EFFECTS OF AIR TEMPERATURE AND OXYGEN DILUTION ON THE
IGNITION BEHAVIOR OF LIQUID FUELS IN AN OPTICAL SPRAY CHAMBER

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ABSTRACT

Spray ignition studies of liquid fuels provide important physical and chemical diagnostic information that support the advancement of combustion simulation models for rapid development of next-generation clean and efficient internal combustion (IC) engines. This work investigated the ignition behavior of n-heptane, ultra-low sulfur diesel (ULSD) and biodiesel blends in an optically-accessible constant volume combustion chamber (CVCC) under “low temperature combustion” conditions. Initial ambient air temperature was varied between 540 and 620°C. To simulate the gas mixture composition in a modern IC engine that utilizes exhaust gas recirculation (EGR), standard air was diluted with nitrogen and carbon dioxide which resulted in oxygen concentrations ranging from 21.8 to 9.6%.

The optical CVCC was built by modifying a Cetane Ignition Delay (CID 510) instrument, manufactured by PAC, l.p. Two optical systems were integrated into the design of the apparatus. A spray visualization system utilized a high speed camera that captured images of the developing liquid fuel spray at 29,197 frames per second via direct optical access through a liquid-cooled borescope. These images were post-processed to calculate liquid penetration length and cone angle. In addition, natural light emissions from excited formaldehyde (CH₂O*), OH*, CH*, and C₂* were captured by a chemiluminescence detection system comprised of a UV/Vis optical probe, dichroic mirrors, band-pass filters, and photomultiplier tube modules.

It was observed for each fuel sample that liquid penetration length and cone angle were insensitive to the changes in temperature and EGR dilution rates tested. A direct
relationship between liquid length and cone angle was observed across transient and quasi-steady spray behavior; the ratio between these values developed a positive linear trend across the transient state followed by a constant value in the quasi-steady state. Increased ambient air temperature shortened ignition delay values for all fuel samples. ULSD and n-heptane displayed negative temperature dependence as temperature exceeded 580°C, consistent with well-understood hydrocarbon oxidation behavior. Higher rates of EGR dilution increased chemical ignition delay in an exponential manner. ULSD was the most sensitive to the decreasing ambient oxygen concentration, while B100 and n-heptane displayed stronger EGR tolerance. This trend was considered to be influenced most by fuel structure, as well as fuel-derived oxygen concentration to a lesser degree.
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Chapter 1

Introduction

1.1 Background and Motivation

Over recent years, government regulations on diesel engine emissions have resulted in the implementation of expensive exhaust aftertreatment systems that reduce particulate matter (PM) and nitrogen oxides (NOx) [1, 2]. Researchers have found benefits in premixed or partially-premixed combustion strategies, coined “low temperature combustion” (LTC), as a potential solution toward mitigating the need for aftertreatment while maintaining high energy conversion efficiencies [3]. The introduction of LTC strategies in compression-ignition systems has placed new technological demands on the development of multi-dimensional computer models for combustion simulations [4]. Accurate experimental data that provides a greater fundamental understanding of fuel spray and ignition behavior are needed to support these developments [5].

1.2 Research Objectives

The primary objective of this project was to supply accurate experimental diagnostic measurements of physical and chemical ignition behavior of liquid fuels under relevant diesel engine operating conditions for the verification of computational fluid
dynamics (CFD) model studies. This was to be achieved through development of an optically-accessible constant volume combustion chamber (CVCC) that provided a controlled environment for repeatable studies.

The secondary objective was to investigate ignition behavior of liquid fuels under varied ambient air temperature and oxygen dilution conditions; similar to LTC operating conditions in an IC engine. Liquid fuels of interest included n-heptane, ultra-low sulfur diesel (ULSD), biodiesel (B100), and blends of biodiesel. Ignition tests of n-heptane were completed to compare results with well documented observations in literature. Biodiesel and blends with ULSD were performed to explore the ignition behavior of practical fuels with varying oxygen concentrations under LTC operating conditions.
Chapter 2

Literature Review

2.1 Introduction

Ignition behavior of liquid fuels has been studied by many research groups over the past century through a variety of experimental and computational techniques. In a diesel engine environment, the pathways leading to the phenomenon known as “autoignition” are controlled by physical and chemical processes. The physical aspect of ignition behavior is accounted for by the fuel spray interaction with air under high temperature and pressure leading up to the formation of an ignitable mixture. The chemical aspect covers the complex reaction chemistry that occurs between fuel and oxidizer ultimately resulting in the release of fuel energy in the form of heat. In order to understand the ignition behavior of a fuel, these processes must be studied in detail.

This review initially covers the fundamentals of spray combustion as it occurs in diesel engines. In particular, the unique phenomenon of two-stage ignition and corresponding reaction kinetics are discussed to illustrate the size and complexity of the mechanisms involved. Physical spray behavior is also reviewed on a macroscopic level. This is followed by a survey of experimental combustion methods used to investigate the aforementioned processes of ignition. Lastly, a brief review of research that has investigated ignition behavior under varied ambient gas temperature and charge air composition is completed.
2.2 Combustion Fundamentals in Diesel Engines

Diesel engines (also referred to as “compression ignition” engines) differ from gasoline engines in that they do not use a spark to ignite the fuel and air mixture, rather they use the heat generated by compression of the moving piston. Combustion in an engine is controlled by an internal computer that varies the timing and rate of fuel injection according to the employed combustion strategy. A deep understanding of the ignition behavior for a given fuel under a range of operating conditions is desired in order to improve the design of IC engines. Physical processes such as liquid to gas phase transition and mixing, as well as chemical processes play a significant role in the efficient conversion of fuel energy to mechanical energy. The following section will cover the physical and chemical processes present in compression ignition engine environments.

2.2.1 Ignition Delay

Ignition delay ($\tau_{\text{ign}}$) in a compression ignition engine is the time duration between start of injection (SOI) and start of combustion (SOC)[6]. During this short period of time (on the order of milliseconds) physical and chemical processes take place in overlapping series leading to the autoignition (“self-ignition”) phenomenon. The physical ignition delay ($\tau_{\text{phys}}$) is the time required for liquid spray jets to undergo atomization, entrainment, vaporization, and mixing within the hot combustion chamber air. The chemical ignition delay ($\tau_{\text{chem}}$) is the time required for chemical reactions to take place that lead to the onset of the high temperature heat release known as SOC, as will be discussed below. The
physical and chemical ignition delay periods are summarized in Figure 2-1, an illustration adapted from Caton et al. [7].

To simplify the understanding of $\tau_{\text{chem}}$, the complex reaction mechanism that occupies this time period can be broken down into three temperature regimes loosely referred to as “low” (<850K), “intermediate” (850-1100K), and “high” (>1100K) as illustrated by Morley and Pilling in Figure 2-2 [8]. The temperature designations are only meant to give a general reference as they can vary between fuel composition and operating conditions in practical applications.
The importance of the three temperature regimes as it relates to $\tau_{\text{chem}}$ is amplified by the existence of a two-stage ignition process created by certain hydrocarbon species in modern diesel engines that utilized exhaust gas recirculation (EGR). Figure 2-3 illustrates the two stage ignition phenomenon in the form of apparent heat release rate and bulk temperature data for ultra-low sulfur diesel (ULSD), of which the behavior can be explained by the dominate reaction chemistry of each temperature regime. The “first stage” of ignition represents exothermic proxy chemistry resulting in increased reaction rates leading to a sharp rise in system temperature. The increase in temperature pushes the system into the intermediate region where $\text{HO}_2$ and $\text{H}_2\text{O}_2$ chemistry dominates and overall reaction rates drop as a result [9]. The slow temperature rise rate accounts for a significant time portion of $\tau_{\text{chem}}$. As the system temperature crosses a threshold (~1000K) into the high temperature regime, stable peroxy intermediate species rapidly decompose to small radicals that readily consume the remaining fuel via aggressive chain-branching
reactions. The onset of small radical chemistry is what leads to the high temperature heat release, the accepted definition of SOC [10]. The reaction chemistry involved in these three regimes is discussed in further detail in Section 2.2.3.

![Diagram of apparent heat release rate (AHRR) and bulk temperature data for two-stage ignition process with reaction temperature regimes labeled](image)

**Figure 2-3:** Example apparent heat release rate (AHRR) and bulk temperature data for two-stage ignition process with reaction temperature regimes labeled

### 2.2.2 Physical Spray Behavior

Investigating the physical spray behavior of a liquid fuel injection is the first step toward characterizing the ignition process in an internal combustion engine. Fuel injectors with multiple jets are used in diesel engines to mix a specific quantity of fuel with compressed air quickly and as completely as possible. Liquid fuel enters the chamber at a very high velocity due to the high pressure gradient (on the order of 1000 bar) that drives the fuel through small circular orifices (diameters on the order of tenths
of a millimeter). The high velocity jets atomize into small droplets followed by rapid evaporation; Figure 2-4 [11] shows a diesel spray image taken by Pastor et al. In addition, the high velocity liquid jets permit the fuel to mix with air more thoroughly and quickly prior to ignition [6].

![Diesel spray image](image)

**Figure 2-4: Diesel spray image taken from an optical engine [11]**

Macroscopic fuel spray behavior has most commonly been characterized by measurements of liquid penetration length and cone angle [12-14]. Figure 2-5 illustrates these measurement definitions for a liquid fuel jet. The liquid penetration length (also referred to as “liquid length”) is measured from the tip of the injector to the end of the jet where liquid droplets undergo vaporization. Cone angle is measured as the angle between two fitted lines at each edge of the jet, focused on the portion that extends one half the liquid length from the injector nozzle [13].
Major factors that affect spray structure are the gas density ratio between fuel and air, injector orifice geometries, and the mechanical action of the needle lift [15]. The first measurements of spray penetration of diesel in an IC engine were reported by Browne et al. in 1986 [16]. They found that the length of the spray reached a maximum value axially, of which was dependent on the volatility of the fuel (i.e., lower fuel volatility resulted in longer maximum penetration lengths). Siebers investigated the dependence of liquid length on injection pressure, orifice geometries, and fuel temperature and volatility [12]. Injection pressure was found to have no significant effect on liquid length, although increasing ambient gas density decreased liquid length. Secondly, greater fuel volatility produced shorter liquid lengths as expected; additionally multi-component fuel (i.e. conventional diesel) liquid lengths were controlled primarily by the lower volatility fuel fraction. Naber et al. observed that air entrainment in the liquid jet resulted in a wider cone angle [13]. More importantly, the penetration velocity decreased due to the increased mass of the jet; a relationship that followed the conservation of jet momentum. Fuel surface tension and viscosity have been seen to hinder the atomization process,

Figure 2-5: Diagram of penetration length ($S$) and cone angle ($\theta$) definitions

$S = \text{Liquid Penetration Length}$

$\theta = \text{Cone Angle}$
although these values do not vary enough in typical diesel blends to produce significant effects [17].

