

Investigation of the autoignition behavior of liquid hydrocarbon fuels using diagnostic absorption measurement techniques

Overview: The study of the in-engine combustion behavior of liquid hydrocarbon fuels involves many complex and distinctive processes including fuel injection, jet break up and atomization, ignition, and flame propagation. To improve upon the performance of existing engines, develop more advanced engine technologies, and increase the safety of fuel transport and storage devices, an improvement in the fundamental understanding of each of these phenomena is critical. This proposal focuses on the ignition process, primarily in the low temperature autoignition regime which is of interest for advanced engines and hazard mitigation in fuel transport and storage. It is in this regard that this proposal connects directly to the propulsion and energetics section of the Army Research Office's BAA (W911NF-17-S-0002-03). A key component of this study lies also in the development of simplified fuels, called surrogates, which can be made to mimic certain behaviors of real fuels in order to simplify their study. I will propose utilizing this tool along with a novel experimental approach employing controllable heating rates along with absorption spectroscopy of the C-H bond to temporally resolve species concentrations during the ignition process which will thereby enable a better fundamental understanding of hydrocarbon ignition.

Background (Ignition): Although ignition has been heavily studied in the past, the fundamental low temperature chemical kinetic processes leading to autoignition are still poorly understood at both high and low pressures. This gap in the literature is significant as low temperature autoignition is critical both to the understanding of combustion in advanced engines and to the design safety and certification of fuel storage and transport technologies. The phenomenon known as autoignition occurs when a substance spontaneously ignites in the absence of an external ignition source like a flame or spark. This occurs in many existing applications of interest including diesel engines and the steady state operation of jet engine combustion chambers. The lowest temperature at which autoignition occurs in a normal atmosphere is called the autoignition temperature (AIT) of that fuel and it is defined by an empirical test developed in the 1950s, referred to as the ASTM-E659 [1]. However, this testing approach is not quite up to present day standards of scientific rigor as many important variables that are known to play critical roles in ignition behavior such as heating rate, pressure, mixture composition, and chamber volume are not well controlled or arbitrarily defined. As a result, the AIT derived from this test is inherently irrelevant to the actual autoignition behavior of a substance in practical situations.

More recent studies of autoignition behavior of real fuels have been conducted using heated shock tubes and rapid compression machines (RCMs) to observe ignition delay times but not minimum AIT. These ignition studies have mainly been conducted in the high pressure regime across a range of temperatures ($P = 8\text{-}51$ atm, $T = 651\text{-}1381$ K) with a few notable exceptions [2-6]. Tang et al. studied ignition at low pressure and high temperature ($P = 2\text{-}4$ atm, $T = 1100\text{-}1500$ K) and Valco et al. studied ignition at high pressure and low temperature ($T = 625\text{-}735$ K at $P = 20$ atm) [7, 8]. The regime of low temperature and low pressure ignition however has largely been overlooked in the literature. Moreover, these recent studies in the high pressure regime do not provide any data relevant to the minimum AIT of the studied fuels at elevated pressures as the temperature ranges studied were far too high to observe the critical temperature regime between ignition and non-ignition (for reference, at 1 atm, the AIT of jet fuel is 505 K and the AIT of diesel fuel is 529 K as determined by the E659 test). Additionally, the minimum AIT has been shown to decrease with increasing pressure which means far lower temperatures than those studied previously must be achieved in order to observe the transition between ignition and non-ignition [9].

An additional consideration that has been ignored since the standardization of the ASTM E659 test is the effect of heating rate on autoignition behavior. Many methods used in the study of AIT prior to this

standardization employed a so called “rising temperature” approach to ignition temperature determination where the surroundings would be heated at a controlled rate rather than being held at a constant temperature. However, these were done away with in favor of the constant temperature method of the E659 mainly due to the early complications in accurately controlling heating rate. This selection was justified by the misguided desire to ignore low temperature reactions of liquid fuels which occur in practice but result in differences in the measured AIT as compared to the constant temperature approach due to the production of some relatively stable compounds [10]. The methods of heated shock tubes and RCMs are also unable to control fuel heating rate as they are both relatively rapid compression processes. More recent studies from our group do indeed show that varying heating rate can change the characteristics of ignition reactions so it is not realistic to ignore heating rate in the study of ignition behavior [11,12]. To address both the heating rate issue and the lack of low temperature experimental work, a new test method for the determination of minimum AIT at a variety of pressures and heating rates will be developed. The accurate measurement of physically relevant AIT that will be achieved with this method is crucial both for fundamental understanding and for designing accurate operational envelopes for future applications including advanced engines. To further aid this effort, suitably simple but representative fuels, called surrogates, will be developed to facilitate experimental repeatability and the development of efficient numerical models to compare with experimental results.

