

Ignition Studies of Diisopropyl Ketone, A Second-Generation Biofuel

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IGNITION STUDIES OF DIISOPROPYL KETONE,
A SECOND-GENERATION BIOFUEL

by

OWEN M. PRYOR

A thesis submitted in partial fulfillment of the requirements
for the Honors in the Majors Program in Aerospace Engineering
in the College of Engineering and Computer Science
and in The Burnett Honors College
at the University of Central Florida
Orlando, FL

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Thesis Chair: Dr. Subith S. Vasu

Abstract

This thesis focuses on ignition of diisopropyl ketone (DIPK), a new biofuel candidate that is produced by endophytic conversion. The ignition delay times behind reflected shockwaves were modeled in a high-pressure shock tube. The ignition delay times were compared to other biofuels and gasoline surrogates. Parametric studies of the ignition delay experiments were performed between 1-10 atm and 900 -1200K. An OH optical sensor was developed in conjunction for the ignition delay experiments. The OH optical sensor uses a microwave discharge lamp to generate light at 308 nm that will then be shined through the combustion reaction. Using Beer-Lambert law the concentration of OH can be obtained during ignition and oxidation of hydrocarbon fuels in a shock tube. DIPK ignition delay time experiments are planned in two shock tubes (located at UCF and UF) to provide ignition and OH time-histories data for model validation.

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Chapter 1: Introduction and Background

Ideally, an engine is designed to produce the greatest amount of energy for the lowest cost and minimal environmental effects. Research into the improvement of engines is focused on several interconnected areas. These areas include engine prototypes, fuel combustion and exhaust emissions. The development of detailed models is highly important for the improvement of current engine performance. These models combine information on the chemistry, fluid dynamics and thermo dynamics of a system.

Chemical kinetic modeling is one method to interpret the decomposition of fuel in a combustion sequence. Programs like Chemkin Pro[1] are capable of reducing a complex series of chemical reactions and predicting the combustion process. These models are then able to estimate parameters such as the ignition delay time or the fuel composition as it leaves the system. Using this information, improvements in engine and fuel performance could cause a dramatic shift in the use of modern engines.

1.1 Background

This thesis has incorporated a chemical kinetic model of diisopropyl ketone (DIPK) to model the ignition delay times and OH production in a shock tube. Shock tube modeling was then performed in order to match the initial conditions of the combustion process with those simulated by the chemical kinetic model. These simulations were performed in order to study the combustion of DIPK so that it may one day be applied to an engine.

1.1.1 Diisopropyl Ketone

Until recently, research into ketones has focused on their use as a tracer in the combustion of other biofuels [2]. Ketones were considered an intermediate species and the majority of research focused on alcohols and esters that were proven. This has changed with the advent of 2nd generation biofuels. This new generation focuses on the use of endophytic fungi to produce volatile organic compounds [3]. One such fungus that produces heavy ketones has recently been discovered. This fungus, named NRRL 50072, produces a variety of different compounds that could be used as a fuel including DIPK and other heavy ketones [4]. This new development has drastically raised the desirability of ketone research.

DIPK was chosen as a representative of the branched ketone family that is produced by endophytic fungi. Understanding the combustion of DIPK through the use of chemical kinetic modeling would allow for greater understanding of the entire family of ketones. Another reason for the importance of DIPK is that it has the potential to be a mass produced renewable source. Research into the genetic engineering of DIPK is currently being performed at Sandia National Laboratory [3]. By manipulating the DNA of this simple organism, the production of DIPK and other branched ketones can be increased. The combination of chemical kinetic modeling and the creation of an abundant source could allow for branched ketones to be a viable solution to a global problem.

1.1.2 Chemical Kinetic Modeling

Chemical Kinetic Modeling incorporates several engineering disciplines to model chemical reactions. Chemical Kinetic modeling takes information on the chemical mechanisms and combines it with fluid dynamics and thermodynamics to recreate the combustion process. Chemical Kinetic Models are created by looking at every single reaction possibly present in a reaction process and eliminating those that are deemed insignificant. By eliminating reactions that do not affect the overall combustion process, models are able to be produced. For this work, Chemkin Pro was used to model a shock tube as a closed-batch homogeneous reactor. This modeling assumes that for any infinitely small portion of the reaction in a shock tube, the properties within the control volume would be constant throughout the volume. This approach allows researchers to model a complex reaction like the combustion of DIPK at stoichiometric conditions (Equation 1).



Chemical Kinetic Modeling can also be used to understand the production of a species throughout the combustion process. By understanding the time histories of species like OH, the model is capable of being refined and improved.

1.1.3 Applications of Modeling and Use in Next-Generation Engines

Researchers are then able to determine critical engine parameters like the ignition delay times or to measure the production of individual species. Ignition delay times is the amount of time it takes for a fuel/air mixture to combust once it reaches the necessary conditions of pressure and temperature at top dead center (TDC) in a diesel engine. This time is dependent on several

factors including the concentrations, equivalence ratios, pressure, and temperature of the combustion chamber.

Ignition delay times are important for the operation of engines. Engines that utilize the auto-ignition of the fuel must be timed precisely. If the ignition occurs too fast or too slow, then the total energy of the reaction cannot be utilized. This phenomenon, known as knocking, has the potential to damage the engine. By understanding when the ignition will occur, the combustion process is capable of being timed precisely. For diesel engines, this helps with timing the engine cycles but for future engine designs, like a homogeneous charged compression ignition (HCCI) engine, this timing is absolutely crucial.

The HCCI engine combines concepts from the spark ignition engine and the diesel engine. Like a gasoline engine with spark ignition, it injects the fuel in the intake stroke. As the piston is compressed, the fuel auto-ignites as if it were a diesel engine. This process allows for several important conditions to occur. By injecting early in the cycle, the fuel has the opportunity to vaporize and disperse creating a uniform distribution of fuel. Since the fuel is dispersed throughout the entire chamber before ignition, an HCCI allows for more efficient and complete combustion. This requires excellent modeling of the ignition delay times in order to ensure that the fuel ignites at the desired time.

Another important aspect of the HCCI is the lower initial temperature. Unlike in other engine types where the ignition process occurs at a specific location and propagates outward, the uniform conditions of an HCCI engine allow for combustion to occur across the entire volume.

Therefore the heat is released in a much smaller time frame and allows for the initial temperature to be lowered dramatically. The lowered initial temperature has a dramatic effect on the emissions produced during the combustion process. NO_x , pollutants formed in the combustion process that lead to the depletion of the ozone [5], are produced at high temperature combustion.

1.1.4 Shock Tubes

Shock tubes are a device for understanding fuel combustion. A shock tube is a device that creates a normal shock through the sudden contact of two gasses at different pressures. The two different sections are separated using a diaphragm, made of metal or plastic, which is designed to rupture at a prescribed pressure. The regions are generally referred to as the driver and driven sections for the high pressure and low pressure sections, respectively. When the diaphragm ruptures, a normal shockwave propagates down the driven side pushing the gas in the driven section towards the end wall. As the shockwave approaches the end wall, the gases compress causing a near instantaneous rise in the pressure and temperature in this region. If a fuel located in this region reaches its critical conditions then autoignition will occur. Later on, the pressure and temperatures will be quenched by expansion waves that were created in the opposite direction during the diaphragm rupture. Figure 1 represents a typical shock tube during an experiment [6].

