throughout the experiment. Despite these limitations, the heaters were controlled to maintain fuel temperature. Fuel temperature was estimated to be measured with a relative error of (±5 K).

The oxidizer stream temperature was 300 K, as measured directly before the lower burner. Ozone production from an ozone generator is inversely proportional to the oxygen flow rate. Feed oxygen flow rates must be maintained throughout all measurements to keep the ozone concentration constant. Since ozone concentration in an oxidizer stream is directly influenced by controlling oxygen volumetric flow rate to the generator, three different oxygen flow rates were tested in this experiment. Table 1 summarizes the corresponding ozone concentration measured by the ozone analyzer of oxidizer stream at different oxygen flow rates just before the lower burner. Measurements were taken at 300 K; the ozone generator was operated for one hour.
Table 1: Corresponding ozone concentrations of feed oxygen flow rates measured by 2B Technology Model 106-H ozone analyzer.

<table>
<thead>
<tr>
<th>Oxygen Flow Rate (SLM)</th>
<th>Ozone Concentration (wt %)</th>
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<tbody>
<tr>
<td>5</td>
<td>5.94</td>
</tr>
<tr>
<td>7</td>
<td>5.02</td>
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<tr>
<td>8</td>
<td>4.64</td>
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</tbody>
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5.3.2 Strain Rates and Momentum Calculations

The fuel mole fraction, temperature, fuel jet density, and the component of the fuel jet velocity normal to the stagnation plane at the exit of the fuel outlet were $X_{f,1}$, $T_1$, $\rho_1$, and $V_1$, respectively. The oxygen mole fraction, oxidizer temperature, oxidizer jet density and the flow velocity normal to the stagnation plane at the exit of the oxidizer outlet, were $X_{O2,2}$, $T_2$, $\rho_2$, and $V_2$, respectively. Plug flow conditions were assumed in conducting all experiments, while balancing momentum of the counterflowing streams according to the following Eq. 2:

$$\rho_1 V_1^2 = \rho_2 V_2^2$$

(2)

Since oxidizer stream was fixed during experiment, momentum was balanced by changing fuel side flow rate (nitrogen and fuel) accounting for density changing with fuel dilution. The local strain rate, $a$, is defined as the normal gradient of the normal component of the axial flow velocities accounting for the density variation between fuel and oxidizer jets. This value changed from the exits of the fuel to the oxidizer nozzles, respectively [68]. Local strain rate of oxidizer side was calculated according to the modified Eq. 3. Strain rate, calculated by changing the separation distance between two nozzles, was between 9 to 25 mm.

$$a_2 = \frac{2|V_2|}{L} \left( 1 + \frac{|V_1|\sqrt{\rho_1}}{|V_2|\sqrt{\rho_2}} \right)$$

(3)
5.3.3 Cool Flame Ignition and Extinction

Initially, oxygen flow should be fixed according to the ozone concentrations that will be tested (Table 1). The experiments were done using three different oxygen flow rates (5, 7, and 8 SLM). The separation distance was fixed each time during the running experiment to determine the influence of a particular strain rate on ignition. Strain rate remained constant at fixed separation distances while changing fuel mole fraction. To achieve ignition, the fuel concentration in the fuel jet was increased gradually, while adjusting the nitrogen flow slightly to maintain the momentum balance between the two jets. Calculations were performed each time to set the appropriate fuel and nitrogen flow according to the set fuel concentration while momentum was maintained. The fuel mole fraction was increased slightly and gradually until the ignition was observed, to avoid pseudo-ignition, which can be caused by a sudden increase in fuel concentration. After observing the flame, the fuel flow was stopped to extinguish the flame. The nitrogen curtain flow was closed to release any remaining radicals in the reaction zone. This was repeated, with smaller increasing steps of fuel concentration, to precisely specify the ignition concentration. To confirm the repeatability of the experiment, the procedure was repeated several times and the average was taken. The fuel ignition concentration was recorded at a particular strain rate and ozone concentration. The same experiment was tested for several strain rates. The entire procedure was repeated for other oxygen flow rates and different ozone wt% and to determine ignition limits under different strain rates and three levels of ozone addition for both n-butane and iso-butane fuels.
Following a similar procedure, extinction limits were measured after full establishment of cool flame. The fuel extinction mole fractions of n-butane and iso-butane were obtained as a function of several strain rates. After establishing a stable cool flame, the fuel mole fraction gradually decreased while the nitrogen flow was adjusted slightly to maintain momentum balance between the two jets until extinction. This was repeated several times to measure the precise fuel extinction concentrations at every strain rate. The experiment was repeated for other separation distances to account for different strain rates. Measuring the extinction strain rate, instead of the fuel extinction mole fraction, is another possible approach, performed by fixing the fuel concentration at a specific value and changing the separation distance instead, until flame extinction. This model is challenging because the separation distance is not automatically controlled; it must be fixed manually every time, which disturbs the flame and makes it difficult to monitor the extinction. Both methods target measuring the extinction limits.