Researchers have developed correlations for liquid length and cone angle in quiescent environments, although there is limited understanding of the effects in turbulent mixing for a transient spray [18]. Recent work by Eagle et al. found that current spray theory predicted penetration length well, however it struggled during the transient period of spray formation where fluctuations in liquid length were observed [19]. Johnson et al. concluded liquid length fluctuations are a result of turbulent eddies created at the edges of the spray tip in a transient diesel jet [20]. Further investigations of transient spray behavior are needed to resolve modelling issues under these conditions.

2.2.3 Hydrocarbon Oxidation

Hydrocarbon oxidation involves the production of radical species that produce additional radicals in a chain reaction. The four major classifications of chain reactions involved in hydrocarbon oxidation are initiation, propagation, branching, and termination[21]. Initiation reactions generate radicals from stable species. Propagation reactions create new forms of radicals while the net production of radicals is zero. Chain-branching reactions result in a net increase in radicals which results in new chains of reactions that “branch” off of the parent pathway. Westbrook determined that the key to understanding the reaction kinetics of hydrocarbon oxidation is done through identifying the chain-branching steps present under the conditions studied [22]. Lastly, termination reactions occur when multiple radicals recombine to produce stable species. Table 2-1
summarizes these classifications with example reactions. The chain reactions that
dominate each stage (low, intermediate, and high temperature regimes) of hydrocarbon
ignition are discussed in this section.

| Table 2-1: Examples of chain reaction classification for hydrocarbon oxidation |
|-------------------------------|---------------------------------|
| Initiation                    | \( \text{H}_2 + \text{O}_2 \rightarrow \text{OH}^* + \text{OH}^* \) |
| Propagation                   | \( \text{H}_2 + \text{OH}^* \rightarrow \text{H}_2\text{O} + \text{H}^* \) |
| Branching                     | \( \text{H}^* + \text{O}_2 \rightarrow \text{OH}^* + \text{O}^* \) |
| Termination                   | \( \text{H}^* + \text{OH}^* \rightarrow \text{H}_2\text{O} \) |

Note: Species marked with an * represent radical (unstable) species

The low temperature regime is primarily comprised of a combination of straight
chain propagation reactions with alkyl peroxy radicals playing a major role. The “back-
bone” chemical mechanism for hydrocarbon oxidation in the low temperature regime is
illustrated in Figure 2-6. At the heart of this mechanism is the \( \text{R} + \text{O}_2 \rightarrow \text{RO}_2 \)
propagation reaction which dominates in the forward direction. The \( \text{RO}_2 \) radical
isomerizes to create the \( \text{QOOH} \) radical; an event that has been accepted as the most
important reaction leading to chain branching in this regime [4, 23]. \( \text{QOOH} \) picks up
another \( \text{O}_2 \), followed by another isomerization reaction. The \( \text{HOOQOOH} \) radical
decomposes into meta-stable ketohydroperoxide (KHP) and \( \text{OH} \). Below 800K the
production of KHP dominates over decomposition, which results in the “pooling” of
KHP [22]. As the system temperature rises between 800-850K the \( \text{R} + \text{O}_2 \rightarrow \text{RO}_2 \)
reaction begins to shift toward the reverse direction that slows the production of KHP [24]. Likewise, the second O₂ addition reaction begins to shift in equilibrium, favoring dissociation. The rapid depletion of the KHP pool results in a spike in heat release due to the creation of many radical species that accelerate oxidation; a process identified as the first stage of ignition in a practical system [9]. The rise in temperature pushes the system into the negative temperature coefficient (NTC) region, where overall reaction rate reduces as temperature increases [25]. This unique behavior is due to slow non-branching, low-exothermicity reactions that produce stable intermediate species such as aldehydes, peroxides, and alcohols [26]. Of the aldehydes, formaldehyde (CH₂O) accounts for roughly half of the production [27]. At this point the temperature has transitioned from the low to intermediate temperature regime.

![Figure 2-6: Simplified low temperature hydrocarbon oxidation mechanism](image)

The intermediate temperature regime consists predominantly of HO₂ and H₂O₂ chemistry. The abundant supply of HO₂ radicals created by KHP decomposition begin to abstract hydrogen from neighboring alkanes to produce hydrogen peroxide (H₂O₂) in a
thermodynamically neutral fashion [28]. HO$_2$ also reacts with the significant presence of formaldehyde to produce HCO and more H$_2$O$_2$. Also, the available OH radical supply oxidizes formaldehyde exothermically, adding to the slow rise in temperature. A small portion of the H$_2$O$_2$ pool decomposes, contributing to the OH radical pool, although production is more dominant at these temperatures. It is not until the system temperature crosses $\approx$1000K that the large pool of H$_2$O$_2$ intermediates rapidly decompose to a large supply of OH radicals. This is the key point where the run-away oxidation of the remaining unburned hydrocarbons occurs, marked as the transition to the high temperature regime.

The high temperature regime consists of high heat release reaction chemistry involving OH, O, and H radicals. The majority of fuel energy is released during this stage due to runaway chain reactions that consume parent hydrocarbons via hydrogen abstraction, carbon-carbon cleavage, and beta-scission reaction mechanisms [21]. The heat release rate increases exponentially as more OH radicals are produced via the most important chain-branching reaction, H + O$_2$ $\rightarrow$ O + OH [22, 29, 30].

Hydrocarbon oxidation is a complex mechanism that releases a significant amount of fuel energy in a very short time period. Researchers continue to discover new pathways, particularly in the low temperature regime that guide development of more accurate computational models for advanced combustion strategies [31]. More detailed reviews of hydrocarbon oxidation kinetics have been published by Pilling [32], Zádor [4], Battin-Leclerc [33], and Westbrook [22].
2.3 Progress in Combustion Research Techniques

Combustion research has progressed greatly in the past few decades in part due to the development of kinetic models for practical application intended for internal combustion (IC) engine design [22]. This has largely been accomplished by the modeling of laboratory observations of ignition systems ranging from relatively-simple shock tubes to the more complex experimental engines. Advances in optical diagnostic methods have brought greater understanding to the physical and chemical behavior of combustion in an IC engine environment. In the following section these apparatuses and analysis methodologies are discussed.

2.3.1 Shock Tubes and Rapid Compression Machines

Two common experimental apparatuses used to investigate combustion behavior of fuels under IC engine conditions are the high-pressure shock tube and rapid compression machine (RCM) [33]. Their application in combustion research has helped researchers derive activation energies for gaseous fuel/air mixtures since the early 1950’s [34].

Shock tubes are used as a means to investigate combustion temperatures and ignition delays of many gaseous fuel types. A simple setup consists of a tube that is sectioned off by a diaphragm disk with a high pressure driver gas on one side and the sample gas on the other, see Figure 2-7 (from ref. [35]) and Figure 2-8 (from ref. [36]). When the diaphragm is ruptured the driver gas creates compression waves that coalesce to create a uniform wave called the shock front. The shock front rapidly elevates
temperatures over the course of microseconds that ignites the sample gas in an isothermal environment [36]. Measurements from pressure sensors and optical devices such as photomultiplier tubes (PMTs) have been used to calculate ignition delay profiles and temperatures with very high accuracy [37]. Although accurate, shock tubes are typically limited to ignition delay measurements below 10 milliseconds.

While designs vary, a standard RCM consists of a driving air tank, driver piston, hydraulic motion control chamber, reactor piston, and end reaction chamber, see Figure 2-9 (adapted from ref. [38]). RCMs function by driving a pneumatic piston in a closed cylinder to rapidly heat and pressurize an air/fuel mixture with very little heat loss [39]. The reaction chamber can be observed with pressure sensors and optical equipment to...
investigate the ignition period between end of compression and start of combustion. However, RCMs outfitted with optical diagnostic equipment are difficult to control and can create intense vibrations that may result in non-ideal measurements [40, 41]. A shock tube apparatus is more suitable for high temperature studies with short ignition delay fuels than an RCM because the time interval of compression in an RCM can be on the same order as the ignition delay which leads to greater errors in measurements [37]. However, Donovan et al. demonstrated that RCMs are excellent instruments for high temperature and pressure ignition studies of fuels that have ignition delays greater than 10 milliseconds due to the sustained temperature and pressure environment created by the instrument [42].

![Figure 2-9: Illustration of a basic rapid compression machine (RCM)](image)

### 2.3.2 Constant Volume Combustion Chambers

Constant volume combustion chambers (CVCC) are research apparatuses used for accurate spray ignition studies because they provide greater control and quality of measurements than what can be achieved in a real engine environment. Unlike shock tubes and rapid compression machines, which are limited to gas-phase premixed combustion studies, CVCCs use liquid fuel injectors that allow for the measurement of
The basic function of a CVCC is to create a high temperature and pressure environment for liquid spray ignition to take place. Many designs have incorporated optical access to investigate physical and chemical behavior of the ignition sequence. Sandia National Lab has developed a chamber design that has multiple viewing windows for Mie scattering, chemiluminescence, and Schlieren spray studies, see Figure 2-10 [44]. The cube-like chamber is heated by igniting a premixed gas mixture of acetylene and air, followed by a cool down period (see Figure 2-11 from Higgins et al. [45]). At the precise moment that the temperature and pressure conditions are met, the liquid fuel sample is injected into the chamber and subsequent ignition measurements can be conducted [46].
Commercial CVCC instruments have been developed to derive the cetane number (DCN) of diesel-relevant fuels by correlating ignition pressure traces to reference fuels. The CVCC of AET’s ignition quality tester (IQT) has provided a means for experimentalists to investigate a fuel’s ignition behavior under stable initial conditions which are much more repeatable than engine-studies [47]. Some researchers have chosen...
to model the IQT’s CVCC to develop CFD combustion models from gathered experimental data with great success [43, 48]. The PAC Cetane Ignition Delay (CID) instrument was introduced to the market in the late 2000’s as a direct competitor to the IQT, offering a more user-friendly design with strong cetane index correlation. Both of these instruments are pictured in Figure 2-12 [49, 50]. The CID in current literature has not been used for research purposes other than ignition delay derived from pressure traces.

![Figure 2-12: Commercial derived cetane number instruments; IQT (left [49]) and CID510 (right [50])]()

The design and controllability of commercial CVCCs appear to offer a strong platform for optical ignition studies. The CVCC in the CID and IQT both use electric heaters to heat the pressurized combustion air prior to the injection of fuel (see Figure 2-13). The use of cooled-borescopes to gain optical access in electrically-heated CVCCs has not been reported, although this application to IC engine apparatuses has been demonstrated successfully [51-53]. Fuel spray characterization of the IQT in the CFD modelling study previously mentioned were completed by removing the injection system
and filming the spray behavior in a chemical fume hood under standard room temperature and pressure conditions [43].

![Diagram](image.png)

**Figure 2-13:** Constant volume combustion chamber diagrams for IQT (left, adapted from Bogin et al. [43]) and CID (right, adapted from ref. [50])

### 2.3.3 Spray Characterization

Quantification techniques of spray behavior have progressed significantly due to the capabilities of computational fluid dynamic (CFD) spray models under development for efficient engine design [54]. Researchers in this field utilize high speed cameras and optical combustion facilities to supply accurate spray characterization, as well as test current spray theory [12]. The techniques commonly used to accomplish these goals can vary significantly between apparatuses as there is not a single standard, although a brief overview of the most prominent will be covered in this section.