Background (Surrogate Fuels): Any real fuel is difficult to study since they typically consist of hundreds of different hydrocarbons in varying quantities even between different batches of the same fuel. This complexity makes it difficult both to accurately reproduce experimental results across distinct fuel batches and to model the reaction mechanisms that take place during ignition. As an alternative, suitably representative mixtures of hydrocarbons, called surrogates, can be developed to mimic a few isolated real fuel characteristics like ignition delay time, cetane number and distillation curves while consisting of only a handful of species in well controlled concentrations [13-15]. This makes surrogates much more amenable to experimental reproducibility as well as numerical modeling because the species and reaction pathways to consider are both far fewer in number and typically much better known than those of real fuel components. Several surrogate fuels have been developed in the past to mimic real fuel ignition behavior at high pressures and a range of temperatures similar to the real fuel studies previously mentioned ($P = 8.5\text{-}20$ atm and $T = 645\text{-}1750$ K) [15-17]. However fewer studies have been in the low temperature regime which is characteristic of autoignition even at elevated pressures. It is therefore unknown if previously developed surrogates for the study of ignition have any relevance to real fuel studies at these conditions. The methodology of surrogate component selection developed in the literature may however still prove relevant and will be used in the proposed work to develop surrogate fuels which match real fuel ignition behavior at low temperatures. This procedure involves reducing the real fuel to its major functional groups (alkanes, cycloalkanes, arenes, etc.) and using 1-2 species to represent the averaged properties of the hundreds of species actually present within each group [13-15]. Using the ASTM E659 test procedure as a first step in this surrogate study will be crucial to qualitatively compare ignition characteristics of existing surrogates from the literature with real fuel samples and determine necessary composition modifications needed to provide better representation of the real fuel in the vicinity of the AIT. Once this is accomplished, a more controlled testing environment will be needed to provide quantitative verification of the surrogate behaviors under different pressures, mixture compositions and heating rates.

Methodology: An experimental vessel will be developed to facilitate the use of absorption spectroscopy techniques which can measure the vapor phase composition of liquid fuel samples throughout a controlled heating process and autoignition. This will allow the levels of certain chemical species of interest to be quantified and temporally resolved throughout the process. This approach can be used along with temperature and pressure measurements to paint a clear picture of the low temperature chemical processes

leading to auto ignition which are taking place within the vessel. A previous study from our group utilized UV absorption, Fourier Transform Infrared (FTIR) spectrometry, scanned wavelength modulation spectroscopy (WMS) and infrared laser absorption spectroscopy at 3.39 μm to temporally track the concentrations of several important species of single component fuels undergoing chemical reactions near the AIT [18,19]. Eventually each of these methods will be incorporated into the proposed study but for now the use of a 3.39 μm He-Ne laser to track the

concentration of C-H bonds present in the fuel is all that will be considered and discussed. The C-H bonds in a variety of hydrocarbons have been shown to readily absorb at 3.39 μm which provides a powerful tool in measuring the time evolution of the composition of a reactive mixture [19]. A schematic of the proposed setup is shown in Figure 1 which illustrates a 3.39 μm He-Ne laser being split into two beams, one of which travels through a heated test cell containing the fuel-air mixture and the other which is the reference beam. The signal detector measures the intensity of light that has passed through the test cell without being absorbed. The measured intensities can be related to quantities of interest via the Beer-Lambert law

$$I = I_0 e^{-LC_f\sigma_v} \quad (1)$$

where I and I_0 are the test and reference intensities respectively, L is the length of the test cell, C_f is the fuel concentration, and σ_v is the absorption cross section. Using this formula and a known concentration, the absorption cross section for a given species can be determined which can then be used in determining the fuel concentration in an unknown mixture based on the measured intensities. This procedure was used in our group to determine a convenient empirical relation for the absorption cross section given a fuel's chemical structure but this relation and the procedure itself have not yet been extended to the study of multicomponent fuels [19].