5.3.4 Influence of Temperature on Cool Flame Ignition

The ignition temperature of various fuel concentrations can be investigated under several conditions. This could be achieved by checking the minimum fuel concentration responsible for ignition of cool flame. The fuel stream should be heated to low temperature, which is expected to be beyond the cool flame temperature range. In this experiment, the fuel stream was initially heated to 400K, then, the temperature of the fuel was increased gradually in small increments. Prior to the establishment of the flame, the temperature was stabilized until steady; then the fuel concentration was increased gradually to ignition, while maintaining the momentum balance with the oxidizer stream by adjusting both the
fuel and nitrogen flow rates simultaneously. Fuel mole fraction at ignition and corresponding temperatures were recorded. The ignition was tested up to approximately 600 K; this procedure was repeated at every temperature. The maximum fuel mole fraction was tested up to 90 percent. Flowing large amounts of high fuel in the existence of ozone was avoided as a safety consideration by following this procedure, it was observed that the lowest temperature could cause ignition.

5.3.5 Safety Considerations

Safety is the most important consideration in any experiment. All the necessary safety precautions were considered and implemented in this experiment. Because this investigation included the release of flammable and dangerous gasses, the entire model was placed under a well-isolated ventilation hood connected to a large exhaust system. All released gasses were effectively vacuumed to the exhaust and, since CH$_2$O is a main product of cool flame, and a carcinogenic irritant, all involved personnel wore protective equipment, including a respirator with special cartridges for aldehydes and other hydrocarbons. An ozone sensor was used near the working area during the experiment to monitor its concentration in case of leakage; an alarm sounds if ozone concentration exceeds permissible exposure limits.

5.4 Simulation Procedure and Software Package

CHEMKIN-PRO® software package was used to perform numerical calculations and to simulate process inlet conditions, as shown in Fig. 14. It is necessary to solve complicated partial conservation equations for energy, mass, and momentum, used to describe the
reactor system (rarely solved analytically). The OPPDIF solver is used for ignition simulation. For extinction simulation, the CHEMKIN PRO extinction solver was used; this solver utilizes an arc length continuation method to generate an S-CURV [69]. All the conservation equations were already built into the reactor model. The Aramco Mech 1.3 was used to characterize kinetic and thermochemical properties [70]. This chemistry design included gas-phase kinetics, thermodynamics data and gas transport data files to solve the gas energy problem. The ozone chemistry subset developed by Ombrello et al. was also incorporated into this design [71]. Numerical simulation is applied to discuss the accuracy of the chemical model to describe the cool diffusion flame of the butane isomers in diffusive systems.

![Figure 14: CHEMKIN PRO simulation of intended counterflow conditions using OPPDIF solver.](image)

The computational procedure is similar to experiments in which ignition and extinction are achieved by changing fuel concentration at a fixed temperature of 570K. All inlet conditions, including oxidizer and fuel velocities, strain rate, ozone concentration, pressure and temperature were set according to the corresponding experimental conditions to be simulated. For each imposed fuel mole fraction, the convergent solution requires substantial CPU time on the workstation. For simulation properties, 700 uniform number of grid points was used, with 1500 maximum number of grids allowed. The adaptive gradient and curvature were 0.05 and 0.1 respectively. Ten adaptive grid points were used.
Chapter 6: Data Analysis

6.1 Experimental Results and Discussion

The main deliverables on this project were self-sustaining n-butane and iso-butane cool flames in a counterflow facility, specifying the set of conditions under which cool flame could be observed. In this project, work was extended to investigation of cool flame ignition and extinction limits at different strain rates. The influence of fuel dilution, temperature, and ozone concentration on the initiation of cool diffusion flame were also tested. The experimental procedure described was used successfully in the study of cool flame ignition and extinction in a counterflow model.