Acquiring spray images for characterization has commonly been achieved through either light-scatter or light-extinction methods. The main difference is in the illumination of the spray jet where orientation and delivery vary. Researchers have illuminated the spray in light-scatter techniques by directing the light source from the
side [12] and the head [55]. In light-extinction, the light source is directed from the back, initially passing through either a diffuser [19] or collimating lens (Schlieren imaging)[56]. An investigation into the uncertainty of liquid length measurements by Pickett et al. found that light-scatter methods are sensitive to illumination source orientation, therefore creating varied maximum intensity locations. They also concluded that the preferred method may be to use light-extinction because the maximum intensity is referenced by direct observation of the source light [57].

Post-processing of spray images is commonly achieved by following a basic algorithm to pre-process raw images, segment important image objects, and measure the physical features [11-13, 58]. Common pre-processing techniques involve reducing the impact of background objects (or artifacts) that could be falsely identified as the spray by either mitigating noise or manually removing background features [11]. Image segmentation is an operation that analyzes a pre-processed image to identify objects of interest [59]. The most common technique for spray images is to use image thresholding which converts grayscale pixels (values ranging from 0 to 255) to black and white (values of 0 and 1, respectively) according to a selected “threshold” value. Given that spray movies consist of many images in sequence, most researchers elect to use a statistical method for determining an “optimal threshold” for each image to greatly reduce the processing time traditionally involved in manual selection. Macian et al. evaluated the two most common statistical methods employed in spray characterization, Otsu’s thresholding method (OTM) and Likelihood Ratio Test (LRT), and found that LRT was more reliable than OTM due to the inaccuracies of OTM created by a significant sensitivity to mean luminosity variations [60]. LRT was first adapted to spray
characterization by Pastor et al. which calculated optimal thresholds by fitting independent Gaussian distributions to the spray and background histograms [58]; later they expanded the method to cover non-Gaussian probability density functions (PDFs) that were characteristic of background distributions observed in newer experimental setups [11]. Lastly, measurements of physical features are calculated according to a specified definition and converted to standard units with a pixel/mm ratio determined with reference images.

2.3.4 Natural Luminescence Measurement Techniques

Researchers have observed the chemiluminescence of excited CH$_2$O*, OH*, CH*, and C$_2$* as markers for the presence of known intermediate chemical reactions throughout the two-stage ignition process [61, 62]. An illustration of measured emission spectra for these species is displayed in Figure 2-14, adapted from work by Sheinson [63] and Docquier [61]. Chemiluminescence is the spontaneous emission of a photon from an electronically-excited molecule produced as the result of a chemical reaction [64]. Excited formaldehyde (CH$_2$O*) chemiluminescence, first observed by Gradstein [65], is characterized by a broadband emission spectrum which overlaps the emission spectra of high temperature radical species (CH* and C$_2$*); however, these species are not intrinsic to low temperature flame chemistry [63, 66]. For this reason, excited formaldehyde emission is a strong marker for the first-stage of two-stage ignition. OH* chemiluminescence is most commonly used as the marker for high temperature combustion chemistry with a strong emission at 307nm [64, 67]. The key reaction
responsible for the formation of excited OH* has been studied by Dandy [68] to be \( \text{CH} + \text{O}_2 \rightarrow \text{OH}^* + \text{CO} \) in methane/air combustion. CH* and C\(_2\)* chemiluminescence (strong emission peaks at 431nm and 516nm, respectively) have also been measured in conjunction with OH* to investigate possible correlations of light emission intensity to equivalence ratio and heat release rates with limited success [69]. In addition, accurate measurement of OH*, CH*, and C\(_2\)* formation provides valuable validation data to support CFD modelling efforts.

![Figure 2-14: Illustration of hydrocarbon emission spectra for OH*, CH*, CH\(_2\)O*, and C\(_2\)*](image)

Optical equipment used to observe the natural luminescence of combustion include high speed cameras, optical filters and photomultiplier tubes (PMTs) [69, 70]. Gated high speed cameras with band-pass filters have been used to capture OH* chemiluminescence of mixing-controlled combustion flames for the purpose to measure the length between the fuel injector nozzle and first observation of OH* chemistry [71, 72]; the “lift-off length” measurement is a useful diagnostic for CFD model verification. PMTs have been used in many ignition studies [67, 73, 74] due to their high sensitivity
and signal response rate to photon emissions. When a photon enters a PMT it excites the electrons in a photocathode that emits photoelectrons towards a system of dynodes in series. The photoelectrons reflect between dynodes, multiplying after each interaction, and collect at an anode that produces a measurable signal [75]. The time resolution for measurements is ideal for recording detailed emission profiles of specific wavelengths during ignition. As well as with high speed cameras, PMT systems commonly use band-pass filters to detect a specific wavelength range of interest.

2.4 Ignition Behavior Sensitivity

2.4.1 Ambient Gas Temperature

The effect of ambient gas temperature on ignition behavior has been studied by many researchers, which in particular has led to the greater understanding of low temperature reaction kinetics over the years. It has been well documented that as ambient gas temperature increases, the ignition delay of hydrocarbon fuels decreases [76]. Interestingly when ambient temperatures are lower than 1000K, the chemical ignition delay can undergo negative temperature coefficient (NTC) dependence as mentioned in previous sections. Higgins et al. observed the location of first and second stage ignition chemistry in relation to the liquid diesel spray at varied ambient temperatures. They observed that ignition delay decreased as temperature increased as expected, although the spatial location of ignition transitioned upstream to surround the liquid spray jet in locations characterized by “shear and radial temperature gradients” [45]. Longer ignition
delay conditions appeared downstream of the spray where a more uniform temperature gradient was present. This may have interesting implications for two-stage ignition chemistry at higher temperatures in that there may be a mass-transfer limitation present during low temperature chemistry.

2.4.2 Charge Air Composition

Charge air is the fresh air that fills the combustion chamber of an IC engine (or experimental combustion apparatus) prior to fuel injection. The primary constituents of dry fresh air are O₂ (21%vol), N₂ (78%vol), Ar (0.9%vol), and CO₂ (0.03%vol) [77]. However, modern diesel engines typically utilize exhaust gas recirculation (EGR) to dilute the O₂ concentration of charge air. This lowers the flame temperature during combustion potentially resulting in the reduced production of regulated toxic emissions (i.e., nitrogen oxides) [6]. Kook et al. observed that decreasing O₂ concentration increased ignition delay values, particularly due to the reduced low-temperature heat release (LTHR). Also, they observed that increased dilution decreased the temperature rise rate during low temperature chemistry due to the increased diluent heat capacities and lowered reactant concentrations [78]. The lower temperatures due to diluent heat capacities results in a need for an increased mixture equivalence ratio for complete combustion of lean mixtures [79]. Karim and Ward investigated the effect of varying inlet oxygen concentration 15-55% in a single cylinder engine, concluding that any observed ignition behavior variations to oxygen concentration can be attributed to the sensitivities of the chemical, not physical, portion of ignition delay [26]. Oakley et al.
found that alcohols performed with greater tolerance to EGR dilution than hydrocarbon fuels [80]. The recorded tolerance of oxygenated fuels to EGR dilution in literature suggests that the potential application of biofuels in the next generation IC engines is promising.
Chapter 3

Experimental Method

3.1 Introduction

Optical access to a constant volume combustion chamber (CVCC) was designed and constructed for the purpose of investigating the physical and chemical ignition behavior of liquid fuels. This chapter begins with a description of the experimental apparatus and the sub-systems that were integrated into the design. This is followed by an overview of the post-processing methodology used to extract diagnostic ignition behavior data. Thereafter, the liquid fuels investigated using these systems are discussed. A section on the thermal characterization method performed to investigate the CVCC’s temperature profile is completed. Lastly, the procedure for the ignition sensitivity studies performed is defined.

3.2 Experimental Apparatus

The constant volume combustion chamber (CVCC) within a commercially available Cetane Ignition Delay (CID) 510 manufactured by PAC l.p., was chosen as a foundation for ignition studies due to its ease of control and design, of which mimicked the combustion chamber of a diesel engine. The CID unit utilized a Bosch light-duty diesel injector that delivered fuel at 1000 bar, a pressure similar to an automotive
common-rail injection system. The entire system was controlled by an internal computer that had the capability to deviate from standard operating conditions that had been calibrated for the derivation of cetane number (the CID’s primary function). With the operating controls open for modification, this provided the opportunity to change chamber temperature, chamber pressure, injection pressure, and injection duration as needed.

The CVCC in the CID was modified to add optical access for physical and chemical ignition behavior investigations. Three ports were welded to the bottom of the chamber for an optimal view of the spray during fuel injection. Two sub-systems occupied these ports including a high speed camera system for physical spray characterization and a photomultiplier tube system for chemiluminescence detection of intermediate chemical species. In addition, a gas mixer system developed by Polycontrols was installed upstream of the CVCC to dilute air with nitrogen and carbon dioxide to simulate exhaust gas recirculation (EGR) commonly utilized in modern IC engines. A simplified version of the experimental apparatus is illustrated in Figure 3-1. Each optical sub-system is briefly covered in this section.
The operating procedure for a standard ignition test cycle was as follows. Liquid fuel sample (160mL) was loaded into the CID’s sample reservoir and sealed with a screw cap. The user initiated a run by using the keypad of the CID’s human-machine interface (HMI), first by specifying a name and description of the run. Nitrogen gas (10 bar) forced the fuel from the reservoir through a 5μm particulate filter and a one-way valve to a pneumatic pressure multiplier tube. During the moments leading up to fuel injections, the multiplier tube was designed to pressurize the fuel to 1000 bar. The air inlet solenoid valve opened to fill the CVCC with a specified gas mixture from the 1.0 liter reserve tank. The chamber pressure was regulated to 20±0.1 bar by actuation of the CVCC inlet.
and exhaust solenoid valves. The process paused for approximately 80 seconds to allow for the air to equalize to the specified operating temperature, monitored by two type-K thermocouples embedded in the side walls of the CVCC. When the temperature, air pressure, and fuel pressure conditions were met, the computer initiated fuel injection by sending a 2.5ms 5V TTL pulse to the fuel injector that subsequently opened a solenoid valve, unseating a pin inside the tip of the injector. This allowed for fuel to flow around the pin and through six circular orifices (0.1mm diameter) into the chamber. The resulting high velocity fuel jets mixed with the air and ignited via physical and chemical processes. The pressure transducer located at the bottom of the CVCC recorded 250ms of pressure rise from ignition with a sample every 20μs. These data were automatically smoothed by the CID’s computer using a 9-point moving average before they were exported to an attached USB thumb-drive; the smoothed data were automatically re-scaled to a 40μs time step. After the combustion process was completed, the exhaust solenoid valve opened to release the hot pressurized air out an exhaust tube located at the rear of the instrument. The chamber was quickly refilled to 10 bar with fresh air and successively evacuated to flush out any remaining combustion products that may contaminate the next test. The complete injection process was repeated 15 times, which was defined as one test cycle. Multiple cycles could have been run if desired, however only one was completed for each test condition in this work.