In order to make this method viable for the study of real fuels and surrogates, the extension of this method to multicomponent fuel mixtures must first be verified. As the light at this wavelength is highly susceptible to absorption by C-H bonds in a mixture, it is expected that a similar approach can be used to monitor the bulk fuel concentration via the C-H bond concentration during the reaction and that a similar empirical relation for evaluating the cross section of a known multicomponent mixture given the single component chemical structures can be developed. The test cell shown in Figure 1 will consist of two concentric cylindrical shells with the outer shell acting as an insulator and the inner shell being connected to a power supply with variable amperage to control the rate of heating via conduction. Using this method, we hope to control the heating rate across a wide range (10-1000 K/s). Sapphire windows on either side of the test cell allow for optical access through the heated cavity where a premixed blend of fuel and oxidizer is added after the cell is evacuated via a pump. This mixture will be prepared in a separate heated container to ensure complete evaporation of the liquid sample prior to injection into the test cell so as to simplify the problem to one of studying only the ignition process rather than the more complicated process of ignition in combination with injection, atomization, and evaporation. The concentration will be controlled via the method of partial pressures and thermocouples will be used to monitor temperature inside the vessel. Results will show the fuel concentration as a function of time which will allow for the tracking of low temperature reaction progression and determination of ignition delay times and minimum AIT at a controlled pressure. The results of this study will validate the novel approach to the study of ignition behavior and enable a better understanding of the fundamental physical and chemical processes leading to ignition in the low temperature regime.

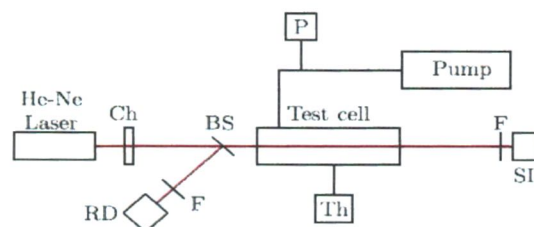


Figure 1: Schematic of proposed test setup with Ch: Chopper, BS: Beam Splitter, F: Bandpass filter (3.39 μm), RD: Reference detector, SD: Signal Detector, Th: Thermocouple, P: Pressure Transducer (adapted from [19])

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Answer the following: What are your short and long-term professional goals? How did these goals develop? How have you already begun to lay the foundation for these goals? How does this fellowship fit into these goals? (500 Words)

The study of combustion has been an interest of mine long before I knew it could be studied as a science. A fascination with rockets, jets, car engines and anything that burned really has been ever-present throughout my life and was further reinforced whenever I heard stories about my grandfather's work as an engineer on the Nike missile program during the cold war. The overwhelming appeal of these marvels of human creation did not waiver through undergrad or into graduate school and now that I have begun seriously considering my goals for the rest of my PhD in Aerospace Engineering and beyond, I am more certain than ever that this is the profession I am meant to be in. In the short term I hope to complete my PhD within the next 3-4 years while cultivating an expertise in fluid and thermal sciences in addition to advanced optical diagnostic techniques. With this experience gained I would hope to continue researching combustion science upon graduation but on a more applied level. Therefore, in the long term I would hope to work for a national research laboratory like Sandia or in the R&D department of a major U.S. aerospace company on advanced propulsion technologies like Scramjets.

These goals have developed mostly since I began to study engineering in undergrad. There I came to realize how deeply the body of knowledge on the subject of combustion has grown while at the same time beginning to understand the areas like supersonic combustion, flame stability, and ignition where progress has been slow. It is my goal to make contributions in these areas which represent not only improvements to fundamental understanding of chemistry and fluid mechanics, but also the advancement in the safety, speed, and efficiency of industrial processes, energy generation, and transportation which are each critical to the support and prosperity of our national interests and defense forces.

When I joined my first research project as an undergrad under Dr. Yoo in the Micro and Mesoscale Combustion Laboratory, I began developing the foundation necessary to tackle these difficult problems by reading extensively into combustion literature in search of a topic for my new project. As I progressed through this and other projects, I designed and refined novel experimental devices for studying small scale flames and probing in-engine combustion processes while applying for and receiving several research grants to fund my work. In graduate school, I have continued to strengthen this foundation through advanced coursework and new experiences working with advanced optical techniques like interferometry and spectrometry. This includes building my own UV spectrometer from scratch because as my advisor, Dr. Shepherd, likes to say; "Why buy what you can build yourself?". Progress towards my goals will be rapid with this spirit of learning by doing and with the NDSEG fellowship providing me the intellectual freedom to focus on the pursuit of my own research ideas as well as providing an excellent stepping stone to a career supporting our nation through the aerospace industry.