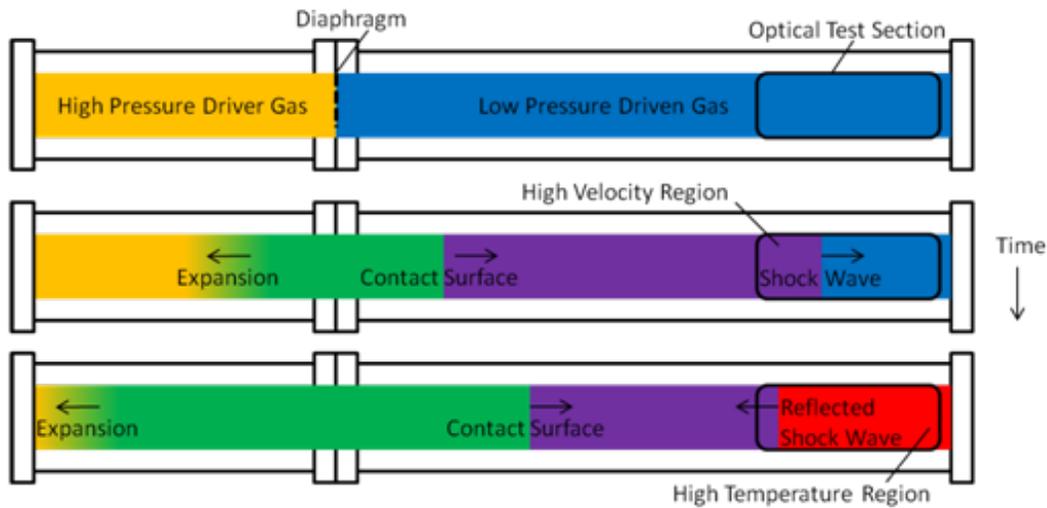


Figure 1: Example of Shock Tube Rupturing [6]. The first image is before the diaphragm ruptures, the second is immediately following rupture and the third is after the shockwave reflects from the end wall. Image taken without permission from the High Combustion Research Lab at the University of Calgary

Shock tubes are based on the normal shock equations to produce the desired initial conditions for combustion. As the shock propagates down the tube at a constant Mach number several important interactions take place. These interactions, like the contact surface between the driver and driven gases or the reflection of the incident shockwave are represented using a wave diagram. Figure 2 represents a typical wave diagram and the locations of each event with respect to a shock tube [7].

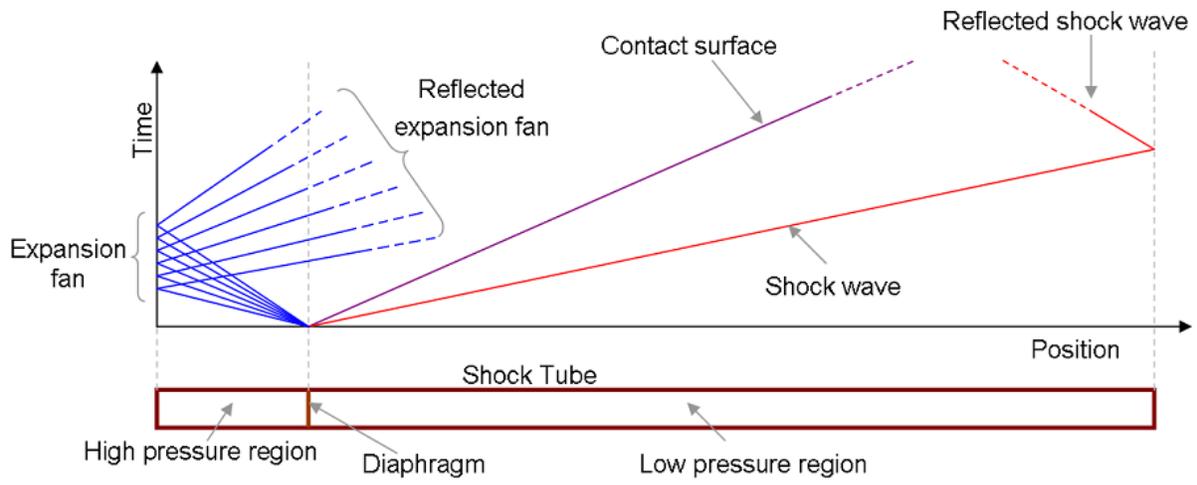


Figure 2: Wave Diagram of a Basic Shock tube [7]

Chapter 2: State of the Art Review

Combustion research focuses on both the improvement of the mechanism and the fuel. Modeling is used to help predict how a fuel will react under varying conditions. The following sections examine how current research is conducted on biofuels. A majority of the research focused on the validation of models through ignition delay times. The ignition delay time is the time it takes for a fuel to undergo combustion after the shock wave has reflected from the end wall. The ignition delay time calculated in shock tubes is the same for an engine at similar conditions. The ignition delay time is important to optimize engines in order to maximize efficiency and minimize engine knock. These were performed for a variety of fuel types, each of which is examined in detail here.

2.1 Ketones

There have been several important studies on ketones in the last few years. These papers focus on acetone, butanone and pentanone. The majority of the articles have focused on the validation of models for both oxidation and pyrolysis, although others have focused on the thermal decomposition and comparison to other fuels.

2.1.1 Ketone Oxidation

Oxidation is the combustion of a fuel with oxygen. Since oxygen is present in engine combustion these studies represent an important area of research.

In 2010, Serinyel et al. [2] examined 3-pentanone oxidation. It presents a chemical kinetic model to address this topic. The research was conducted between the temperatures of 1250 - 1850 K, at

a pressure of 1 atm. Equivalence ratios of 0.5-2.0 were used in the experiments. The paper uses results from shock tube experiments and spherical bomb tests to validate this model and calculate the ignition delay times. It compared the reactivity of 3-pentanone with two other common ketones, 2-butanone and acetone, and they were able to prove that 3-pentanone is the most reactive compound because of its "two ethyl groups attached to the carbonyl carbon." The final set of experiments described was 3-pentanone as a fuel tracer in n-heptane. The authors removed up to 15% of n-heptane and replaced it with 3-pentanone. Serinyel et al. was able to explore several aspects of 3-pentanone oxidation. They were able to validate the proposed model although the authors tended to exaggerate the model's ability to predict ignition delay times. The reaction pathways described will be able to further future research by presenting ideas for possible refinement of the model. The results from the tracer experiments were able to show that in quantities of up to 15% of the total fuel, 3-pentanone had no observable effect on the oxidation of n-heptane. This proves that 3-pentanone can be used as a fuel tracer in other fuels.

A second paper presented by Serinyel et al. [8] describes 2-butanone oxidation. This paper describes 2-butanone (Methyl Ethyl Ketone) oxidation. It presents a chemical kinetic sub-mechanism and validated the approach using data from shock tube experiments. Ignition delay times were recorded in a temperature range of 1250-1850 K at a pressure of 1 atm. The ignition delay time was recorded based on the pressure rise after the shockwave reflected from the end wall. The data were analyzed using the reaction flux method to determine the dominant reaction pathways. A sensitivity analysis was also performed to ensure validity of the model. The model was compared to data for a wide range of fuels, including ethanol. Problems with the model occurred at high temperature for the rich fuel mixtures. The last part of the experiment was to

determine whether or not 2-butanone could be used as an effective fuel tracer when added to n-heptane. It was determined that for up to 15% 2-butanone in a balance of n-heptane there was no observable difference in the combustion characteristics of n-heptane. This means that 2-butanone could also be used as a fuel tracer.

2.1.2 Ketone Pyrolysis

Pyrolysis is the combustion of a fuel without the presence of oxygen. These studies help identify key features of fuels and can also be used to validate chemical kinetic models through the ignition delay time.