In addition to the procedure covered above, either the spray visualization or chemiluminescence detection system (CDS) was operated in parallel. Since the visualization system introduced high intensity external light (discussed later) into the chamber which would add noise and possibly damage the photomultiplier tube modules
of the CDS, separate test cycles were completed for each sub-system to perform their respective measurements. These systems, including the gas mixer system, are covered in the following sub-sections.

3.2.1 Spray Visualization

Optical access to the stainless steel CVCC of the CID was achieved with a rigid Karl Storz endoscope and custom liquid light guide, each outfitted with liquid-cooled AVL Aquashfts. Each probe entered the chamber through access ports welded to the bottom (Figure 3-2). A Vision Research Phantom v7.1 monochrome camera equipped with a 50mm f/1.2 lens was mounted to the eye-piece of the endoscope to capture spray images at a rate of 29,197 frames per second (resolution of 128 x 384 pixels, exposure of 20μs). Spray movies were captured using Vision Research’s PCC v2.3 software, triggered via the 5V TTL fuel-injection pulse that was measured with a 1X oscilloscope probe at the injector computer board. The first 100 spray-images were exported in AVI format for further analysis. A Karl Storz NOVA 300 Xenon light source was used to supply high-intensity illumination to the fuel jet at a direct angle for light-scatter studies. Due to increased cooling demands of the optical probes, the original Lauda 300W circulating thermostat was replaced with a Polyscience 1000W circulating thermostat that supplied both the fuel injector and optical probes with a constant 50±2°C flow of 50/50 (by volume) ethylene glycol/water mixture.
3.2.2 Chemiluminescence Detection System

A custom chemiluminescence detection system (CDS) was designed and constructed to observe the presence of known intermediate chemical species throughout the ignition delay period. An air-cooled, UV/Vis optical probe designed by SMETec was installed through the third access port at the bottom of the combustion chamber. The probe was equipped with a 90° wide-angle, quartz observation lens for quality global measurements (Figure 3-3). The photons emitted from excited chemical intermediates passed through the optical probe and fiber to the CDS. A collimating lens aligned the light rays in parallel order as they exited the fiber tip. This homogeneous beam of light was directed towards a system of dichroic mirrors, band-pass filters, and photomultiplier...
tube (PMT) modules (Figure 3-4 illustrates the preparation of light rays prior to interaction with the PMTs). Two dichroic mirrors in series segregated the light according to their cut-off wavelengths of 340 and 460nm. The three resulting channels of light were individually filtered by wavelength with Edmund Optics band-pass filters of 307±5nm, 430±5nm, and 515±5nm which represented excited OH*, CH*, and C2* photon emission, respectively. In addition, excited formaldehyde (CH2O*) emissions (which overlapped the 431 nm wavelength of CH*) were captured during the first stage of two-stage ignition; a situation discussed in Section 2.3.4. Positioned after each filter was a Hamamatsu PMT module (sensitive to the 230-700nm range); each generated an amplified voltage signal (0-5V, via Hammamatsu power supplies) when photons were present. A National Instruments high-speed data acquisition (DAQ) card (USB-6366, mass termination) simultaneously acquired 40,000 samples at 1MHz (1 sample every microsecond) from each of the three PMT signal channels. The 40 millisecond acquisition period was triggered by the 5V TTL pulse read off the CID injector board with a 1X oscilloscope probe. At the end of the 15 test injection cycle, data was saved to a text file for further analysis. The complete CDS is pictured in Figure 3-5.
Figure 3-3: Close-up image of the SMETec UV/Vis optical probe’s 90° wide-angle quartz glass optics

Figure 3-4: Schematic of light pathway in the chemiluminescence detection system (CDS)
3.2.3 Gas Mixer

A custom high pressure gas mixer, manufactured by Polycontrols, was installed upstream of the CVCC to provide on-demand, simulated engine intake air with exhaust gas recirculation (EGR). Three computer-regulated mass flow controllers (MFCs) diluted standard compressed air with pure nitrogen and carbon dioxide, each of which were fed from gas cylinders regulated to 550psi. A 1.0 liter reserve tank downstream of the MFCs was maintained at 500 psi by a proportional-integral-derivative (PID) controller, which provided a constant supply of air to the CID throughout a test cycle. The selection of MFCs was completed by matching their optimal flow rate specification with the air consumption of the CID over one injection process in order to ensure high
mixing accuracy and timely replenishment of the reserve tank in-between fuel injections. An annotated picture of the gas mixer is shown in Figure 3-6.

![Figure 3-6: Annotated picture of the Polycontrols gas mixer used to supply charge air to the CID’s combustion chamber](image)

### 3.3 Post-Processing Programs

In order to quantify the physical and chemical autoignition behavior of each fuel, computer programs were developed in Matlab to ensure all data was handled in a similar and efficient fashion. Image analysis code was developed to measure physical properties
of a single liquid fuel jet by analyzing the digital pixels of each frame in the captured spray movie. Voltage signals measured from the PMT modules were analyzed to calculate physical and chemical ignition delay. Thermodynamic information, such as apparent heat release rate, was calculated from the pressure trace data collected by the CID’s internal computer. This section provides more detail into the algorithms and equations used to quantify these observations.

3.3.1 Image Analysis

After the spray images were captured by the Phantom v7.1 camera at 29,197 frames per second, they were post-processed in a Matlab program written to quantify macroscopic physical spray behavior described by liquid length and cone angle. An image analysis algorithm adapted from Pastor et al. [11] was used in this code as it provided greater threshold accuracy over the more commonly implemented Otsu’s method. The complete image analysis algorithm used is shown in Figure 3-7.
Since images were captured with a monochrome camera, each image was an independent matrix of values ranging 0-255 that corresponded to the grayscale with 0 and 255 representing black and white, respectively. Initially, each image was pre-processed by subtracting out the averaged value matrix for the first 8 images (averaged background) which lacked the presence of a spray. This corrected for global exposure gradients and lessened the impact of light spots created by reflections at the chamber walls. A histogram of the pixel values for each image revealed a logarithmic shape of which spray and background pixels could be identified (see example in Figure 3-8). 1-D log-
likelihood ratio testing was used to calculate an optimal threshold value for image segmentation, as detailed by Pastor et al. [11]. Each image was converted to a binary matrix by changing all values greater than the threshold to a 1 (spray) and every value below to a 0 (background). Only one complete spray jet was of interest, so the other identified spray pixel groupings were removed through spatial selection of known coordinates leaving a single spray object, as seen in Figure 3-9. Edge detection was accomplished by converting all inner spray pixels values from 1 to 0. A sequence of original spray images with their edges highlighted was saved in AVI format for visual inspection (a sample n-heptane image sequence is shown in Figure 3-10).

Figure 3-8: Histogram of n-heptane spray image with background and spray pixels annotated
Liquid length was defined as the distance between the injector orifice (selected by the user) and the furthest point classified as a spray pixel along the central spray axis. Cone angle was derived by first calculating the best fit of two vectors to the edge pixels that represented 50% of the liquid length via linear regression analysis. The cone angle was calculated as the angle between the two resulting line positions.
3.3.2 Chemiluminescence and Pressure Trace Analysis Program

A Matlab program was written to efficiently extract quantifiable information from the PMT and pressure data. Physical and chemical ignition delay, apparent heat release rate, and bulk temperature were calculated using algorithms and equations detailed in this sub-section.

3.3.2.1 Ignition Delay from PMT data

The PMT data (voltage signals) captured by the CDS was analyzed to derive the time values at the end of the physical and chemical ignition delay periods. An example of the raw PMT voltage signals captured during ULSD ignition under 600°C and 0%EGR is shown in Figure 3-11. Ignition delay values were calculated from the captured data at a reduced scale (as shown in Figure 3-12) where a clearer distinction between low and high temperature ignition could be made; often on the order of $10^{-3}$ volts.

Figure 3-11: Raw PMT signals from ignition of ULSD
Ignition delay ($\tau_{\text{ign}}$) was defined as the first significant measurement of OH* chemiluminescence represented by the 307±5nm PMT signal, as shown in Figure 3-13. This was completed by taking the derivative of the smoothed voltage signal (2000Hz low-pass filter) and analyzing the result to find when the signal began to show a positive rate of increase.
As mentioned in Section 2.2.1, the end of the physical ignition delay ($\tau_{\text{phys}}$) period occurred at the onset of low temperature combustion chemistry. This time point was calculated as the first observation of excited formaldehyde chemiluminescence, which was measured by the first significant voltage increase seen in the $430\pm5$nm PMT signal. Due to the high signal fluctuations, a 2,000Hz low-pass filter was used to smooth the data for accurate calculation of $\tau_{\text{phys}}$, as shown in Figure 3-14. Only the data captured between start of injection and $\tau_{\text{ign}}$ were analyzed to identify $\tau_{\text{phys}}$. The first derivative of the smoothed data was used to measure $\tau_{\text{phys}}$ as the first positive deviation from zero that led to the local maximum value in this data range. The difference between $\tau_{\text{ign}}$ and $\tau_{\text{phys}}$ was calculated as the chemical ignition delay ($\tau_{\text{chem}}$).

![Figure 3-14: Example 430±5nm signal smoothed with 2000Hz low-pass filter used to derive $\tau_{\text{phys}}$](image)

### 3.3.2.2 Thermodynamic Calculations from Pressure Data

Apparent heat release rate was derived from the pressure trace data collected by the CID’s internal computer. Often the saved pressure trace would reveal pressure fluctuations near peak combustion pressures of which were identified to be the result of
characteristic acoustic waves (an audible “ping” sound during ignition) created by large pressure-rise rates, as illustrated in Figure 3-15. The fluctuations were not representative of the actual heat release process and therefore created noise that affected the quality of the heat release derivations. To accurately calculate apparent heat release rates, a 2,500Hz low-pass filter was used to smooth the pressure signal, as illustrated in Figure 3-16.

![Figure 3-15: Sample pressure trace data from ignition of ULSD](image)

![Figure 3-16: Sample smoothed pressure trace data using low-pass filter](image)
Apparent heat release rate (AHRR) was calculated from the smoothed pressure trace data. The term “apparent” is meant to indicate that the values are approximate, given that the exact values cannot be quantified solely from the pressure trace data captured here. For the calculation, the air temperature throughout the chamber was assumed to be uniform at each time step of ignition. The “bulk temperature” \( T_{\text{bulk}} \) was calculated using Equation 3-1. Volume \( V \) was specified as the internal CVCC volume to be 0.473 liters. Instantaneous chamber pressure \( P \) was taken from the smoothed pressure data. The specific gas constant \( R_{\text{specific}} \) of air was assumed to be 0.287 kJ/kg-K.