I intend to pursue a career in organic chemistry research by synthesizing useful and interesting molecules and improving the methods by which organic synthesis is carried out. My decision to pursue intensive study of organic chemistry stems from a fascination with the subject which developed over the course of my undergraduate career. I thoroughly enjoy the way that organic chemistry encourages me to think - solving puzzles, investigating patterns, and gaining fluency in the language of chemical structure and bonding. This led me to pursue opportunities to conduct undergraduate research.

My first research experience was a 10-week summer research fellowship at my home institution following my sophomore year. Under the direction of Dr. Allan Nishimura, I investigated the ability of small organic molecules to percolate through an amorphous layer of naphthalene and induce a disorder-to-order transition. This project familiarized me with the process of conducting original research. Designing experiments, troubleshooting problems, and communicating results in presentations and publications were all integral components of my project.

I remained passionate about organic chemistry, prompting me to join Dr. Amanda Silberstein in the fall of 2015. My work with Dr. Silberstein focused on synthetic methodology development, where we investigated a method for synthesizing boronic esters via nickel catalysis. As one of Dr. Silberstein's first research students, I was involved in designing the project from the ground up by synthesizing substrates of interest and choosing initial reaction conditions. As the project moved into the optimization phase, I took on a leadership role in the group. I perused relevant literature and discussed potential new experiments with Dr. Silberstein at the beginning of each week. She helped to refine my ideas, and together we distributed the week's experiments among the four student researchers. Our efforts were ultimately successful: I spearheaded a series of experiments that improved reaction yield from 0-5% to 70-95%. This project culminated in my Major Honors Thesis, which I defended before a committee, and the results were exhibited as a poster presentation at the Spring 2017 ACS Conference.

In addition to my work with Dr. Nishimura and Dr. Silberstein at Westmont College, I also conducted research at the University of California, Los Angeles as part of the Amgen Scholars Program. I worked with Dr. Neil Garg to probe the scope of a nickel-catalyzed Suzuki-Miyaura coupling of aliphatic amides, part of a series of reactions developed in the Garg group to increase the utility of amides in organic synthesis. This experience reaffirmed that graduate study in organic chemistry was an endeavor I wanted to pursue. I enjoyed interacting with graduate students, discussing chemistry at a high level, and working on high-impact projects.

My love of chemical research is not merely a product of academic interest; I am also drawn to research as a means for effecting positive change in the world. By working in the chemical industry, I can play a role in addressing the underlying problems that make life more difficult for those at the bottom of the pyramid, such as climate change, food waste, and preventable illness. I had the opportunity to experience this kind of work during a six-month postgraduate internship at Apeel Sciences, a Santa Barbara based startup that aims to extend the shelf life of produce by applying thin, plant-based barriers to its surface. During my time at Apeel I worked with the Process Development team to develop methods for the selective monofunctionalization of glycerol at either the 1 or the 2 position. I designed my own experiments and presented my results to a group of chemists and materials scientists weekly. I ultimately left my position at Apeel to pursue my graduate studies, but I exited with an appreciation for the challenges of industrial research, which will inform my research in graduate school.

I have begun to lay the foundation for my goal of a career in synthetic organic chemistry by enrolling in Caltech's Ph.D. program under the advisement of Dr. Sarah Reisman. Graduate school in organic chemistry will prepare me for a career in chemistry by honing my ability to design scientific experiments and conduct independent research. This fellowship would help fund my graduate studies, allowing me to focus on conducting research and furthering my training. After obtaining a Ph.D. in organic chemistry, I intend to undertake postdoctoral work in organic chemistry or a related field, such as drug discovery or materials science. I will then seek a career as an industrial research scientist or professor, where I can direct my knowledge of the subject I love toward finding solutions to the issues I care deeply about. I have come to understand that chemical research is a powerful way to effect positive change in the world, and I look forward to supporting our nation through a career in organic chemistry.

Objective:

Nitrogen-containing organic compounds are ubiquitous among biologically active molecules such as fertilizers, pesticides, and pharmaceuticals.¹ As a result, efficient strategies for C–N bond formation are required to construct these valuable chemical tools. The development of carboamination reactions is an area of growing focus in synthetic organic chemistry, and this proposal delineates a novel strategy for olefin carboamination.