Lam et al. [9] investigated high-temperature pyrolysis of acetone and 2-butanone. The experiments were performed in a shock tube using laser diagnostics. The experiments were performed at a pressure of 1.6 atm for a temperature range of 1100 to 1600 K. Kinetic models from Serinyel et al. [8] and Pichon et al. [10] were modified using the data to create more accurate models. The species measured were ketone, CO, CH₃, C₂H₄, and CH₄. The model by Serinyel et al. was improved by discovering that a previously ignored reaction was causing some of the inconsistencies with that model. The use of laser ignition was relevant to my research in order to better understand the implementation of optical techniques. The weakness of this paper is that it fails to understand the models limitations to an adequate extent. The authors ignore the significant differences between the model and the data that exists at certain instances. An example of this can be seen in Figure 3. The model struggles to predict the CH₄ time-histories at

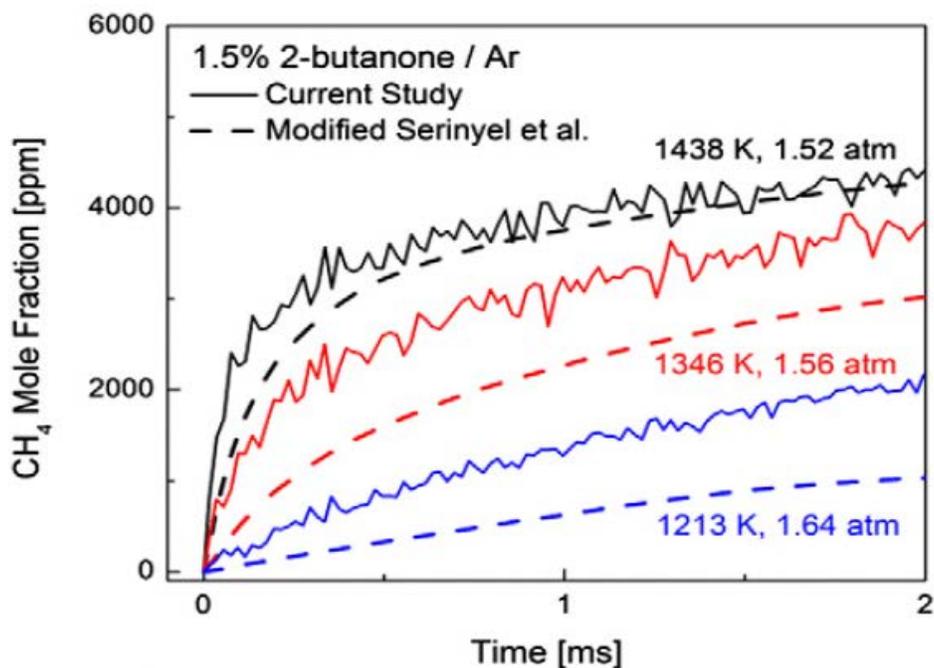


Figure 3: CH₄ time-histories for 1.5% 2-butanone in Ar by Lam et al. [9] (Used without permission).

low temperatures. The description of the laser diagnostic system utilized in the experiments was pivotal for my research. The authors provided an excellent example of how to improve a model through the use of optical diagnostics.

Another study that examined both the oxidation and the pyrolysis of 3-pentanone oxidation was presented by Lam et al. [11]. 3-pentanone was studied at high temperatures in a shock tube. The authors focused on the pyrolysis and oxidation of 3-pentanone. Laser diagnostics were performed to determine the time-histories of 3-pentanone, CH₃, CO, C₂H₄, OH and H₂O. Ignition delay times were also recorded for 3-pentanone. The experiments were performed at low pressures, no greater than 1.6 atm. The authors developed an overall decomposition rate coefficient for 3-pentanone. The data were compared to the chemical kinetic model created by

Serinyel et al. [2]. The model was modified to include the decomposition of methyl ketene. The last part of the paper compares the results for 3-pentanone to previous data on 2-butanone and acetone to determine reactivity. It was determined that 3-pentanone is the most reactive of the three and has the shortest ignition delay times because of the much larger initial OH plateau level compared to the other two ketones. The paper is the first study to use laser diagnostics to study 3-pentanone analysis. The information on laser diagnostics was important for a reference. The authors were able to significantly improve the model that this study was based on. The improvements were caused by the inclusion of a methyl ketene decomposition pathway.

2.1.3 Thermal Decomposition Studies

Thermal decomposition is the analysis of how the components break down. These types of experiments are also compared to kinetic models. These types of experiments are important for ketones because they are often intermediate species themselves. Thermal decomposition can help determine new pathways to be added to improve models.

An example of a paper that describes thermal decomposition of ketones is Lam et al. [12]. This paper describes the thermal decomposition of a series of ketones as it reacts with OH radicals. Acetone, 2-Butanone, 3-Pentanone, and 2-Pentanone were the fuels studied. The experiments were performed under a temperature range of 870–1360 K at pressures of 1–2 atm. Laser diagnostics were used to record the OH time-histories. The time-histories were compared to the chemical kinetic models of Pichon et al [10] and Serinyel et al. (1) [2]. The Arrhenius Equations were created for each of the compounds. A detailed error analysis was performed and yielded uncertainty values of between 20-28% for each of the four fuels. Uncertainty values of this

nature are not uncommon and the authors not overstate their accomplishments. This paper is important in its use of ketones at low pressures.

2.1.4 Comparisons with other fuels

One of the studies focused on comparing acetone with other fuels from different types. The authors, Akih Kumgeh and Bergthorsen [13], studied various C3 oxygenated hydrocarbons in a shock tube. The fuels studied were propanal, acetone (propanone), isopropanol, and ethyl formate. Ignition delay times were measured at a temperature range of 1100-1800 K with pressures at 1 and 12 atm. The data were compared with each other. It was determined from the data that propanal has a shortest ignition delay time of the studied fuels. Furthermore, the authors developed a chemical kinetic model for propanal with the data collected. The authors describe several trends at the end of the paper. Acetone, methyl acetate and isopropanol all have comparable ignition delay times. This is most likely because of the terminal methyl groups that each possesses. Other structural similarities such as C-C bonds could play a role in this. Another trend is that the two most reactive fuels studied, ethyl formate and propanal, both have ethyl groups. These groups form compounds that improve chain branching and thus speed the reaction.

2.2 Alcohols

Alcohols are the most heavily experimented fuel category. This is because of the importance of ethanol. Alcohol has been the focus of many different types of studies. These studies include oxidation, pyrolysis, emission, and speciation.

2.2.1 Oxidation of Alcohols

The oxidation of two alcohols is described by Heufer, Bugler, and Curran [14]. The paper focuses on the combustion of n-pentanol and n-hexanol. The experiments were conducted between the temperatures of 640 to 1200 K for the range of pressures of 9 to 30 atm. The article used both a shock tube and an RCM to conduct the experiments and produce the data at the temperature range. Ignition delay times were recorded using the rise in pressure. The results of the experiment were compared to that of similar n-alkanes. Arrhenius equations were created from the chemical kinetic models. One important finding from this paper is that the reaction rates for alcohols and alkanes were similar for the larger carbon chain lengths. The authors also reason that this similarity may hold true for other types of fuels.

2.2.2 Alcohol Pyrolysis

The pyrolysis and oxidation of butanols were conducted by Yasunaga et al. [15]. The paper describes experiments conducted for four types of butanol (n-, sec-, iso- and tert-). The experiments were conducted in two different shock tubes at a pressure range of 1 to 4 atm. The temperatures of the experiments ranged from 1000 - 1800 K. The ignition delay times were recorded using both the pressure and CH* emission. A detailed chemical kinetic model was produced from the results of the experiments. One interesting observation that the authors noted was that acetone was seen to be created in the process. Ketones are commonly found as intermediates in the combustion process and this is an example of such a case. The use of two shock tubes was different from the others and was able to provide an increased level of certainty in the experiments and was the basis for the planned experiments in two facilities presented later.