The summation of fuel and air mass \( m_{\text{air+fuel}} \) was calculated using the ideal gas law equation for air mass and unit conversion equations with the known injection volume (125 mm\(^3\) for 2.5ms injection) and fuel density properties for fuel mass.

\[
T_{\text{bulk}} = \frac{PV}{R_{\text{specific}}m_{\text{air+fuel}}} \quad \text{(3-1)}
\]

Apparent heat release rate (AHRR) was calculated assuming an ideal gas using Equation 3-2. Gamma \( \gamma \) was the ratio of specific heat capacities (Equation 3-3), a value that is commonly between 1.3 and 1.4 in diesel combustion systems.

\[
\frac{dQ}{dt} = \frac{1}{\gamma - 1}V\frac{dP}{dt} \quad \text{(3-2)}
\]

\[
\gamma = \frac{c_p}{c_v} \quad \text{(3-3)}
\]

where,

\( c_p \) = constant pressure heat capacity

\( c_v \) = constant volume heat capacity
Often gamma is left constant in AHRR calculations although this is rarely true under real environments. A correlation of gamma to temperature (Equation 3-4) [6] was used to correct for changes in heat capacity ratio as the air mixture transitioned from unburned to burned.

\[
\gamma = \frac{1}{1 - \frac{1}{a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4}} \quad (3-4)
\]

where,

\[
\begin{align*}
  a_1 &= 3.6359 \\
  a_2 &= -1.33736 \times 10^{-3} \\
  a_3 &= 3.29421 \times 10^{-6} \\
  a_4 &= -1.91142 \times 10^{-9} \\
  a_5 &= 0.275462 \times 10^{-12}
\end{align*}
\]

The first derivative of smoothed pressure data was calculated using the five-point method as shown in Equation 3-5.

\[
\frac{dP}{dt} \approx \frac{-P(t + 2h) + 8P(t + h) - 8P(t - h) + P(t - 2h)}{12h} \quad (3-5)
\]

where,

\[
h = \text{time step}
\]

A typical AHRR profile is shown in Figure 3-17 of which was derived from the ULSD pressure data presented in Figure 3-15. The low and high temperature exothermic reaction stages were highlighted to point out the two-stage ignition phenomenon characteristic of this fuel under these conditions.
3.4 Fuel Samples

3.4.1 n-Heptane

Chevron Phillips primary reference fuel (PRF) n-heptane was tested in all ignition studies. The purity of PRF-grade n-heptane was a minimum of 99.78% by volume, with a maximum lead and isoctane concentration of 0.0020 g/gal and 0.10 %vol, respectively [81]. The molecular structure of n-heptane is shown in Figure 3-18.
3.4.2 Diesel and Biodiesel Blends

Peter Cremer NEXSOL BD-0100 Biodiesel (ASTM D 6751, EPA 4627) derived from soybeans was blended with ultra-low sulfur diesel (ULSD) produced by ExxonMobil. Fuel properties for the soybean biodiesel and ULSD are listed in Table 3-1. The blend matrix tested is summarized in Table 3-2.

Table 3-1: Chemical properties of biodiesel fuel blend components

<table>
<thead>
<tr>
<th>Property</th>
<th>Ultra Low Sulfur Diesel</th>
<th>Soybean Biodiesel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lower Heating Value, MJ/kg</td>
<td>42.6</td>
<td>--</td>
</tr>
<tr>
<td>Density @ 20°C, kg/m³</td>
<td>831.8</td>
<td>--</td>
</tr>
<tr>
<td>Kin. Viscosity @ 40°C, mm²/sec</td>
<td>--</td>
<td>4.0c</td>
</tr>
<tr>
<td>Cetane Number</td>
<td>45.1a</td>
<td>48b</td>
</tr>
<tr>
<td>T90, °F (°C)</td>
<td>593.8 (312.1)d</td>
<td>667.4 (353.0)e</td>
</tr>
</tbody>
</table>

aASTM D6890; bASTM D613; cASTM D445 ; dASTM D86; eASTM D1160

Table 3-2: Biodiesel blend compositions

<table>
<thead>
<tr>
<th>Fuel Name</th>
<th>Soybean Biodiesel (Volumetric Fraction)</th>
<th>Ultra Low Sulfur Diesel (Volumetric Fraction)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B100</td>
<td>1.00</td>
<td>0.00</td>
</tr>
<tr>
<td>B80</td>
<td>0.80</td>
<td>0.20</td>
</tr>
<tr>
<td>B60</td>
<td>0.60</td>
<td>0.40</td>
</tr>
<tr>
<td>B40</td>
<td>0.40</td>
<td>0.60</td>
</tr>
<tr>
<td>B20</td>
<td>0.20</td>
<td>0.80</td>
</tr>
<tr>
<td>ULSD</td>
<td>0.00</td>
<td>1.00</td>
</tr>
</tbody>
</table>
The composition of a separate batch of Peter Cremer soy biodiesel (BD-0100) was characterized by Mueller et al. [82] in an unrelated study and found to be composed of methyl palmitate (C16:0), methyl stearate (C18:0), methyl oleate (C18:1), methyl linoleate (C18:2), and methyl linolenate (C18:3); of which methyl linoleate (C18:2) and methyl oleate (C18:1) accounted for over 75% of the mole fraction. The structures of these molecules are illustrated in Figure 3-19.

![Structures of major molecular compounds present in Peter Cremer BD-0100, soy-derived biodiesel](image)

Figure 3-19: Structures of major molecular compounds present in Peter Cremer BD-0100, soy-derived biodiesel

The composition by mass of a typical ULSD #2 found in the US market has been illustrated in Figure 3-20 by Mueller et al. [83]. These general compositions were considered to be closely representative of the ULSD samples tested in this study. The
total aromatic content of the ULSD used in these studies was tested to be 31.54% (ASTM D5186), which aligned well with these estimations.

Figure 3-20: Molecular composition (by mass) of a typical ULSD #2 fuel in the US market as illustrated by Mueller et al. [83]. Representative molecules of each classification are displayed.

3.5 Thermal Analysis of the Combustion Chamber

A thermal analysis of the combustion chamber was conducted after initial pressure trace data revealed that the ignition delay of n-heptane at 600°C increase by 1-2ms compared to previous tests with the original combustion chamber installed. The thermal analysis package within Solidworks 2012 was used to simulate the temperature profile of the heated combustion chamber at steady state. A solid mesh model of the closed chamber with 620,844 nodes and 420,171 elements was constructed, see Figure 3-21. Heat was applied via a 900W power source to the cylindrical outer wall where the electrical heater was located. Convective heat losses were accounted for at the cooled
injector assembly and three probe access ports by adjusting their respective heat transfer coefficients until the final steady state results matched experimental data taken at specific locations around the chamber walls. The remaining mesh surfaces were considered fully insulated, contributing no heat loss to surroundings. Furthermore, the temperature profile of air inside the chamber was not simulated, only the solid metal body was. Material properties of the chamber was set to AISI 316 stainless steel, accounting for a thermal conductivity of 16.3 W/m-K, specific heat of 500 J/kg-K, and mass density of 8000 kg/m³.

In addition, temperature profiles of the gas within the chamber were investigated experimentally under 550, 575, 600, and 625°C operating conditions. A multi-point type-K thermocouple was used to measure temperature at six points spaced 0.5 inches apart along the centerline axis of the chamber, beginning from the injector’s tip. An Omega thermocouple data acquisition (DAQ) card with cold junction compensation (CJC) was used to record eight temperature locations (accuracy within ±0.1°C) of the air during the
heating stage of the injection process. A simulated air heating process was controlled manually through pneumatic actuation of the inlet and exhaust valves. The pressure transducer was relocated with a T-fitting to accommodate the thermocouple; this change did not adversely affect pressure measurements. A diagram of the measurement locations within the chamber and image of the installation are shown in Figure 3-22.

![Figure 3-22: Experimental setup for internal gas temperature characterization; diagram (left), installation (right)](image)

The manually-controlled air heating cycle was developed to mimic the automatic air preparation process controlled by the CID’s computer boards during a standard test run. The first 10 seconds were spent filling the chamber with fresh air by opening the inlet valve until the pressure inside the chamber reached 20.0±0.1 bar. This was followed by an 80 second settling time. Once completed, the exhaust valve was immediately
opened to release the heated air as if ignition had occurred. Each temperature condition was repeated five times and averaged temperature profiles were calculated.

### 3.6 Ignition Sensitivity Studies

Investigations into the effects of ambient air temperature and oxygen dilution (via simulated EGR) were completed using the optically accessible CVCC. The spray visualization system and CDS where both used at each operating condition, although the only pressure data used for thermodynamic calculations were from the CDS tests. Each test condition was run for one cycle (15 injections) per fuel sample. The detailed test parameters are discussed in this section.

#### 3.6.1 Ambient Air Temperature

The sensitivity of ignition behavior to ambient air temperature was investigated by spanning the initial chamber temperature at 540, 560, 580, 600, and 620°C. Chamber temperature was easily adjusted via the HMI keyboard of the CID unit. Other initial test conditions included: 20bar chamber pressure, 2.5ms injection duration, and 1000bar injection pressure. Combustion air composition was set to 20.8% oxygen (by volume), balance nitrogen, using the Polycontrols air mixer explained in the next section. The fuels tested under these conditions were n-heptane, ULSD, and B100.

#### 3.6.2 Oxygen Dilution
The combustion air used in each ignition study were mixed to a set concentration of oxygen, carbon dioxide and nitrogen using an automated gas mixing system developed by Polycontrols. The unit had a proportional-integral-derivative (PID) controller that adjusted the mass flow rates of three mass flow controllers (MFC) that were fed by compressed air, nitrogen, and carbon dioxide gas cylinders (regulated to 550 psi). The mixture was stored in a 1 liter reserve tank that was maintained at 500 psi by the PID controller. The operation allowed for an on-demand feedstock of special gas mixtures upstream of the CID instrument. An annotated photo of the gas mixer apparatus is shown in Figure 3-23.