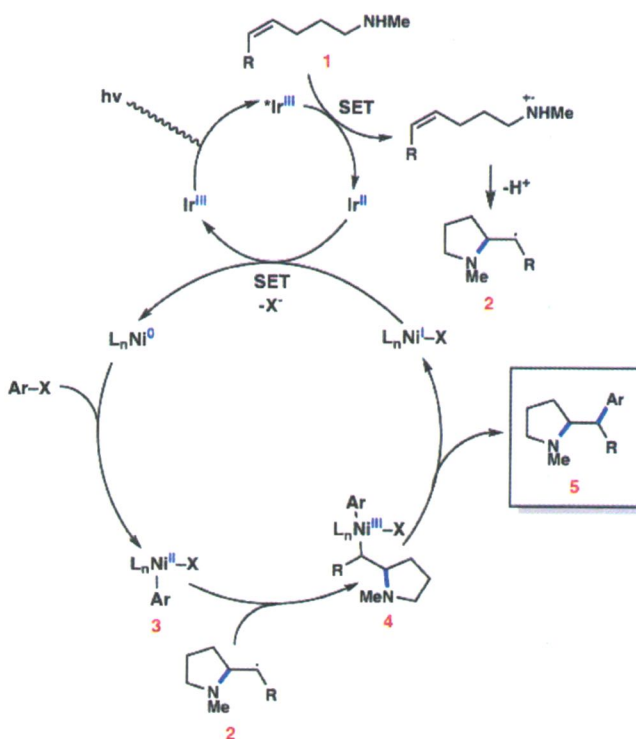
Introduction:

Despite the prevalence of C–N bonds in molecular targets, methods for their construction remain somewhat elusive. Known amination methods include alkylation, reductive amination, and transition metal-catalyzed cross-coupling.¹ These methods are effective, but can require the use of harsh or toxic reagents. An exciting alternative to canonical C–N bond formation is the direct difunctionalization of olefins, which are readily available feedstocks for chemical synthesis.² However, the addition of simple amines across an olefin is typically thermodynamically unfavorable and therefore difficult to achieve.¹ Nevertheless, some recent advances in olefin carboamination methodology have been made using both palladium catalysis³ and photoredox catalysis.⁴

Research Plan:

I propose an intramolecular carboamination of simple olefins by a tandem radical cyclization/nickel-catalyzed cross-coupling strategy (Figure 1). In the proposed transformation, a nitrogen-centered radical cation would be generated by irradiation of a secondary amine (1) in the presence of a photoexcited catalyst such as an $[*Ir^{III}]$ complex.⁴ This highly reactive radical would cyclize onto a pendant olefin, thereby generating a more stable carbon-centered radical. Knowles et al. recently reported a formal hydroamination of

Figure 1. Catalytic cycle of proposed carboamination.



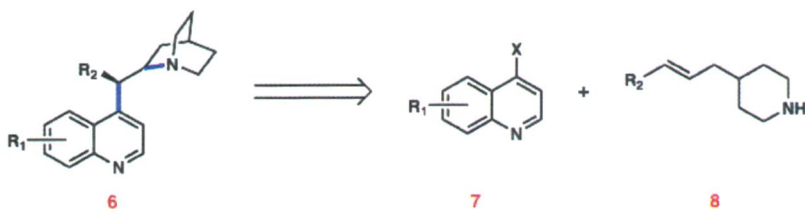
olefins using this strategy, in which cyclization was followed by hydrogen atom transfer to the newly formed carbon radical.⁴

In order to achieve a carboamination reaction, the carbon-centered radical **2** could be intercepted by a transition metal catalyst, such as iron, copper, or nickel. These metals are known to interact with such radicals in cross-coupling reactions.⁵ For example, a $L_nNi^{II}(Ar)X$ complex (**3**), generated by oxidative addition of an aryl or vinyl halide to a Ni^0 complex, could engage with the carbon-centered radical to yield a $L_nNi^{III}(Ar)X$ species (**4**). This high-energy species would undergo facile reductive elimination to give the desired carboamination product (**5**), as well as a L_nNi^IX species. Finally, single electron transfer from the reduced photocatalyst to Ni^I would close both catalytic cycles, regenerating both Ni^0 as well as Ir^{III} .⁵ The proposed method would represent a simple, modular way to generate complex nitrogen-containing molecules from readily available olefins via transition metal catalysis and photocatalysis.

The development of this carboamination reaction will require significant screening of photocatalysts, transition metal catalysts, ligands, and substrates to identify optimal reaction conditions. As a current graduate student at Caltech, I have access to the Caltech Center for Catalysis and Chemical Synthesis, a high throughput screening facility. My background in the discovery and development of nickel-catalyzed cross-coupling reactions, from my undergraduate research at Westmont College as well as my REU at UCLA, will also serve me well as I undertake this project. In addition, this research project should not require any unique resources outside of those generally found in a synthetic chemistry lab; readily available blue LEDs are typically sufficient to activate iridium photocatalysts.