2.2.3 Emissions of Alcohols

Studies of fuel emissions are often carried out in engine models. Emissions are of great concern for the industry as people desire to reduce pollutants found in the air. Emissions studies focus on the creation of pollutants during the combustion process. These studies present important data for the utilization of any fuel. Since alcohols are the most widely studied and utilized fuel, these are even more important.

One example on the study of pollutant formation of alcohols is from Broustail et al. [16]. The authors compared the results of the formation of pollutants of butanol with that of iso-octane. The experiments were carried out in a single-cylinder port-fuel injection spark ignition engine. The pollutants targeted in this study were both regulated and non-regulated. The list of pollutants includes CO, CO₂, NO_x, THC, and CH₄, acetylene, ethylene, benzene, acetaldehyde and formaldehyde. The authors are able to conclude that with increasing alcohol concentrations emissions of CO₂ decreased while there was a decrease of CH₄ and NO_x. Other pollutants were almost entirely eliminated as the concentration of alcohol approached 100%. The authors end the article by comparing the results with that of the standard bearer, ethanol. As this was a fuel compared to DIPK later in the thesis, this provided an interesting example for fuel comparisons. The emission studies are very important if a fuel is to ever be used as an alternative. This study provides a blue print for future studies of DIPK.

2.2.4 Speciation Studies for Alcohols

Speciation is related to emissions. It is the analysis of all the products that are present during combustion. This commonly is measured after combustion has finished. The difference between

emissions is the focus on all products. These data are normally recorded through sampling. One weakness that speciation has is that it normally does not involve time-histories. It also has a problem with recording intermediate species that do not exist after the combustion process has finished.

Karwat et al. [17] is an example of a speciation study for an alcohol. In this paper, n-butanol was tested in a rapid compression machine (RCM) between the temperatures of 920-1040 K at a pressure of approximately 3 atm. Measurements were taken to record the time histories of several intermediate components. These intermediate species were methane, carbon monoxide, ethene, propene, acetaldehyde, n-butyraldehyde, 1-butene and n-butanol. A high speed camera was used to record images of the combustion phenomenon. The time histories were recorded using high-speed gas sampling and gas chromatography. Ignition delay times were recorded based on the pressure trace. The measurements were compared to the chemical kinetic model proposed by Black et al. [18]. The authors used a sensitivity analysis to determine the most significant reactions in the combustion of n-butanol. The model improved the effectiveness of most of the intermediate species. Based on the modifications, the overall reaction rate was improved upon. RCMs are commonly used to provide different and complimentary data to shock tubes. This paper provides an excellent example of a method of model validation for comparisons to shock tubes. Alcohols are the most prevalent class of fuels as well and understanding the combustion of this fuel type can help with other less understood groups. The paper also provides an excellent overview on how biofuels are already impacting society and how new research could benefit the field.

2.3 Esters

Esters are another category that has received a lot of focus. The reason is for its similarities to diesel fuel. Studies for esters have been on oxidation, pyrolysis, emissions and speciation.

2.3.1 Oxidation of Esters

Rotavera and Petersen [19] researched oxidation. The paper describes the ignition delay times of three different fuels separately and then blended together (Two different blends were used). The fuels used were methyl octanoate, n-nonane, and methylcyclohexane. The fuels were tested at pressures of 1.5 atm and 10 atm. The equivalence ratios included in the study were 0.5, 1.0 and 2.0. The ignition delay times were measured using two different shock tube facilities. OH chemiluminescence was the measured compound. Three different chemical kinetic models were used for the pure fuels. "The mechanisms of Dayma et al. [20], Rotavera et al. [21], and Pitz et al.[22] were chosen for methyl octanoate, n-nonane, and methylcyclohexane, respectively." (11). These three models were used to develop the model presented. The ignition delay times of the three compounds and their blends were compared. It was determined that the blending of the fuels had a greater effect at near atmospheric pressure compared to at 10 atm. The information on the blending of biofuels is a possible topic for future investigations.

2.3.2 Pyrolysis of Esters

Grana et al. [23] examined the pyrolysis and oxidation of methyl decanoate and methyl butanoate. The authors focused on the creation of a chemical kinetic model with it being validated through the data from a shock tube study by Hakka et al. [24] and data from a jet-stirred reactor provided by Marchese, Angioletti and Dryer [25]. The shock tube experiments

were conducted at a temperature of 1280 - 1990 K and a pressure range of 7.6 - 9.1 atm. The jet-stirred reactor was operated at a pressure of 12.5 atm for temperatures between 600 and 900 K. The information in this article relates to my research in its creation of the chemical kinetic models. This article provides another example of the use of multiple mechanisms to provide the greatest results and to provide the best possible conclusions.

2.3.3 Emission Studies of Esters

Klein-Douwel et al. [26] describes the formation of soot in a diesel engine. The authors focused on the two types of methyl esters that could be used in the creation of biodiesel. These were jatropha methyl ester (JME) and rapeseed methyl ester. The experiments were conducted in a prototypical diesel engine with capabilities for high speed imaging and spectroscopy. Data was recorded using a chemiluminescent technique to record concentration of OH and CH. A comparison of the formation of soot is described. The authors also determined the NO concentrations. NO is an important emission and is only created at high temperature combustion. The article focuses on the formation of soot which although being outside the purview of the research presented is important to understand. Experiments on the formation of soot during the combustion of DIPK may one day be recorded and this provides an excellent reference.

2.3.4 Speciation of Esters

One example of a study on the speciation of esters is Walton et al. [27]. The paper presented a study on methyl butanoate combustion and the creation of intermediate species. Methyl butanoate is considered a possible surrogate for other more complex biofuels. The experiments were performed in a rapid compression machine (RCM) at pressures of 10.2 atm and a

temperature of 985 K. Ignition delay times were recorded using the pressure time histories. Gas sampling and imaging was conducted to measure the intermediate species. The authors compared their data with data of fuels that this could simulate. The data were also compared to two different models, Walton et al. [28] and Metcalfe et al. [29]. A sensitivity analysis was conducted to insure that the most important reactions were included.

2. 4 Other Types of Fuels

The three types of fuels listed above are not the only ones that are studied. Many different fuels are studied over a variety of conditions. Some examples are described in this section.

Decalin is a fuel that can be classified as a polycyclic alkane. As research into developing new generations of biofuels, Dagaut et al. [30] believes they will be important. The authors studied the oxidation and pyrolysis of decalin. The apparatus used was a jet-stirred reactor. The experiments were conducted at 1 and 10 atm over a temperature range of 750-1350 K. A chemical kinetic model was created and tested with the data from this study and data from a previous shock tube study. The study had equivalence ratios of 0.5, 1, and 1.5. The authors were able to determine that the model is reasonably effective for the overall range. They were able to validate the model with the data recorded and by performing both a sensitivity analysis and a reaction flux analysis. One reason this paper is important is because decalin is often created while burning fossil fuels. Information on its combustion could improve any research that uses biofuel blends.

Dimethyl ether was studied behind reflected shockwaves by Pyun et al [31]. Time-histories of CO, CH₄, and C₂H₄ were recorded in a shock tube for experiments of dimethyl ether (DME) pyrolysis. The experiments were performed for mixtures of 0.5%, 1% and 1.5% DME with argon as the balance. The tests were performed in a range from 1300 to 1600 K at a pressure of 1.5 atm. The authors chose two models to use to compare to the data acquired. The first model was proposed by Curran et al. [32, 33] and the second model was created by Zhao et al. [34]. The authors used laser absorption for each of the species time histories. Ignition delay times were recorded using pressure. The authors compared the two models using simulated results and determined that there were several inconsistencies between the two models. The three species time histories were compared to the two models and modifications were made to both. The modified Curran et al. mechanism was better able to predict the CO concentrations at low temperatures while the mechanism by Zhao was closer to the experimental data for higher temperatures. The modified Curran et al. model was able to predict the concentrations of CH₄ and C₂H₄ better than the other model. Despite the improvements made to the two chemical kinetic models, neither could accurately predict DME combustion throughout a large range of temperatures. The paper describes the use of laser ignition experiments. The focus on creating time-histories of a variety of components helped with the creation of my own experimental design. It also presents a method for improving chemical kinetic models.