6.1.1 Identification of Butane Isomers Cool flames

The existence of cool flames at low temperature has been proved, and self-sustaining cool flames of both butane isomers have been established under a variety of conditions. Fig. 15a shows direct photography of n-butane cool diffusion flame using a Nikon D70 digital camera. Flame was established at 5.02 wt % O₃ in the oxidizer stream, fuel volume fraction was $X_f=15\%$ in the fuel stream, and strain rate of $a_2=71$ 1/s. Cool diffusion flames were found to be located on the oxidizer side near the stagnation plane, as reported previously [65]. Cool flame was characterized by a pale blue light, indicating the absence of soot formation. This shows that the radical chemical species and ions responsible for the bright light of the conventional flame are not produced in large amounts. Heat released from the low-temperature chemical reactions was relatively small; for this reason, cool flames were difficult to observe experimentally, requiring some optical measurement. Deng et al. [44] reported that no bright flame can be observed, and only the instant of cool flame ignition
could be visually detected using optical measurement—especially for NTC-affected ignition. In another work, Deng et al. demonstrated that cool flame chemiluminescence could be suddenly detectable by UV camera [64]. However, when using this new experimental technique, adding ozone to the oxidizer stream enabled direct observation of cool flames by the naked eye. The temperature of cool flame was measured directly by inserting a thermocouple in the flame zone. Temperature found to be around 700 K which is within the cool flame temperature regime. To further distinguish cool from hot flame, Fig. 15b shows a hot flame, initiated from the pre-existing cool flame under the identical flow condition, by an external ignition source. The hot flame is characterized by a bright yellow emission of soot particles from the flame.

To confirm that the observed flame is a cool flame, a special filter (Melles Griot filter with 10 transmission band and 400 nm wavelength) was used to capture CH$_2$O$^*$ chemiluminescence. Chemiluminescence of excited CH$_2$O$^*$ and peroxides are considered to be precursors of cool flame. The filter nearly matches the prominent fluorescence
features of CH$_2$O, found to be excited at 355 nm wavelength [72]. Fig. 16 shows that cool flame is characterized mainly by CH$_2$O—a weak bluish chemiluminescence.

![Figure 16](image)

**Figure 16**: a) Direct photography of n-butane cool flame without a filter. b) n-butane cool flame using formaldehyde chemiluminescence filter with wavelength 400 nm. Flame observed at fuel volume fraction $X_f$ = 0.6, strain rate $a_2$ = 60 l/s, ozone concentration O$_3$ = 5.02 wt%. Shutter speed $f$ = 1s, iso 1250. Exposure time five min.

In this study, ignition of both tested fuels was performed in the absence of ozone. However, no cool flame could be observed experimentally without the addition of ozone. Because it acts as an initiator of LTC at atmospheric pressure, the ozone enabled a self-sustaining stabilized diffusion cool flame. The stabilization of cool flame reaction in an open flowing system is achieved with a complete balance between heat losses at the system’s boundaries, and heat generated from cool flame chemical reactivity. No extensive heat release was observed with increasing fuel concentration, as a result, a steady-state thermochemical operation was achieved, which prevented conventional hot ignition of the hot flame caused by thermal runaway.

The stabilization of cool flame was also clarified by the existence of a nitrogen curtain flow which acted as a guard, isolating the reaction zone from the surrounding environment and maintaining heat balance. Unstable, violent, cool flame was observed experimentally when the nitrogen curtain flow was reduced (Fig. 17). When the nitrogen curtain flow was off,
the cool flame immediately touched the hot surface of the burner, causing hot flame ignition, proving that a well-balanced nitrogen curtain flow is important for cool flame stabilization.