Future work in the area could include the extension of this method to fully intermolecular systems and the development of a stereoselective carboamination. The latter could be accomplished with the use of a chiral ligand on the nickel catalyst. Additionally, the proposed carboamination could be applied toward the total synthesis of natural products, drug molecules, or chiral building blocks. One class of molecules accessible through this transformation is the

Figure 2. Retrosynthesis analysis of cinchona-like molecules.



cinchona alkaloids (Figure 2). These natural products, best known for the potent antimalarial quinine, are privileged catalysts for a variety of asymmetric reactions.⁶ Using the

proposed carboamination, a cinchona-like molecule (**6**) can be disconnected to two much simpler coupling partners: a haloquinoline (**7**) and a piperidine with a pendant olefin (**8**). Following formation of an N-centered radical, the piperidine fragment could cyclize then couple with the haloquinoline fragment to deliver the structural core of the molecule. This strategy provides a

modular route to the cinchona alkaloids, enabling divergent synthesis to form new chiral catalysts.

Broader Impacts:

The proposed carboamination would expand the scope of possible C–N bond formations to streamline access to a wider variety of biologically active natural products. C–N bonds are common in the chemical industry; 84% of small-molecule drugs contain at least one C–N bond, and synthesis of alkyl amines currently accounts for over 10% of reactions performed in industrial medicinal chemistry departments.¹ Improvements in C–N bond construction methodology could therefore facilitate the discovery of new drugs, fertilizers, and other materials of societal interest. Furthermore, novel carboamination methodology could be used to shorten routes to existing synthetic targets, such as quinine or other cinchona alkaloids, reducing the amount of energy required for and waste generated by those syntheses. This would lessen both the cost as well as the environmental impact of synthesizing such products. Green chemistry is of growing significance as the demand for synthetic products increases, making the discovery of novel chemical transformations of the utmost importance.

Developing synthetic chemistry methodology is particularly relevant to the interests of the Department of Defense due to the multitude of potential applications of small organic molecules. The discovery and production of new drugs and vaccines will equip the military to cope with the injury and illness associated with war. Small molecule monomers can be combined to produce new materials, including durable polymers like Kevlar as well as potentially self-healing materials. Organic molecules also have applications in agriculture, an industry intimately connected to national security and vitality. Ultimately, organic synthesis is an enabling technology which has the potential to facilitate scientific advancement in numerous fields of relevance to the Department of Defense.

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Overview: The study of the in-engine combustion behavior of liquid hydrocarbon fuels involves many complex and distinctive processes including fuel injection, jet break up and atomization, ignition, and flame propagation. To improve upon the performance of existing engines, develop more advanced engine technologies, and increase the safety of fuel transport and storage devices, an improvement in the fundamental understanding of each of these phenomena is critical. This proposal focuses on the ignition process, primarily in the low temperature autoignition regime which is of interest for advanced engines and hazard mitigation in fuel transport and storage. It is in this regard that this proposal connects directly to the propulsion and energetics section of the Army Research Office's BAA (W911NF-17-S-0002-03). A key component of this study lies also in the development of simplified fuels, called surrogates, which can be made to mimic certain behaviors of real fuels in order to simplify their study. I will propose utilizing this tool along with a novel experimental approach employing controllable heating rates along with absorption spectroscopy of the C-H bond to temporally resolve species concentrations during the ignition process which will thereby enable a better fundamental understanding of hydrocarbon ignition.

Background (Ignition): Although ignition has been heavily studied in the past, the fundamental low temperature chemical kinetic processes leading to autoignition are still poorly understood at both high and low pressures. This gap in the literature is significant as low temperature autoignition is critical both to the understanding of combustion in advanced engines and to the design safety and certification of fuel storage and transport technologies. The phenomenon known as autoignition occurs when a substance spontaneously ignites in the absence of an external ignition source like a flame or spark. This occurs in many existing applications of interest including diesel engines and the steady state operation of jet engine combustion chambers. The lowest temperature at which autoignition occurs in a normal atmosphere is called the autoignition temperature (AIT) of that fuel and it is defined by an empirical test developed in the 1950s, referred to as the ASTM-E659 [1]. However, this testing approach is not quite up to present day standards of scientific rigor as many important variables that are known to play critical roles in ignition behavior such as heating rate, pressure, mixture composition, and chamber volume are not well controlled or arbitrarily defined. As a result, the AIT derived from this test is inherently irrelevant to the actual autoignition behavior of a substance in practical situations.