Ramirez-Lancheros et al. [35] created a chemical kinetic model for the surrogate biodiesel B30. The authors set about proving that B30 had similar combustion characteristics of biodiesel. Surrogates are used as a substitute to replace a more complicated mixture that could contain many different components with one that reacts similarly and only has a fuel. The article

describes the oxidation of this fuel. The fuel, B30 surrogate, is comprised of 49% n-decane, 21% 1-methylnaphthalene, and 30% methyloctanoate. The ignition delay times were measured in a high-pressure shock tube. The experiments were performed for equivalence ratios of 0.5-1.5 with a temperature range of 700-1200 K. The pressures used were 20 and 40 bar. The ignition delay times were determined using CH chemiluminescence at a wavelength of 431.5 nm. Based on the data collected a detailed chemical kinetic model was created. The model was also validated using data from Wang et al. [36]. A sensitivity analysis was performed for the model. The use of high pressures was particularly important. These pressures are closer to those that will be experienced under engine conditions. This paper provided a basis for how to conduct high pressure experiments using a shock tube.

2.5 Comparison of the fuel types

There are a variety of different fuel types but almost all of them focus on the same problems. Each type of fuel had similar experiments conducted, with the exception of ketones where there has been less research. The focus on oxidation, pyrolysis, emissions, and speciation are for obvious reasons. These are the key questions that pertain to the use of these fuels.

One of the main goals of the field is to predict how fuels will react under combustion conditions. Therefore, almost all studies work at the creation of their own model or the improvement of someone else's. These models were created in order to help with the problem of predicting how fuels will react. One of the most crucial predictions is the ignition delay time. The ignition delay time is important in determining if a fuel can be used in a modern engine and in the creation of such an engine. The models can also predict the emissions generated by the combustion. This

can be seen in the papers presented by Lam et al. [9, 11]. This has become increasingly important with the concern over pollution. Both Karwat et al. [17] and Walton et al. [27] focused on this with their speciation studies.

There are several challenges that exist in the creation of the models. The first problem is to understand the different reactions that take place. A chemical kinetic model could involve thousands of different species and even more reactions. Any model must first determine which reactions to include and to ignore. These decisions lead directly to the differences between the various models. The next challenge when modeling combustion is to perform a sensitivity analysis. The sensitivity analysis is used to determine how important a given reaction is to the model and can help lead people to reactions left out. This is one of the techniques that allowed Lam et al. [9, 11, 12] to modify the different models that they reviewed.

Other challenges involved in combustion research come from the devices used in the experiments. Shock tubes are difficult to use. The tube must be opened after each experiment and the diaphragm must be replaced. Afterwards the tube must be completely evacuated to near vacuum conditions before filling the driven chamber with the fuel being tested. The amount of time between each run makes these studies incredibly long. RCMs have other problems. These facilities do not require as long to setup but it still must be evacuated. It also has problems with heat loss and with the creation of such facilities. These two devices are the best ways to experiment with combustion but both have their unique drawbacks.

The future of biofuel research is in blends. Blends are the combination of a biofuel with a conventional fuel. This already occurs with the addition of ethanol in gasoline. Replacing ethanol with a different biofuel can help lead to reduce emissions through a cleaner burning fuel and increase engine efficiency by developing a leaner mixture. I have decided to focus on ketones because they much potential. Ketones have the potential to be easily produced which has been a concern with other fuels. This class of fuel could help lead the United States to energy independence and help reduce the cost of fuels.

2.6 Roadmap

The remainder of this thesis will focus on the combustion of diisopropyl ketone. This thesis will establish the specific problem and develop a hypothesis to solve it. The approach to the problem will then be explored in detail. The experimental setup will be described, including details on the shock tube and diagnostics. The approach will also include details on the development of the chemical kinetic model and how the data will be collected. A description of how the data was evaluated and model validation will be described after the approach. Finally, conclusions that were drawn from the research and possible topics of future research will be discussed.

Chapter 3: Project Definition

The problem addressed in this thesis is covered in a clear and precise manner in this chapter.

3.1 Technical Area

Fuel consumption has become an increasingly important topic worldwide. As we understand the limitations of current methods as well as the consequences of burning conventional fuels, demands for new fuels have risen. One source of alternative fuels is biofuel research. Research into biofuels has focused on the understanding of its combustion properties. Biofuels possess similar features to conventional fuels and potentially can replace some or all of the petroleum based fuel with little cost to the infrastructure. An example of this is ethanol. Ethanol is currently being blended with gasoline in amounts up to 10% ethanol [37]. Biofuels have the potential to limit the costs associated with burning fuels and maximize the benefits of the fuels.

3.2 General Problem

Fossil fuels account for over 30% of the total energy consumed in the world [38]. The problem is that burning fossil fuels has consequences to the environment. The research into biofuels has focused on limiting emissions while optimizing performance. This is performed through chemical kinetic modeling. Emission studies are able to provide information on the different compounds produced by the burning of biofuels while other studies are capable of predicting performance. The research has generally focused on alcohols and esters. Alcohols, like ethanol, resemble gasoline in structure and therefore are capable of being blended together with it. Many studies on alcohols are trying to develop larger alcohols that would have a greater energy density with the reduced emissions of ethanol. This greater energy density would result in a greater

performance from the fuel. Research into esters is focused on the development of a biofuel for diesel. There has been less research into other types of hydrocarbons as biofuels.

3.3 Specific Problem

Ketones are a possible choice for biofuels. They also resemble diesel fuel with their structures. The problem was the availability of ketones compared to esters. With the discovery of the fungus NRRL 50072 [4], ketones could be easily and cheaply produced in mass quantities. However, there is little information on the combustion of DIPK. Research must be conducted to understand the combustion of this compound. Understanding the compounds created during combustion and the time it takes to combust is important if DIPK is ever to be used as an alternative fuel. DIPK has the ability to be combined with diesel fuel and create a safer product for the environment.

3.4 Hypothesis

The detailed chemical combustion model will accurately be able to predict the combustion characteristics of Diisopropyl Ketone and that the ignition delay times of DIPK will resemble those of iso-octane.

3.5 Major and Minor Contributions

This research could provide several contributions to the state of the art. The first is the validation of a chemical kinetic model by Allen et al. [39]. Another contribution could be from comparisons of DIPK with different fuels. The research will validate heavy ketones as a potential fuel source by showing the similarities to current standards. The work will also detail the creation of an Optical Diagnostic System for the use with shock tubes.

3.6 Novelty, Significance and Usefulness

The research presented by this thesis is novel, significant and useful to the advancement of my field. There has been no research provided on the combustion of DIPK. Before the discovery of NRRL 50072 [4], ketones were not considered to be a viable option for biofuel development. The research is significant because it provides a potential solution to a problem facing humankind. Energy consumption is ever increasing and this research could provide a new source of renewable energy. The development of a model is the first step in the creation of a new biofuel. My research is useful in its creation of this model. Other research can then be based on the model and the findings described in this thesis that could then be applied to new research and possibly create a viable alternative to diesel fuel.

Chapter 4: MODELING AND SIMULATIONS

Two different programs were utilized to understand the combustion of diisopropyl ketone. The ignition delay times and OH time histories were simulated using Chemkin Pro while the program Kasimir 3 [40] was employed to model two different shock tube facilities for future experimentation.