Figure 17: Unstable cool flame. Fuel concentration $X_f = 20 \text{ vol\%}$, strain rate is $a_2 = 60 \text{ 1/s}$, and $T = 570 \text{ K}$.

6.1.2 Ignition Limits of n-butane and iso-butane

The initiation diagram of cool flames was experimentally determined in fuel ignition mole fraction versus strain rate at three different ozone concentrations. To investigate the influence of changing strain rate on the minimum fuel concentration responsible for ignition, the tests were performed while the temperature of the fuel stream was maintained at a constant 570K (±5K). Figs. 18a and 18b show the ignition limits of n-butane and iso-butane respectively; it can be seen from the graphs that ignition of cool flames is favored at lower strain rates than hot flame ignition, which requires very high strain rates. Lower fuel concentration is required to achieve cool flame ignition at lower strain rates. This illustrates that ignition concentrations of the tested fuels were directly proportional to the
strain rate, in agreement with previous cool flame studies in counterflow diffusion systems by Deng et al.[73] and Won et al.[65]. The reason is that as strain rate increases, the width of mixing layer decreases which decreases both radicals’ diffusion and reacting times. Thus, higher fuel concentration is required to cause ignition.

**Figure 18**: Fuel concentrations required for establishment of cool diffusion flames at different strain rates for different ozone concentrations. a) n-butane b) iso-butane. Fuel side temperature \( T_1 = 570 \text{K} \).

It is also evident from Figs. 18a and 18b, that n-butane is more reactive than iso-butane. As shown, n-butane ignition concentration is much less than iso-butane ignition concentration at the same specific strain rate; this could be due to the differences in their octane rating (n-butane-94 and iso-butane-102). It is well known that branched alkanes are less reactive than linear alkanes, due to higher intermolecular forces which require more energy for C-H bond dissociation via hydrogen abstraction to initiate combustion reactions [74].

To further explain the reason why n-butane is more reactive than iso-butane, the total H-abstraction rate was plotted for a low temperature range, as shown in Fig. 19. It can be seen
that the total rate of H-abstraction by OH radical is higher for n-butane due to the presence of more secondary sites, from which it is easier to abstract than primary sites. Moreover, two radicals can be produced by abstracting hydrogen from iso-butane, which are primary radical (IC₄H₀) and tertiary radical (TC₄H₀). TC₄H₀ cannot undergo the second isomerization to form KHP as the main branching step for LTC.

![Graph](image)

**Figure 19**: Total H-abstraction rate by OH for both n-butane and iso-butane.

The effects of ozone concentration on cool flame ignition limits for the tested fuels were also measured. They were examined at three different oxygen flow rates (5, 7, and 8 SLM) corresponding to (5.94, 5.02, and 4.64 wt% O₃) in oxidizer stream respectively. The addition of more ozone to the oxidizer stream dramatically increased the reactivity of both fuels. Ozone decomposition through three body reaction $\text{O}_3 + (M) = \text{O} + \text{O}_2 + (M)$ releases O atom; it works as a trigger to shorten induction time by accelerating H abstraction and increasing fuel radical pool. Fuel radicals are required to proceed with LTC, e.g. R+O₂ reactions; therefore, increasing ozone concentration plays a significant role by
increasing the generation of radicals and enhancing chain-branching reactions. For iso-butane, it was difficult to observe ignition in relatively higher strain rates as shown for n-butane ignition. In addition to the lower reactivity of iso-butane, residence time is too short for chemistry to occur at high strain rates, thus the system exhibited no flame. Neither could ignition be observed for iso-butane in many tested strain rates at low ozone concentration, $O_3 = 4.64$ wt%, implying that iso-butane requires higher ozone concentration to overcome its weak reactivity and enhance radical propagation rates and chain-branching reactions.