More recent studies of autoignition behavior of real fuels have been conducted using heated shock tubes and rapid compression machines (RCMs) to observe ignition delay times but not minimum AIT. These ignition studies have mainly been conducted in the high pressure regime across a range of temperatures ($P = 8\text{-}51$ atm, $T = 651\text{-}1381$ K) with a few notable exceptions [2-6]. Tang et al. studied ignition at low pressure and high temperature ($P = 2\text{-}4$ atm, $T = 1100\text{-}1500$ K) and Valco et al. studied ignition at high pressure and low temperature ($T = 625\text{-}735$ K at $P = 20$ atm) [7, 8]. The regime of low temperature and low pressure ignition however has largely been overlooked in the literature. Moreover, these recent studies in the high pressure regime do not provide any data relevant to the minimum AIT of the studied fuels at elevated pressures as the temperature ranges studied were far too high to observe the critical temperature regime between ignition and non-ignition (for reference, at 1 atm, the AIT of jet fuel is 505 K and the AIT of diesel fuel is 529 K as determined by the E659 test). Additionally, the minimum AIT has been shown to decrease with increasing pressure which means far lower temperatures than those studied previously must be achieved in order to observe the transition between ignition and non-ignition [9].

An additional consideration that has been ignored since the standardization of the ASTM E659 test is the effect of heating rate on autoignition behavior. Many methods used in the study of AIT prior to this

standardization employed a so called “rising temperature” approach to ignition temperature determination where the surroundings would be heated at a controlled rate rather than being held at a constant temperature. However, these were done away with in favor of the constant temperature method of the E659 mainly due to the early complications in accurately controlling heating rate. This selection was justified by the misguided desire to ignore low temperature reactions of liquid fuels which occur in practice but result in differences in the measured AIT as compared to the constant temperature approach due to the production of some relatively stable compounds [10]. The methods of heated shock tubes and RCMs are also unable to control fuel heating rate as they are both relatively rapid compression processes. More recent studies from our group do indeed show that varying heating rate can change the characteristics of ignition reactions so it is not realistic to ignore heating rate in the study of ignition behavior [11,12]. To address both the heating rate issue and the lack of low temperature experimental work, a new test method for the determination of minimum AIT at a variety of pressures and heating rates will be developed. The accurate measurement of physically relevant AIT that will be achieved with this method is crucial both for fundamental understanding and for designing accurate operational envelopes for future applications including advanced engines. To further aid this effort, suitably simple but representative fuels, called surrogates, will be developed to facilitate experimental repeatability and the development of efficient numerical models to compare with experimental results.

Background (Surrogate Fuels): Any real fuel is difficult to study since they typically consist of hundreds of different hydrocarbons in varying quantities even between different batches of the same fuel. This complexity makes it difficult both to accurately reproduce experimental results across distinct fuel batches and to model the reaction mechanisms that take place during ignition. As an alternative, suitably representative mixtures of hydrocarbons, called surrogates, can be developed to mimic a few isolated real fuel characteristics like ignition delay time, cetane number and distillation curves while consisting of only a handful of species in well controlled concentrations [13-15]. This makes surrogates much more amenable to experimental reproducibility as well as numerical modeling because the species and reaction pathways to consider are both far fewer in number and typically much better known than those of real fuel components. Several surrogate fuels have been developed in the past to mimic real fuel ignition behavior at high pressures and a range of temperatures similar to the real fuel studies previously mentioned ($P = 8.5\text{-}20$ atm and $T = 645\text{-}1750$ K) [15-17]. However fewer studies have been in the low temperature regime which is characteristic of autoignition even at elevated pressures. It is therefore unknown if previously developed surrogates for the study of ignition have any relevance to real fuel studies at these conditions. The methodology of surrogate component selection developed in the literature may however still prove relevant and will be used in the proposed work to develop surrogate fuels which match real fuel ignition behavior at low temperatures. This procedure involves reducing the real fuel to its major functional groups (alkanes, cycloalkanes, arenes, etc.) and using 1-2 species to represent the averaged properties of the hundreds of species actually present within each group [13-15]. Using the ASTM E659 test procedure as a first step in this surrogate study will be crucial to qualitatively compare ignition characteristics of existing surrogates from the literature with real fuel samples and determine necessary composition modifications needed to provide better representation of the real fuel in the vicinity of the AIT. Once this is accomplished, a more controlled testing environment will be needed to provide quantitative verification of the surrogate behaviors under different pressures, mixture compositions and heating rates.