4.1 Chemical Kinetic Modeling - Chemkin Pro

Chemkin Pro is a program capable of simulating the combustion process for a variety of different devices. Chemkin Pro takes a gas kinetic model and a thermodynamic model that details every reaction and species in the combustion process for combustion modeling. To model a shock tube, a closed homogeneous batch reactor can be used after several assumptions. The homogeneous mixed reactor treats the combustion process as being perfectly uniform throughout the constant volume vessel. A shock tube can be looked at in this manner through a control volume process. The assumption used for modeling is the constant-volume and internal energy model (constant U, V). By taking a single infinitesimally small point at the center of combustion, a shock tube can be modeled in this manner.

4.1.1 Simulation Conditions and Fuels

Five fuels were examined using Chemkin Pro. The fuels were diisopropyl ketone, iso-octane, n-heptane, n-butanol and ethanol. Each of these fuels was measured at the stoichiometric ratio at an initial pressure of 10 atm. The temperature range for each fuel was 700 - 1400 K using intervals of 50 K.

The model for diisopropyl ketone was created using the reaction mechanism generator from MIT. This model has been described Allen et al. [39]. The Chemical kinetic models used in this thesis have been described by Mehl et al. (2009), Mehl et al. (2011), Vasu and Sarathy, and Saisirirat et al. for iso-octane, n-heptane, n-butanol, and ethanol, respectively[41-44].

Each of these fuels was chosen for a specific reason. Iso-octane and n-heptane are common surrogates for gasoline and diesel fuel, respectively. These fuels behave similarly as the two common liquid fuels but are chemically less complex. Butanol has recently become a popular alcohol. It can be found in abundance and has shown better performance over other biofuels. Ethanol is a current fuel additive in use today. As the most likely start to any biofuel use is as an additive to gasoline or diesel, ethanol is an important fuel to compare the efficiency to.

4.1.2 Ignition Delay Times

Ignition delay times are an important characteristic in the performance of modern engines. For a diesel engine, short ignition delay times are ideal for optimum performance. As the diesel cycle is based on the auto-ignition of the fuel, delays in the fuel ignition reduce the performance and damage the engine. This results from the fuel igniting at a location other than top-dead-center (TDC) which is the location of the piston where the compression ratio is the highest. The reduced performance resulting from the misfiring of ignition is referred to as knock.

Engine timing is even more important for HCCI engines. As HCCI engines inject the fuel before the TDC, the fuel has a higher chance of igniting before reaching the desired location. As a

result, detailed understanding of the ignition delay times is essential for the use in this type of engine.

The ignition delay times were measured for the five different fuels by examining the pressure time history of each simulation. As the ignition delay time is defined as the time difference between start of the simulation and initial pressure rise, pressure was seen as the most meaningful method. The ignition delay times were measured for this thesis as the time it took for half of the pressure difference. This criterion was selected to eliminate inconsistencies with the chemical kinetic models. The OH time histories were also examined for some of the simulations to compare the ignition delay times. Samples of the pressure trace and OH time-histories can be seen in Figure 4 and Figure 5, respectively.

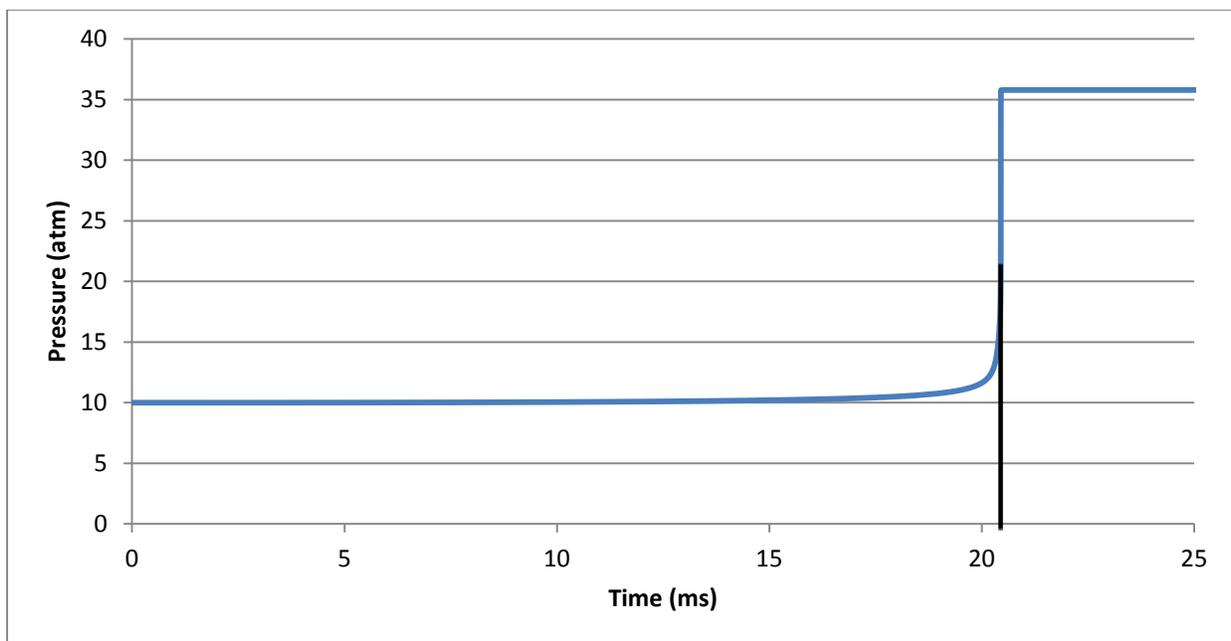


Figure 4: Pressure Trace for Iso-octane, 900 K

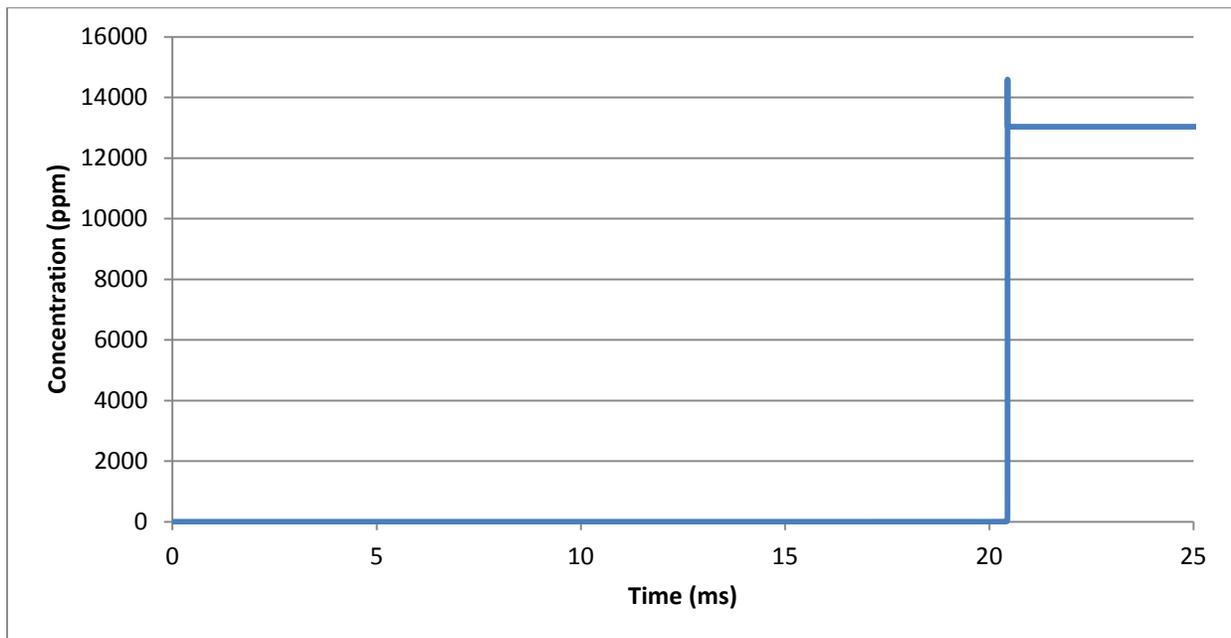


Figure 5: OH Time-history for Iso-octane, 900 K

The ignition delay times can clearly be seen for both figures. The ignition delay times for the above figures were 20.45 ms for both figures. The pressure trace also shows the need for above definition. The chemical kinetic model shows a slow initial rise of the pressure at the start of the simulation. If the ignition delay time was taken as the conventional definition of the initial pressure rise than the ignition delay would have been recorded as early as 10 ms, half of the actual value.