### 6.1.3 Determination of Ignition Temperature

Cool diffusion flame ignition was found to be sensitive to the fuel stream temperature. For this reason, the concentration required to establish a cool flame for n-butane was measured at different fuel temperatures. Fig. 20 shows that the concentration of fuel needed to establish a cool diffusion flame decreases with an increase in the temperature of the fuel stream, demonstrating that cool flame chemical reaction rates increase with temperature due to the increase in heat releases. It is further understood from this result that slowing the reactions does not decrease oxidation reactivity, which can appear due to the competition between chain-branching and chain-termination reactions. This proves that cool flame does not exhibit NTC phenomena in temperature range of 550-590 K; furthermore, no eventual transition of cool flame to hot flame was observed as the temperatures increased in this range. Therefore, the flame is still governed by LTC. No cool flame ignition was observed in fuel side temperature lower than 535 K.
Figure 20: Concentration of fuel required to establish cool diffusion flame at different fuel side outlet temperatures. $a_{z}=50$ l/s, $O_3 = 5.68$ wt%

6.1.4 Extinction Limits of n-butane and iso-butane Cool Diffusion Flames

The extinction limits of both butane isomers (represented by fuel extinction concentration) were measured as a function of strain rate at a constant ozone concentration and temperature. Cool flames were extinguished after a fully developed flame was established. At a fixed strain rate and oxygen flow rate, the fuel concentration was slowly decreased and adjusted while a balanced momentum was maintained until the flame was extinguished. The fuel concentration at extinction was recorded at various strain rates. Fig. 21 shows the extinction limits of n-butane and iso-butane cool flames. The result shows that fuel extinction concentration of both tested fuels was directly proportional to the strain rate. This behavior was found to be similar to the extinction of other fuels, e.g. n-heptane, as well as extinction of hot diffusion flames [65]. At low strain rates, little fuel is required
to sustain the cool diffusion flames; at higher strain rates, however, higher fuel concentration was required for the flame to be sustained. This is because the flame 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, which requires that fuel concentration be increased to sustain the flame. Iso-butane showed a higher extinction limit than n-butane; this is explained by the lower reactivity of iso-butane because there are fewer sites available for H-abstraction by OH, which is the main trigger for LTC. Furthermore, the extinction behavior of iso-butane cool flame showed a rapid increase in fuel extinction concentration with increasing strain rate. Generally, extinction limits of both fuels are much lower than their ignition limits for all strain rates. So, after ignition, cool flames still can sustain lower fuel concentration than those of ignition before extinction can happen. N-butane showed wider flammability limits than iso-butane; however, the kinetic analysis is required to investigate details of the observed trends.

**Figure 21:** Fuel extinction concentration for different strain rates. Fuel side temperature, $T_1 =$ 570K, $O_2 =$ 5.02 wt%
6.2 Numerical Results and Discussion

As previously described, simulations were carried out using CHEMKIN PRO. The OPDIFF solver was used for ignition simulation while extinction solver was utilized for extinction simulation. Figs. 22a and b show the simulated cool diffusion flame ignition for n-butane and iso-butane respectively. Overall, the model qualitatively captured the trends in the experiments for both fuels. However, it overpredicted the ignition limits of the tested fuels at all strain rates by up to a factor of eight. The model was very reactive by showed ignition at very low fuel concentrations for all strain rates.

![Graphs showing simulated cool diffusion flame ignition for n-butane and iso-butane.](image)

**Figure 22**: Comparison of measured and computed ignition limits of a) n-butane b) iso-butane cool flames as a function of strain rates with three different levels of ozone addition. Fuel side temperature T₁=570K.

Similarly, Figs. 23a and b show the simulated extinction strain rates for n-butane and iso-butane respectively. Again, the model captured the experimental trend but overpredicted the extinction limits by up to a factor of two for both fuels. This is not surprising, as all studies of cool flames in diffusion flames by Deng et al. and Ju et al. showed the same
outcome [44][65], indicating that the model cannot accurately describe the cool flame behavior in a diffusive system, despite its ability to reproduce many homogeneous experiments at low temperatures. Also, the chemical kinetics mechanism model was developed for C1-C4-based hydrocarbon and oxygenated fuels; but it has not been validated for butane isomers. So, this kinetic model need to be updated to better predict cool flames behavior in diffusive systems. However, experimental data from this inhomogeneous experiment could be used for the chemical kinetics model validation later.