Methodology: An experimental vessel will be developed to facilitate the use of absorption spectroscopy techniques which can measure the vapor phase composition of liquid fuel samples throughout a controlled heating process and autoignition. This will allow the levels of certain chemical species of interest to be quantified and temporally resolved throughout the process. This approach can be used along with temperature and pressure measurements to paint a clear picture of the low temperature chemical processes

leading to auto ignition which are taking place within the vessel. A previous study from our group utilized UV absorption, Fourier Transform Infrared (FTIR) spectrometry, scanned wavelength modulation spectroscopy (WMS) and infrared laser absorption spectroscopy at 3.39 μm to temporally track the concentrations of several important species of single component fuels undergoing chemical reactions near the AIT [18,19]. Eventually each of these methods will be incorporated into the proposed study but for now the use of a 3.39 μm He-Ne laser to track the

concentration of C-H bonds present in the fuel is all that will be considered and discussed. The C-H bonds in a variety of hydrocarbons have been shown to readily absorb at 3.39 μm which provides a powerful tool in measuring the time evolution of the composition of a reactive mixture [19]. A schematic of the proposed setup is shown in Figure 1 which illustrates a 3.39 μm He-Ne laser being split into two beams, one of which travels through a heated test cell containing the fuel-air mixture and the other which is the reference beam. The signal detector measures the intensity of light that has passed through the test cell without being absorbed. The measured intensities can be related to quantities of interest via the Beer-Lambert law

$$I = I_0 e^{-LC_f \sigma_v} \quad (1)$$

where I and I_0 are the test and reference intensities respectively, L is the length of the test cell, C_f is the fuel concentration, and σ_v is the absorption cross section. Using this formula and a known concentration, the absorption cross section for a given species can be determined which can then be used in determining the fuel concentration in an unknown mixture based on the measured intensities. This procedure was used in our group to determine a convenient empirical relation for the absorption cross section given a fuel's chemical structure but this relation and the procedure itself have not yet been extended to the study of multicomponent fuels [19].

In order to make this method viable for the study of real fuels and surrogates, the extension of this method to multicomponent fuel mixtures must first be verified. As the light at this wavelength is highly susceptible to absorption by C-H bonds in a mixture, it is expected that a similar approach can be used to monitor the bulk fuel concentration via the C-H bond concentration during the reaction and that a similar empirical relation for evaluating the cross section of a known multicomponent mixture given the single component chemical structures can be developed. The test cell shown in Figure 1 will consist of two concentric cylindrical shells with the outer shell acting as an insulator and the inner shell being connected to a power supply with variable amperage to control the rate of heating via conduction. Using this method, we hope to control the heating rate across a wide range (10-1000 K/s). Sapphire windows on either side of the test cell allow for optical access through the heated cavity where a premixed blend of fuel and oxidizer is added after the cell is evacuated via a pump. This mixture will be prepared in a separate heated container to ensure complete evaporation of the liquid sample prior to injection into the test cell so as to simplify the problem to one of studying only the ignition process rather than the more complicated process of ignition in combination with injection, atomization, and evaporation. The concentration will be controlled via the method of partial pressures and thermocouples will be used to monitor temperature inside the vessel. Results will show the fuel concentration as a function of time which will allow for the tracking of low temperature reaction progression and determination of ignition delay times and minimum AIT at a controlled pressure. The results of this study will validate the novel approach to the study of ignition behavior and enable a better understanding of the fundamental physical and chemical processes leading to ignition in the low temperature regime.

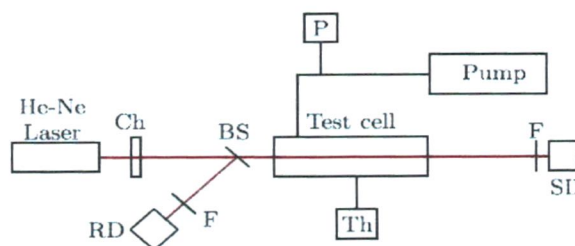


Figure 1: Schematic of proposed test setup with Ch: Chopper, BS: Beam Splitter, F: Bandpass filter (3.39 μm), RD: Reference detector, SD: Signal Detector, Th: Thermocouple, P: Pressure Transducer (adapted from [19])

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