Comparison of Fuels

Each of the five fuels' fifteen simulations was then compared to one another. The ignition delay times were plotted with the inverse of the temperature (multiplied by 1000) as shown in Figure 6. Several interesting trends can be seen when comparing DIPK to the other fuels. DIPK shows a similar trend to iso-octane, a common gasoline surrogate. DIPK does appear to have greater ignition delay times to those of iso-octane but this could be a result of the model. The chemical

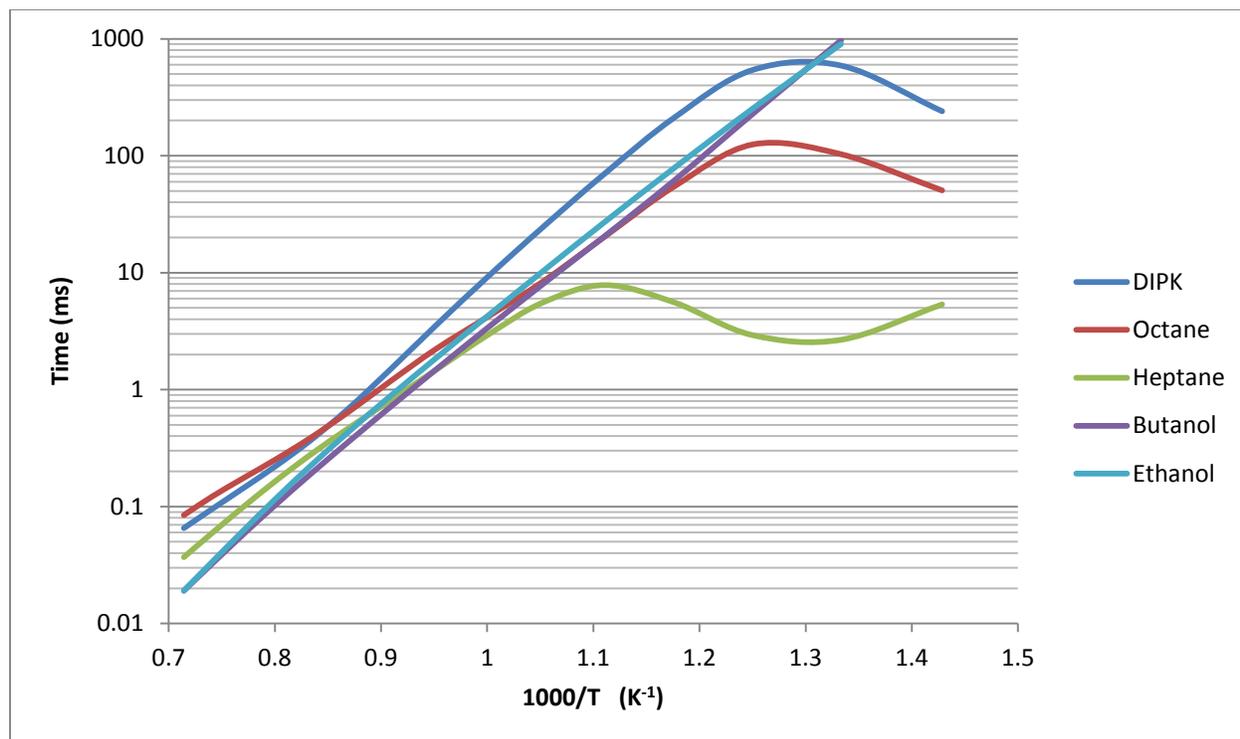


Figure 6: Ignition Delay Times for Five Fuels

kinetic model has yet to be refined using experimentation and the scaling could be reduced in the future. DIPK does not show much relation to n-heptane though. N-heptane is a common surrogate for diesel fuel. Diesel fuel relies on low ignition delay times to reduce knock and improve the efficiency of the engine. A longer ignition delay time like DIPK has shown would be a poor replacement for such a fuel. DIPK also shares trends with both ethanol and butanol. One interesting feature shown by DIPK is the change in the relationship at the lower temperatures. This region is called the negative temperature coefficient region. It is an area seen on many fuels where the ignition delay times again reduce before once again increasing. The full negative-temperature coefficient (NTC) behavior can be seen above in n-heptane.

At low temperatures, DIPK also shows an improvement over both n-butanol and ethanol. The ignition delay times continue to climb for both of these fuels to approaching 1000 ms at 750 K. Neither of these fuels showed any NTC behavior, exceeding 2000 ms simulation time for the lowest temperature. For lower temperatures that are of current interest for application such as HCCI engines, DIPK shows a dramatic improvement over both the current fuel additive as well as another potential biofuel.

Effect of Pressure on Ignition Delay Times

The region of pressures for modern engines ranges between 1 and 60 atm. As a result, the ignition delay times at different pressure must be considered. The effects of pressure were examined for the ignition delay times of DIPK. Simulations were conducted for a stoichiometric ratio for initial pressures of 1, 10, 20, 30, 40, 50 and 60 atm using the same range of temperatures (Figure 7)

As the initial pressure increased, the combustion process quickens. This trend is because at the higher pressures, the conditions for combustion were closer. At the lower end of the pressures, ignition delay times became unacceptable. Combustion did not occur for the two lowest temperatures at the lowest pressure. This result is most likely a result of there being too little energy in the system at these conditions. Another interesting trend that occurs is the increasing definition of the NTC region. Compared to the original simulations at 10 atm where the NTC region was only beginning, the region was clearly noticeable for the other pressures. The NTC region also shifted to the left, occurring at higher temperatures as the pressure increased. This temperature region is an important area of study as it is in the range of temperatures for a

homogeneous charged compression engine (HCCI), an experimental engine design. One final trend of note is the starting and end points for the different pressures. All of the pressures start between the range of 0.01 and 1 ms and the larger pressures all end at the same level of magnitude. These two points show that pressure has little difference at the lower and upper ends of combustion. The main area of concern then is the region where the trend is opposite of the rest, the NTC region.