**Figure 23:** Comparison of measured and computed extinction limits of a) n-butane b) iso-butane cool flames as a function of fuel concentration. O\textsubscript{3} = 5.02 wt%. Fuel side temperature T\textsubscript{1}=570K.

The oxidation chemistry of hydrocarbon depends heavily on free radical generation governed by chain-branching reactions. The rate of radical formation is controlled by chemical kinetics, which is largely determined by temperature. Therefore, chemical kinetics at ignition limits is further analyzed numerically for cool diffusion flame by performing sensitivity analysis. For this reason, sensitivity analyses of n-butane diffusion flame for X\textsubscript{f}= 5%, strain rate a\textsubscript{2} =50 1/s, and 5.02 wt% O\textsubscript{3} were performed to find the
dominant reactions at ignition. The analyses were carried out along the axial distance between the two outlets. Fig. 24 shows that the majority of the sensitive reactions are those that occur at low temperatures.

**Figure 24**: Sensitivity analysis of some important reactions for n-butane cool diffusion flame ignition ($X_f = 5\%$, $a_2 = 50$ l/s, $O_3 = 5.02$ wt%).

Based on sensitivity, ignition of cool diffusion flame is controlled predominantly by LTC. Dominant reactions include the reactions of $\text{ROO}^-$ and $\text{QOOH}^-$ radicals. The most sensitive reactions were abstraction by OH, the most important free radical to initiate low-temperature ignition of fuel. The production of primary radical ($\text{C}_4\text{H}_{10}+\text{OH} = \text{PC}_4\text{H}_9+\text{H}_2\text{O}$) presents the highest positive sensitivity; but the production of secondary radical ($\text{C}_4\text{H}_{10}+\text{OH} = \text{SC}_4\text{H}_9+\text{H}_2\text{O}$) shows negative sensitivity. This is further justified by the highest negative sensitivity shown by the production of olefins from the secondary peroxyalkyl radical ($\text{SC}_4\text{H}_9\text{O}_2 = \text{C}_4\text{H}_8\cdot+\text{HO}_2$). Also, the second addition of QOOH to O$_2$
(C₄H₈OOH₁·₃+O₂=C₄H₈OOH₁·₃O₂, C₄H₈OOH₂·₄+O₂=C₄H₈OOH₂·₄O₂) has positive sensitivity; this is attributed to the production of KHP from produced O₂QOOH, where KHP presents the main branching pathway at LTC. These reactions supply the bulk of the heat at low temperatures. In addition, reactions of ozone appeared as sensitive reactions, indicating the importance of ozone as an ignition accelerator. Both reactions of ozone with molecular oxygen and nitrogen produce an atomic O, which initiates the low-temperature fuel abstraction (O₃+N₂=O₂+O+N₂, O₃+O₂=2O₂+O) because it has a higher rate of H-abstraction from the fuel molecule relative to molecular oxygen. However, another reaction of ozone and atomic O (O₃+O=2O₂) has negative sensitivity as it presents a chain termination pathway by atomic O.
CONCLUSION

This project is intended to provide a basic understanding of the low-temperature reactivity of butane isomers under atmospheric pressure condition via a basic experimental system. This has been achieved by experimentally investigating the critical points of butane isomer cool flames, assisted by ozone addition to oxygen, in a non-premixed diffusive counterflow model. This new experimental method has enabled the establishment of self-sustaining cool flames of both fuels tested under a variety of conditions. Cool flame ignition and extinction limits at different strain rates were investigated. It was observed that ignition and extinction concentrations of both fuels are directly proportional to the strain rate. Higher fuel concentration was required to achieve cool flame ignition, as well as to sustain cool diffusion flames at higher strain rates. Results also showed that establishment and sustenance of cool diffusion flames is favored at lower strain rate and higher fuel stream temperatures. Like previous studies in high-temperature flames, the results showed that the ignition limits of iso-butane cool diffusion flame are higher than n-butane, reflecting the differences in their reactivity. The effects of ozone concentration on cool flame ignition limits for the tested fuels were also measured. The addition of more ozone to the oxidizer stream dramatically increased the reactivity of both fuels. The cool diffusion flame ignition was found to be sensitive to the temperature of the fuel stream. Results showed that fuel concentration necessary to establish a cool diffusion flame is inversely proportional to the fuel stream outlet temperature, demonstrating the increase in fuel reactivity as temperature increases.