![Annotated photo of gas mixer apparatus installed upstream of the CID](image)

**Figure 3-23: Annotated photo of gas mixer apparatus installed upstream of the CID**

All dilution testing was completed with a sweep of simulated EGR at 0%, 25%, 40%, 50%, and 55%. In order to calculate the corresponding O\textsubscript{2}, CO\textsubscript{2}, and N\textsubscript{2}
concentrations for these air mixtures, a method derived by Müller [84] based off the chemical reaction formula for complete combustion (Equation 3-6) was used. The molar coefficient for fresh air (n) was calculated using Equation 3-7. Coefficients of CO₂ (a), H₂O (b), and N₂ (h) were calculated using Equations 3-8, 3-9, and 3-10, respectively. The hydrogen to carbon ratio (y) and oxygen to carbon ratio (z) were derived from fuel property data. The nitrogen to oxygen ratio (ξ) was calculated using Equation 3-11, of which the oxygen percentage of fresh air was assumed to be 20.81%.

\[
\begin{align*}
\text{fuel} & : \text{CH}_y\text{O}_z + n(\text{O}_2 + \xi\text{N}_2) + \frac{\text{EGR}}{100} (\text{aCO}_2 + \text{bH}_2\text{O} + \text{hN}_2) \rightarrow \text{aCO}_2 + \text{bH}_2\text{O} + \text{hN}_2 \\
\text{fresh air} & : (1 - \text{EGR}/100) - \frac{z}{2} \\
\text{recycled exhaust} & : (1 - \text{EGR}/100) \\
\text{exhaust} & : (1 - \text{EGR}/100)
\end{align*}
\]  

\[ n = \left( a + \frac{1}{2}b \right) \left( 1 - \frac{\text{EGR}}{100} \right) - \frac{z}{2} \]  
\[ a = \frac{1}{1 - \text{EGR}/100} \]  
\[ b = \frac{y}{2(1 - \text{EGR}/100)} \]  
\[ h = \frac{n \xi}{1 - \text{EGR}/100} \]  
\[ \xi = \frac{100 - \%\text{oxygen}_{\text{fresh air}}}{\%\text{oxygen}_{\text{fresh air}}} \]

In order to maintain consistency of EGR mixture compositions across fuel types, the selected oxygen, carbon dioxide, and nitrogen concentrations were derived by using n-heptane as the fuel in Equation 3-6. The mixture compositions corresponding to EGR rates used in this work are reported in Table 3-3. For visual interpretation, these values are plotted in Figure 3-24.
<table>
<thead>
<tr>
<th>EGR %</th>
<th>Oxygen, O₂ (% by volume)</th>
<th>Carbon Dioxide, CO₂ (% by volume)</th>
<th>Nitrogen, N₂ (% by volume)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>20.8</td>
<td>0.0</td>
<td>79.2</td>
</tr>
<tr>
<td>25</td>
<td>15.9</td>
<td>3.7</td>
<td>80.5</td>
</tr>
<tr>
<td>40</td>
<td>12.8</td>
<td>6.3</td>
<td>80.9</td>
</tr>
<tr>
<td>50</td>
<td>10.7</td>
<td>8.3</td>
<td>81.1</td>
</tr>
<tr>
<td>55</td>
<td>9.6</td>
<td>9.3</td>
<td>81.1</td>
</tr>
</tbody>
</table>

Figure 3-24: Plot of calculated air compositions at varied exhaust gas recirculation (EGR) rates.
Chapter 4
Results and Discussion

4.1 Thermal Analysis of the Combustion Chamber

A thermal analysis of the modified CID combustion chamber was conducted to characterize the initial temperature profile over the full range of operating temperatures. This provided detailed boundary condition information to support CFD simulation efforts. In addition, the results of this study influenced the test procedure used to observe physical and chemical ignition behavior.

Thermal analysis of the combustion chamber was completed in Solidworks at 550, 575, 600, and 625°C operating conditions. Convective heat transfer coefficients for the optical probe surfaces were adjusted in the Solidworks program until the calculated wall temperatures at two specific locations matched the experimental data taken under the same operating conditions. Figure 4-1 identifies the two locations measured in simulation and experiment. The temperature profile from simulation was considered representative when these measurements agreed within 10°C for each condition. The temperature profile of the cut-away chamber (600°C case shown in Figure 4-2) revealed a large temperature gradient ranging from above 600°C down to as low as ~280°C. A large cold spot (<400°C) accounted for the majority of the wall at the bottom of the chamber. It is worth noting that the portion of chamber near the pressure transducer location was not defined
accurately by simulation, as this portion is not insulated and heat transfer to the surrounding room air was not accounted for. In all cases, the lowest temperatures were located in the region between the two liquid-cooled AVL video probe mounts. The overall surface temperature at the bottom of the chamber was greatly affected by this cool region due to the large footprint of the probes. A lesser impact was attributed to the UV/Vis probe.

Figure 4-1: Combustion chamber temperature profile for 600°C steady-state simulation model, with all optical probes installed; experimental measurement locations are annotated.
Air temperature measurements were taken in the real combustion chamber at different points along the central chamber axis. The average temperature for each point at the end of the 80 second settling time is plotted in Figure 4-3 for each operating temperature case. Overall, the values were roughly 150-250°C lower than the specified operating temperature. The highest temperatures were measured at one inch from the injector tip, closely located to the 3-dimensional center of the inner chamber volume. The shape of the temperature curves indicated that the lower temperatures measured above the central point was likely due to heat loss at the cooled fuel injector assembly. A more aggressive temperature drop was observed below the central point partly due to heat loss at the three cooled probes. In addition, it is reasonable to assume that hotter air transferred to the upper half of the chamber as a result of density gradients, therefore slowing convective heat transfer in the downward direction.
Visual inspection of the combustion chamber’s internal walls exposed an interesting spectrum of colors centered at the bottom near the probe windows. Figure 4-4 shows the discoloration of the internal chamber walls observed after testing. The transition from yellow-brown to purple to deep blue can be explained by well-known surface oxidation reactions between air and stainless steel at elevated temperatures. Although the exact alloy of the chamber was unknown, temperature color charts indicated that yellow-brown, purple, and blue correspond to heat treatments at temperatures roughly around 245-270°C, 280-310°C, and 320-370°C, respectively [85]. With the assumption that the color correlations were accurate, the experimental observations appeared to agree well with the Solidworks simulation results.
Due to the major cold spot created by cooling all three optical probes, the implementation of another heat source was considered as a means to reduce their impact. A 120V high-temperature heating tape from Omega was wrapped around the external
wall and probe mounts at the bottom of the chamber. The temperature of the tape was
controller by an Omega control unit with a type-K thermocouple placed between the
heating tape and chamber wall. The heating tape was unable to exceed 490°C throughout
testing. A modest increase in temperature at 2.0 and 2.5 inches from the injector tip was
observed, accounting for roughly a 20-25°C increase over the previous measurements. It
was concluded that significant modification to the design of the heating system would be
required to reduce the impact of the cold spot created by the cooled optical probes.

In order to investigate the impact the cooled-optical probes on ignition behavior,
individual test cycles of n-heptane at 600°C and 0%EGR were completed in three
different chamber configurations, as summarized in Table 4-1. The resulting pressure
trace data are plotted in Figure 4-5. Ignition occurred later as more optical probes were
installed at the bottom of the chamber. It was reasonable to conclude that the temperature
at the bottom portion of the chamber significantly affected ignition behavior. In fact,
CFD simulations of Configuration 1 revealed that the air and fuel vapor began to mix in
the top half of the chamber but continued into the bottom half where the main ignition
phenomenon actually occurred. Considering these results, it was determined that the
longer ignition delay values were due to lower temperatures imposed by the optical
probes at the bottom of the chamber.
Table 4-1: Descriptions of combustion chamber configurations for thermal analysis tests

<table>
<thead>
<tr>
<th>Configuration Number</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Original chamber with no probes installed</td>
</tr>
<tr>
<td>2</td>
<td>Modified chamber with air-cooled UV/Vis probe installed</td>
</tr>
<tr>
<td>3</td>
<td>Modified chamber with air-cooled UV/Vis and water-cooled AVL probes installed</td>
</tr>
</tbody>
</table>

Figure 4-5: Pressure trace data for n-heptane ignition at 600°C in varied chamber configurations

The results of the thermal analysis provided important boundary condition information to the CFD modelers and furthermore influenced the test method used for the remainder of this work. It was decided that spray visualization measurements were to be completed using Configuration 3, under the assumption that the air temperature gradient in the upper half of the chamber (where liquid spray interacted) was not as significantly impacted by the cooled-probes at the bottom. CFD simulations loosely supported this
assumption. Ignition delay and pressure measurements were to be conducted using
Configuration 2, which provided a compromise between boundary condition complexity
for CFD simulations and experimental accuracy for ignition delay measurements.

4.2 Ambient Air Temperature Effects

4.2.1 Spray Liquid Length and Cone Angle

Measurements of liquid length for n-heptane sprays at operating temperatures
between 540°C and 620°C were completed by analyzing spray images captured at 29,197
frames per second. The effect of temperature across this range was statistically
insignificant as shown in Figure 4-6. Here 540°C and 620°C conditions are plotted with
error bars representing two standard deviations. Although statistically insignificant, the
mean liquid length data was slightly shorter at higher temperatures during the early stages
of quasi-steady behavior. During the later stages, both the mean and distribution across
all temperature conditions overlapped entirely.
Captured spray images of ULSD and B100 made it difficult to measure liquid length of the quasi-steady state due to the fact that the spray jet consistently extended beyond the camera’s viewing angle across all test conditions. Figure 4-7 displays a spray image of ULSD captured when the spray jets extended beyond the view angle. The photo was taken with a 25mm lens rather than the 50mm lens to emphasize that the greatest viewing angle provided by the optical setup still failed to capture a complete spray jet under the conditions tested. Future studies may benefit from reducing the fuel pressure to below 1000 bar, as this may shorten the liquid length enough to capture the fully developed jet.
Regardless of the camera viewing angle issue, liquid length was measured for the transient spray of B100 and ULSD, as shown in Figures 4-8 and 4-9, respectively. The effect of air temperature did not play a significant role for both fuels in transient spray development across the 540-620°C temperature sweep tested. The spray tip fluctuations seen in these plots occurred in the same manner between temperature points, suggesting air temperature does not significantly affect the behavior of these fluctuations under transient conditions.
A comparison of liquid length between each fuel’s transient spray at 540°C is shown in Figure 4-10. n-Heptane reached quasi-steady state earlier than B100 and ULSD (at around 0.22ms). Each fuel displayed liquid length fluctuations during this period; however they were greatest with B100 and ULSD. Similar fluctuations in liquid length in
transient sprays were observed by Eagle et al. and suggested that they may be due to asymmetrical, time-dependent structures within the spray [19].

![Graph showing liquid length values of transient spray for B100, ULSD, and n-heptane at 540°C](image)

**Figure 4-10: Liquid length values of transient spray for B100, ULSD, and n-heptane at 540°C**

Calculation of cone angle was completed for n-heptane, as well as ULSD and B100 since the error in liquid length at their length-scales did not significantly affect cone angle calculation errors. The effect of ambient air temperature on cone angle was similar to its effect on liquid length in that there were statistically similar results. Figures 4-11, 4-12, and 4-13 present the mean cone angle at 540°C and 620°C for n-heptane, B100, and ULSD, respectively. Qualitative inspection of the cone angle and liquid length traces revealed a trend that as the cone angle decreased, liquid length increased. According to a study by Siebers a decrease in cone angle results from the decrease in ambient gas entrainment and therefore longer liquid lengths are required to supply enough energy to vaporize the fuel [12].
Figure 4-11: Mean cone angle profiles for n-heptane at 540°C and 620°C

Figure 4-12: Mean cone angle profiles for B100 at 540°C and 620°C
The mean cone angle data for the 540°C case of all three fuels without error bars are plotted in Figure 4-14 to illustrate some qualitative observations. First, the cone angle for all cases began very wide and fluctuated significantly during the transient period; similar to what was observed with liquid length. Once quasi-steady behavior was achieved, the cone angle fluctuations reduced greatly. n-Heptane appeared to reach quasi-steady state sooner than B100 and ULSD, which may be due to significant differences in surface tension and viscosity as these properties are known to hinder the atomization process in liquid sprays [17].
Due to the apparent connection between liquid length and cone angle fluctuations, the ratio of liquid length to cone angle (LL/CA) was calculated for n-heptane, B100, and ULSD at 600°C. The results for n-heptane in Figure 4-15 revealed a positive increase between start of injection and end of transient behavior before it leveled off during quasi-steady state with an average of 1.8±0.1 mm/deg. The ratios for B100 and ULSD were only calculated for the portion of transient behavior leading to the camera’s viewing angle limitation. The LL/CA ratio calculations for each transient fuel spray are plotted in Figure 4-16. n-Heptane produced larger LL/CA ratios than B100 and ULSD during transient; however quasi-steady behavior resulted in much lower values. The trend was roughly linear, suggesting that the fluctuations in liquid length and cone angle are likely directly linked.
Figure 4-15: Liquid length to cone angle ratio of n-heptane spray at 600°C

Figure 4-16: Liquid length to cone angle ratio of transient spray for n-heptane, B100, and ULSD at 600°C
4.2.2 Ignition Delay

Physical and chemical ignition delay values for n-heptane, B100, and ULSD were calculated from the PMT voltage signals as described previously. The results for physical ignition delay ($\tau_{\text{phys}}$) are plotted in Figure 4-17. The Arrhenius plot revealed a relatively linear dependence of $\tau_{\text{phys}}$ on ambient air temperature. Increased ambient air temperature resulted in shorter physical ignition delays across the complete temperature range tested. $\tau_{\text{phys}}$ values were ordered from shortest to longest by n-heptane, ULSD, and B100. This result was thought to be due to increasing viscosity and decreasing volatility associated with these fuels, a trend that would decrease mixing rates and therefore increase $\tau_{\text{phys}}$, as discussed by Obert [86].