Numerical simulations involving molecular transport data and Aramco detailed chemistry were performed using CHEMKIN PRO, where the OPDIFF and extinction solvers were
utilized for both ignition and extinction simulation. Overall, the model captured the trends in the experiments for both fuels. However, it showed bad agreements with experimental data by overpredicted both ignition and extinction limits of tested fuels at all strain rates, which has also been observed in previous studies of cool flames. The model used could not describe the cool flame diffusion chemistry well. It requires more attention to be updated for better predicting LTC ignition in inhomogeneous systems. Furthermore, sensitivity analyses of n-butane diffusion flame were performed to determine the dominant reactions at ignition. It was found that ignition of cool diffusion flame was predominantly controlled by LTC, where dominant reactions include the reactions of alkyl peroxy (ROO-) to hydroperoxy alkyl peroxy (QOOH-) radicals, and subsequent decomposition into keto hydro peroxyl (KHP) and hydroxyl (OH-) radicals. Also, ozone reaction appeared as a sensitive, indicating the importance of ozone as an ignition accelerator. Both reactions of ozone with molecular oxygen and nitrogen to produce an atomic O, which initiates the low-temperature fuel abstraction. Finally, the existence of ozone played a significant role by increasing radical generation and enhancing the chain-branching reactions required to proceed with LTC.
FUTURE RESEARCH

It is foreseeable that this work will be extended to additional research. Some possible future studies are the investigation of cool flame ignition and extinction characteristics of other fuels, such as propane, pentane isomers, etc. On the subject of cool diffusive flames and investigations of liquid fuels, liquid fuel vaporization systems have already been built and integrated into the counterflow setup, which could be used for further studies. Investigating cool flames’ critical points of ignition and extinction of gasoline face fuels have begun as new projects with work in progress. This study could be supported with quantitative species measurements by sampling cool diffusion flame and obtaining species profiles. The speciation data is necessary to validate kinetics models and establish a well-developed comprehensive mechanisms. Optical detection could be used for better temperature and heat release measurements, rather than thermocouples, which can introduce a disturbance to the flow field. Single-point laser doppler velocimetry (LDV) could be used for axial flow velocity along the centerline to determine local strain rates. Furthermore, because low-temperature chemical kinetics can be promoted at high pressures, cool diffusion flames can be investigated at elevated pressures.

This study can be extended to a higher temperature range to investigate the NTC region, offering the opportunity to identify NTC-affected chemical reactivity coupled with transport in low to intermediate temperature ignition in counterflow systems. Recent focus on oxyfuel/oxygen-enriched combustion and low-temperature combustion requires information on the effect of dilution of fuel and oxidizer streams on sooting behaviors in diffusion flames. A high temperature counterflow facility for HTC studies has been built, capable of performing other high temperature ignition and extinction experiments.
Counterflow experiments can also provide valuable information regarding fuel dilution and strain rate effects on soot formation. In addition to cool flame chemistry investigations, this could provide an opportunity to study cool flame dynamics and structures. Planar laser-induced fluorescence (PLIF) measurements would be used to give precise qualitative measurements of the concentration and temperature fields of cool flames. To understand cool flame behavior, the aerodynamic effect on the flow field could be investigated by measuring flow gradient velocity along the flame centerline, and by flow mapping visualization. Finally, plasma assisted combustion could be applied to counterflow as a new kinetic path to enhancing low temperature fuel oxidation. It is expected to be a promising and effective way to accelerate fuel oxidation at low temperatures, as well as enabling the establishment of stable cool flames [67].

Regarding the numerical simulation, chemical kinetics model requires more attention and deep investigation in the future. It needs to be updated for better predicting the cool flame behaviors and LTC ignition in diffusive systems.
BIBLIOGRAPHY