![Figure 4-17: Plot of physical ignition delay against ambient air temperature for n-heptane, B100, and ULSD](image-url)
The Arrhenius plot of chemical ignition delay ($\tau_{\text{chem}}$) presented a non-linear trend for each fuel, as shown in Figure 4-18. Initially there appeared to be a linear trend from the lowest temperature to about 580°C (853 K), although at higher temperatures the data diverged in a manner similar to the NTC behavior commonly observed under these pressure conditions [28]. ULSD and B100 displayed similar $\tau_{\text{chem}}$ values between 540 and 580°C however ULSD exhibited NTC behavior at a lower temperature, more representative of the n-heptane trend. The n-heptane physical and chemical ignition delay results were very characteristic of trends observed by Ciezki et al. across these conditions [37].

Figure 4-18: Plot of chemical ignition delay against ambient air temperature for n-heptane, B100, and ULSD
4.2.3 Apparent Heat Release Rate (AHRR)

Apparent heat release rate (AHRR) was calculated from the pressure trace data captured during the tests under chamber Configuration 2, as discussed previously. The effect of ambient air temperature was investigated by viewing the AHRR profiles for each fuel across the 540-620°C temperature range tested, as plotted in Figure 4-19. Initial inspection revealed that n-heptane was most reactive at any given temperature. This was attributed to the short ignition delays between the start of injection (SOI) and the high temperature heat release (HTHR) peak. Lower ambient temperatures greatly increased the delay between SOI and the low temperature heat release (LTHR) peak, with B100 appearing to be affected the most. The shape of HTHR for ULSD and B100 became very short and wide with decreased temperature, indicating a very “lazy” heat release behavior. n-Heptane maintained seemingly “sharp” HTHR shapes across all temperatures.
Figure 4-19: Apparent heat release rate profiles for n-heptane, ULSD and B100 ignition at 540-620°C

The maximum LTHR values for each fuel across the temperature span are plotted in Figure 4-20. Some data are missing for n-heptane and B100 due to the appearance of single-stage ignition at those conditions. Ambient air temperature imposed an interesting effect on ULSD and B100, in that maximum LTHR increased with temperature up to 580°C before gradually decreasing as 620°C was reached. This behavior may be shared by n-heptane, although maximum LTHR at 560 and 580°C were not determined. The increased value at 540°C suggested that there may be a linear trend; however this conclusion cannot be made without further testing.
The maximum HTHR data for each fuel appeared to be more conclusive, as plotted in Figure 4-21. The maximum HTHR for n-heptane once again was significantly greater than ULSD and B100 ignition. As temperatures reached 620°C, maximum HTHR for n-heptane seemed to reach a limit and level off. Tests at higher temperatures would confirm this perceived trend. Maximum HTHR for ULSD and B100 appeared to increase linearly with ambient air temperature above 560°C. Additionally their calculated values were very similar at each temperature condition.
4.3 Oxygen Dilution Effects

4.3.1 Spray Liquid Length and Cone Angle

The sensitivity of liquid length and cone angle have been attributed to changes in gas density that are directly proportional to the rate of mass entrainment of the jet, as discussed by Naber and Siebers [13]. The effect of oxygen dilution on the liquid jet in this case, tested with simulated EGR, was accredited to the physical properties of the ambient gas. The gas densities achieved during these studies were very low, ranging between 7.95 to 8.23 kg/m³ for 0% to 55% EGR, respectively (see Table 4-2).
Table 4-2: Air density values of simulated EGR gas mixtures at 600°C

<table>
<thead>
<tr>
<th>EGR %</th>
<th>O₂ (%vol)</th>
<th>CO₂ (%vol)</th>
<th>N₂ (%vol)</th>
<th>Gas Density At 600°C (kg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>20.8</td>
<td>0.0</td>
<td>79.2</td>
<td>7.95</td>
</tr>
<tr>
<td>25</td>
<td>15.9</td>
<td>3.7</td>
<td>80.4</td>
<td>8.06</td>
</tr>
<tr>
<td>40</td>
<td>12.8</td>
<td>6.3</td>
<td>80.9</td>
<td>8.14</td>
</tr>
<tr>
<td>50</td>
<td>10.7</td>
<td>8.3</td>
<td>81.0</td>
<td>8.21</td>
</tr>
<tr>
<td>55</td>
<td>9.6</td>
<td>9.3</td>
<td>81.1</td>
<td>8.23</td>
</tr>
</tbody>
</table>

The liquid length profile for n-heptane at 0% and 55% EGR is plotted in Figure 4-22. The results did not show any significant differences across EGR conditions. This outcome was also observed for B100 and ULSD as well (transient liquid length measurements shown in Figures 4-23 and 4-24, respectively). Due to the small window of gas density across EGR rates, the effect of oxygen dilution on liquid length was almost non-existent.

Figure 4-22: Plot of liquid length measurements of n-heptane spray under 0% and 55% EGR dilution
Inspection of the corresponding cone angle values yielded identical results to the liquid length cases, which was expected due to the direct relationship of cone angle to liquid length. No trends of gas density effects on cone angle could be made under these conditions. Plots of cone angle from n-heptane, B100, and ULSD are shown in Figures 4-
25, 4-26, and 4-27, respectively. Differences in cone angles across fuel types at these conditions were consistent to observations discussed in Section 4.2.1.
Although the effect of oxygen dilution on physical spray properties was not conclusive due to the narrow gas density window tested, the results produced here were still valuable to CFD modeling efforts.

4.3.2 Ignition Delay

The ignition delay values of the physical and chemical processes were calculated for ULSD, B20, B40, B60, B80, B100, and n-heptane across the complete EGR dilution range. Results for physical ignition delay ($\tau_{\text{phys}}$) are plotted on a linear scale in Figure 4-28. There appeared to be a linear trend that increased $\tau_{\text{phys}}$ as EGR rates increased. n-Heptane produced the shortest $\tau_{\text{phys}}$, likely attributed to its significantly different physical properties such as higher volatility and lower viscosity. The $\tau_{\text{phys}}$ for each blend of ULSD and B100 increased with increasing EGR rates. The biodiesel blends were expected to reveal an increasing $\tau_{\text{phys}}$ trend with biodiesel content at all conditions as seen in the
temperature study, although the average results incurred large errors in measurement that possibly masked this trend.

![Plot of physical ignition delay against EGR dilution for all fuel samples](image)

\textbf{Figure 4-28: Plot of physical ignition delay against EGR dilution for all fuel samples}

The effect of EGR dilution on $\tau_{\text{phys}}$ raised questions about whether this was the result of physical or chemical sensitivities. We observed earlier that liquid length and cone angle appeared unchanged under these conditions, attributed to insignificant variations in mass entrainment rates. This may point to changes in physical mixing behavior between air and gaseous fuel. However, the end of physical ignition delay was measured as the first observation of excited formaldehyde which occurs after pre-ignition KHP chemistry in the low temperature regime; a process not detected by the chemiluminescence system in these studies. Longer ignition delays as a result of EGR dilution were discussed by Musculus et al. [9] and suggested that that EGR dilution has
insignificant effect on mixing but reduces low temperature reaction rates. Further work is needed to investigate the possible linear trend in $\tau_{\text{phys}}$ with increasing EGR dilution. A possible explanation might be that the linear increase in heat capacity associated with increasing EGR dilution might slow temperature rise rates thereby delaying the decomposition of KHP and formation of excited-formaldehyde (the marker for end of $\tau_{\text{phys}}$ in these studies).

The chemical ignition delay ($\tau_{\text{chem}}$) for each fuel is plotted in Figure 4-29. A seemingly exponential relationship with oxygen dilution was observed across all fuel types. n-Heptane produced the shortest $\tau_{\text{chem}}$ values and displayed high tolerance to EGR dilution, similar to the trend of B100. The $\tau_{\text{chem}}$ values for each ULSD/B100 blend were statistically similar at 0%EGR; however as EGR rates increased, $\tau_{\text{chem}}$ increased at varied exponential rates according to blend ratios.
Researchers have suggested the high tolerance of biodiesel to EGR dilution is due to the significant portion of fuel-derived oxygen which may result in less of a dependence on ambient oxygen concentration. Figure 4-30 displays a contour plot of $\tau_{\text{chem}}$ data from Figure 4-29 as it varied across biodiesel blend concentration and EGR dilution rate. Higher concentration of ULSD in biodiesel blends displayed greater $\tau_{\text{chem}}$ sensitivity to EGR dilution. The results here agree with suggestions that higher EGR tolerance of biodiesel could be due to the availability of fuel-derived oxygen, however further work is needed to investigate this relationship.

Since n-heptane and B100 displayed very similar behavior across EGR dilution, it is worth considering the effect of long unbranched hydrocarbon structures shared by the two fuels. Higher concentration of straight chain paraffins increases reactivity of HTHR
leading to shorter ignition delays [87]. In the same token, aromatic structures impose the opposite effect. The trends observed in Figure 4-29 may suggest that the high sensitivity of ULSD to EGR dilution may not be due to the lack of fuel-derived oxygen, but more strongly to the dependence of aromatic content on ambient oxygen concentration. Further testing with varying aromatic and biodiesel content may shine some more light on this behavior.

Figure 4-30: Contour plot of chemical ignition delay against volumetric percentage of biodiesel content and EGR dilution at 600°C. Actual measured data are marked with dots.
4.3.3 Apparent Heat Release Rate (AHRR)

The apparent heat release rate (AHRR) for n-heptane ignition across the EGR dilution range at 600°C is plotted in Figure 4-31. The classic two-stage ignition was observed for all conditions, represented by two heat release spikes. The smaller spike accounted for low temperature chemistry and the larger for the high temperature chemistry, as discussed previously. As EGR dilution rates increased, the time delay for high temperature heat release (HTHR) increased at a greater rate than low temperature heat release (LTHR). In addition, the maximum rate of HTHR dropped significantly as EGR dilution increased; however integration over the complete HTHR curve revealed that cumulative heat release did not change significantly with respect to EGR dilution (signifying combustion efficiencies were sustained). The LTHR spike occurred later as EGR increased, similar to the trend of $\tau_{phys}$ under these conditions.
The AHRR profiles for ULSD, B100, and blends between the two are plotted in Figure 4-32. Increased EGR dilution reduced HTHR rates for each fuel; blends with a greater concentration of ULSD displayed wider and shorter heat release curves. Shibata et al. concluded that HTHR advances due to the concentration of hydrocarbon species as ordered from the greatest to least effect: n-paraffins > iso-paraffins > olefins > naphthenes = aromatics [87]. The ULSD from ExxonMobil was composed of ~30% aromatic content which may have amplified the effect of reduced HTHR. Therefore high concentrations of aromatic content and lack of fuel-derived oxygen maybe both promote a fuel’s sensitivity to increased EGR dilution.

AHRR of B100 at 0% EGR revealed single-stage ignition; although true, both low and high temperature chemistry was observed by the chemiluminescence detection
system. It was possible that the transition between LTHR and HTHR may have occurred more rapidly than could be detected by the pressure transducer. The emergence of two-stage ignition for B100 occurred as EGR rates increased to 25% and greater.
Figure 4-32: Apparent heat release rate profiles for ULSD and B100 blends under varied EGR dilution rates at 600°C
The maximum LTHR rates were calculated for each fuel and plotted against EGR dilution in Figure 4-33. n-Heptane displayed the greatest LTHR values with the effect of EGR dilution appearing to be largely insignificant. In contrast, maximum LTHR values for ULSD/B100 blends decreased more rapidly as EGR dilution increased. Blends with higher concentrations of biodiesel resulted in greater LTHR than for neat ULSD.

![Figure 4-33: Maximum low temperature heat release rates for all fuel types across EGR span at 600°C](image)

Maximum HTHR for all fuels were plotted against EGR dilution in Figure 4-34. n-Heptane again produced the highest HTHR out of the group, with a decreasing trend as EGR increased. At 0% EGR, the maximum HTHR rates (ignoring n-heptane) were ordered greatest to least as ULSD, B20, B40, B60, B80, and then B100. As EGR rates increased to 25% this order reversed completely. Then as EGR reached 55%, the HTHR
values began to converge again. A recent study by Zhang et al. [88] observed that HTHR of diesel was greater than biodiesel at 21% oxygen; however as EGR dilution lowered oxygen concentration below 18%, biodiesel displayed stronger HTHR. Interestingly, the flip in HTHR trends observed in Figure 4-34 may have occurred around 18% ambient oxygen (~14% EGR). The reason for this observed behavior for maximum HTHR dependence on increasing EGR dilution was unknown. Additional testing to investigate the 0-25% dilution range may reveal more conclusive trends.

![Figure 4-34: Maximum high temperature heat release rates for all fuel types across EGR span at 600°C](image)

Figure 4-34: Maximum high temperature heat release rates for all fuel types across EGR span at 600°C
Chapter 5
Conclusions and Future Work

5.1 Conclusions

The increase in demand for cleaner and more energy efficient IC engines has driven combustion researchers to investigate unconventional combustion strategies that utilize lower ambient air temperatures and greater oxygen dilution rates. An optically-accessible constant volume combustion chamber (CVCC) was successfully designed and constructed to investigate ignition behavior under similar operating conditions. The results provided accurate physical and chemical ignition data of select liquid fuels that supported computational modelling efforts at Penn State.

The first recorded attempt to convert a CID 510 instrument to an optical ignition research apparatus was completed with measured success. Due to the tight packaging of the CID, rigid optical probes were selected for spray visualization and chemiluminescence detection. The probes required cooling to protect the glass from heat damage, although the effect of introducing cooled surfaces to the bottom of the chamber was not appreciated until initial ignition tests of n-heptane were unable to reproduce previous experimental results. The shift in ignition delay was attributed to the development of a large cold spot (<400°C) created by the cooled probe assemblies mounted to the bottom of the combustion chamber. Thermal analysis of the chamber via simulation and experiment confirmed that lower wall temperatures in this region retarded ignition.
The effect of ambient air temperature on ignition behavior of n-heptane, ULSD, and B100 concluded with reasonable results. The following conclusions were constructed from observations made during these studies:

1. The cone angle of n-heptane, ULSD, and B100 were largely insensitive to ambient air temperature variations between 540 and 620°C. Liquid lengths of n-heptane appeared shorter during the early stage of quasi-steady behavior, although these measurements proceeded to converge to very similar lengths in the later stages. Additionally, the liquid length fluctuations for each transient spray were insensitive to the ambient air temperature.

2. Fluctuations in liquid length and cone angle are shared through a direct relationship that can be explained by the conservation of momentum. Quasi-steady behavior produced a nearly constant liquid length to cone angle ratio for n-heptane sprays. It was suggested that this would also hold true for ULSD and B100. Additionally, a positive linear trend for this ratio was observed for transient sprays of ULSD and B100. n-Heptane also shared this trend during transient, but at an increased slope.

3. Physical ignition delay ($\tau_{\text{phys}}$) decreased linearly with increasing ambient air temperature on the Arrhenius plot. This was observed for each fuel sample, with B100 accounting for the longest delays. As discussed, the order of ignition delay across fuel types is likely attributed to fuel volatility and viscosity as discussed by Obert [86].
4. Chemical ignition delay ($\tau_{chem}$) decreased with increasing ambient air temperature non-linearly on the Arrhenius plot. At measurements above 580°C $\tau_{chem}$ begins to increase for n-heptane and ULSD, a behavior that was attributed to well-documented NTC tendency [37]. B100 appeared to follow the same trend as 620°C was reached, although tests at higher temperatures are needed to confirm the emergence of NTC behavior.

5. The HTHR for ULSD and B100 were slowed significantly with decreasing temperatures. n-Heptane followed this trend with decreasing temperature to a lesser extent, however its shape of HTHR maintained a sharp peak; a behavior not observed with ULSD and B100.

The effect of oxygen dilution on ignition behavior of n-heptane, ULSD, B100, and ULSD/B100 blends were investigated across 0-55% exhaust gas recirculation (EGR) rates. Oxygen dilution was accomplished by diluting standard air with carbon dioxide and nitrogen to gas compositions that correlated to the different rates of EGR utilized by some IC engines. The following conclusions were made for observed ignition behavior:

1. Liquid length and cone angle were not affected by EGR dilution. Gas density is known to affect these parameters significantly, although the gas density window between 0 and 55% EGR was not large enough to observe any significant trends.

2. The observed linear increase in physical ignition delay with EGR dilution was proposed to be a function of heat capacity as it increased linearly with EGR dilution. Additionally, higher heat capacities may slow temperature rise rates therefore delaying the onset of first-stage ignition.
3. The chemical ignition delay period for B100 and n-heptane displayed similar tolerance to EGR dilution. ULSD was much more sensitive to decreased ambient oxygen content than what was observed with B100. Although this is commonly attributed to fuel-derived oxygen effects, fuel structure effects (i.e., aromatic rings) were suggested to increase sensitivity to ambient oxygen content to a greater extent as these are known to control HTHR strongly.

4. ULSD displayed very “lazy” HTHR profiles at higher rates of EGR dilution than what was seen by B100. n-Heptane maintained a “sharp” HTHR profile throughout the complete EGR test range. This was likely connected to the higher reactivity of long chain paraffins, known to increase HTHR rates.
5.2 Future Work

Future investigations into liquid length behavior of heavier fuels (i.e., ULSD and B100) with the current experimental setup will require modification to the spray visualization system. Addition of a larger window for the AVL Aquashift tip may allow for the larger viewing angle by the borescope, which might alleviate the current liquid length measurement limitation of the system.

An investigation into the effects of molecular structure on ignition sensitivity to EGR dilution with comparison of varying fuel-derived oxygen content might explain the underlying reasons for the benefit of B100’s tolerance to high EGR rates. Additionally, the ignition apparatus developed in this work provides great potential for investigations over a large range of liquid fuel types (i.e., gasoline, diesel, and oxygenated species). Investigations that focus on chemical structure effects to EGR dilution may help guide fuel formulation development for the next generation of IC engines.
References


38. Mittal, G. and C.-J. Sung*, *A RAPID COMPRESSION MACHINE FOR CHEMICAL KINETICS STUDIES AT ELEVATED PressURES AND


Appendix A

Error Analysis

A.1 Experimental Uncertainties

Each test condition for the ignition studies was repeated 15 times per fuel sample. As discussed by Moffat [89], sample sizes less than 30 can benefit from statistical corrections as to avoid overinflated error values; therefore the student t-test was used to calculate the conference interval with 95% confidence (discussed in A.2 ).

Outliers were removed from data sets by using the reduced Thompson tau test (discussed in A.3 ). This test was necessary for the collected ignition data because occasionally a sample pressure trace would exhibit very uncharacteristic behavior, possibly due to fuel management errors. Removal of such data was done prior to calculations of confidence intervals to avoid possible misrepresentation of behavior.

A.2 Student T-Test

The student t-test was used to calculate the 95% confidence interval (CI) for sample sizes less than 30, as described in Equation A-1. The t-test was used for these smaller sample sizes to create a bell-shaped distribution that was based off of the degrees of freedom. The confidence interval as a result was more representative of the population, and therefore reduced the occurrence of reported value with overinflated errors.
\[ CI = \bar{x} \pm t_{\alpha/2,n-1} \frac{s}{\sqrt{n}} \] 

\[ \bar{x} = \text{sample mean} \]
\[ t_{\alpha/2,n-1} = \text{student t-test multiplier} \]
\[ s = \text{standard error} \]
\[ n = \text{sample size} \]

### A.3 Test for Outliers

The “modified Thompson Tau Technique” was used to test data sets for possible outliers. The statistical method determined if a suspected outlier in a sample of a single variable should be discarded or not [90]. Given each test condition was repeated 15 times, the modified Thompson \( \tau \) value was calculated to be 1.8579 as shown in Equation A-2. The absolute value of the deviation was calculated for each value according to Equation A-3. Additionally the sample standard deviation (S) was calculated.

\[ \tau = \frac{t_{\alpha/2}(n-1)}{\sqrt{n} \sqrt{n-2 + t_{\alpha/2}^2}} \]  

\( n = \text{number of data points} \)
\( t_{\alpha/2} = \text{critical students t value (} \alpha = 0.05 \text{ and df = n-2)} \)

\[ \delta_i = |x_i - \bar{x}| \]
The test to determine if an outlier was discarded or not was as follows: If $\delta_i > \tau S$, then reject the data point because it is an outlier. If $\delta_i \leq \tau S$, then keep the data point because it is not an outlier.
Appendix B

Additional Results

B.1 Ignition Data – Ambient Temperature Span

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### B.2 Ignition Data – EGR Dilution Span

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B.3 Camera Settings and Calibration

Figure B-1: Camera capture settings in PCC v2.3 program
Figure B-2: Reference image used to determine pixel to mm ratio