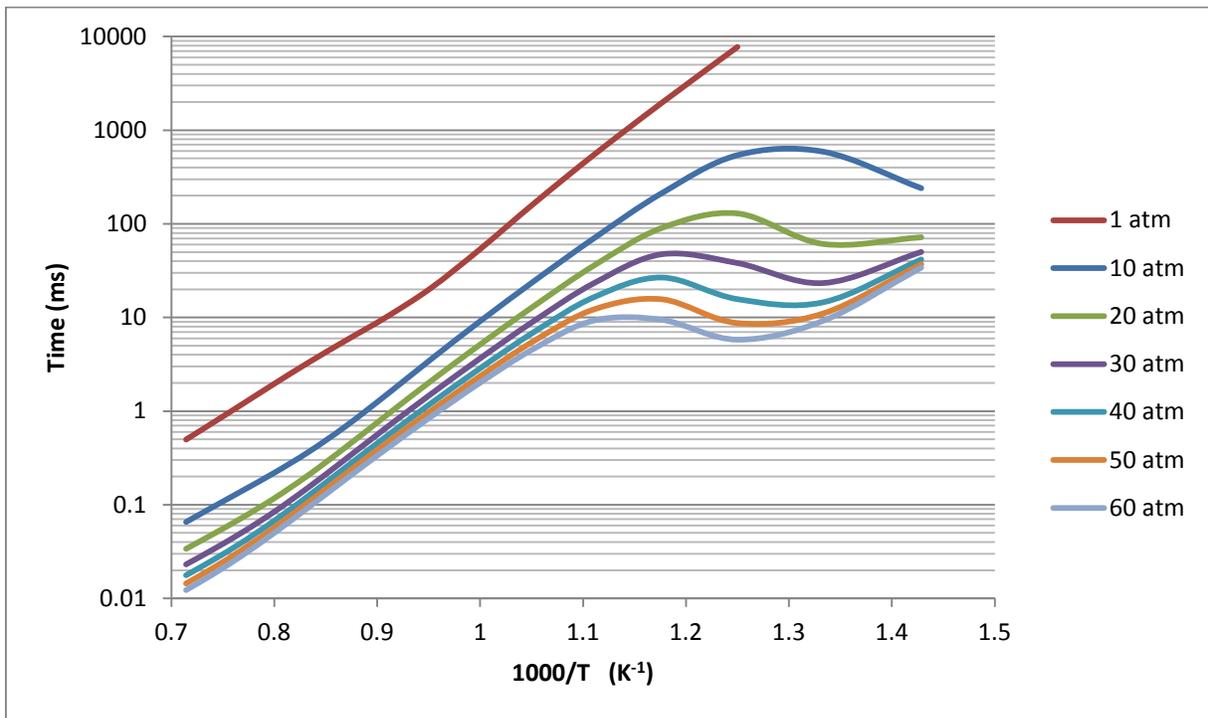


Figure 7: Ignition Delay Times of DIPK for Various Pressures

DIPK showed poor performance at low pressures. Such pressures are not common engine conditions but are still important to study. At this pressure, DIPK resembled the poor performances of DIPK.

The decrease in ignition delay times at the higher pressures is an important trend. As the initial pressures of HCCI engines are typically closer to the upper range of engine conditions, DIPK may be a potential fuel additive for such engine types.

Effect of Equivalence Ratio on the Ignition Delay Times of DIPK

The equivalence ratio is the ratio of fuel compared to the stoichiometric equation. Four different equivalence ratios were examined, $\Phi = 0.5, 1.0, 1.5$ and 2 , using the Chemkin Pro software. Figure 8 shows the effect of equivalence ratio on the Ignition delay times of DIPK. The initial pressure was held at 10 atm for all simulations and the initial temperature ranged from 700 - 1400 K. The ignition delay times show little variation over the various equivalence ratios with almost none for ratios at or above the stoichiometric level. This is an understandable trend as there is not enough oxidizer to burn any more of the fuel. There is a slight increase in the ignition delay times for the lean fuel mixture. This mixture has twice as much oxidizer as fuel and the combustion process would be slowed. As lean fuel mixtures are becoming more desirable to help regulate greenhouse emissions, this trend shows positive signs for DIPK.

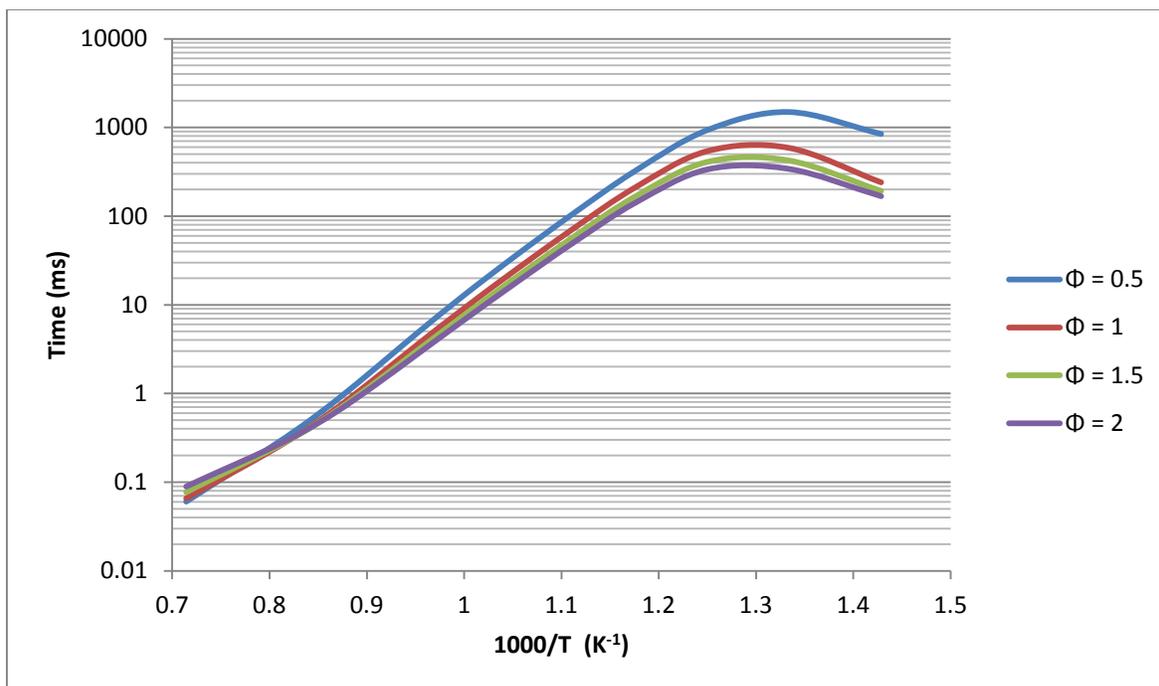


Figure 8: Ignition Delay Times of DIPK for Various Equivalence Ratios

4.1.3 OH Production in the Combustion of Diisopropyl Ketone

A second set of simulations was conducted to examine the production of OH in the diisopropyl ketone. OH is a common intermediate product in combustion. The production of OH helps facilitate other reactions including products such as water. Understanding the production of OH is also important in the decomposition of ketones. H-abstraction of OH molecules is a common pathway for the breakdown of the fuel. Understanding the OH time-histories during the combustion process allows for improvements in the chemical kinetic models which will allow for improved engine performance from more accurate modeling of parameters such as the ignition delay times.

The production of OH was compared with the other four fuels. The chemical kinetic models for all of the simulations were the same as previously.

The conditions for the production of OH were explored at temperatures between 1500 and 2000 K. The pressures examined for OH generation ranged between 1 and 5 atm. The amount of fuel for the production of OH was 50 ppm at stoichiometric conditions. Argon was used as a bath gas for all experiments. These conditions were chosen to match with planned experiments with the OH optical sensor.

Comparison of Fuels

The production of OH in the combustion of DIPK was compared to that of the other four fuels (Figure 9). The simulations were performed at 1500 K and a pressure of 1 atm. All reactions occurred at the stoichiometric ratio. DIPK again shows similar trends to iso-octane as well as butanol. All three fuels have an almost immediate initial rise before dropping off suddenly and picking up later with DIPK in the middle for both the plateau and the bottom. One difference of DIPK and the other two fuels is the time that it takes DIPK to rise to its plateau.

Further information on the production of OH is revealed by examining the initial OH peak (Figure 10). The initial rate of production of OH is the same as it is for both iso-octane and n-heptane. The main difference that can be seen between DIPK and iso-octane is the location of the peak. The initial peak of DIPK is almost twice the amount of iso-octane. This relationship shows that Although DIPK and iso-octane originally are generated at the same rate; iso-octane is

consumed at a much more rapid rate early in the process. The opposite comparison can be made for the second peak where iso-octane increases much more rapidly and reaches a higher plateau.

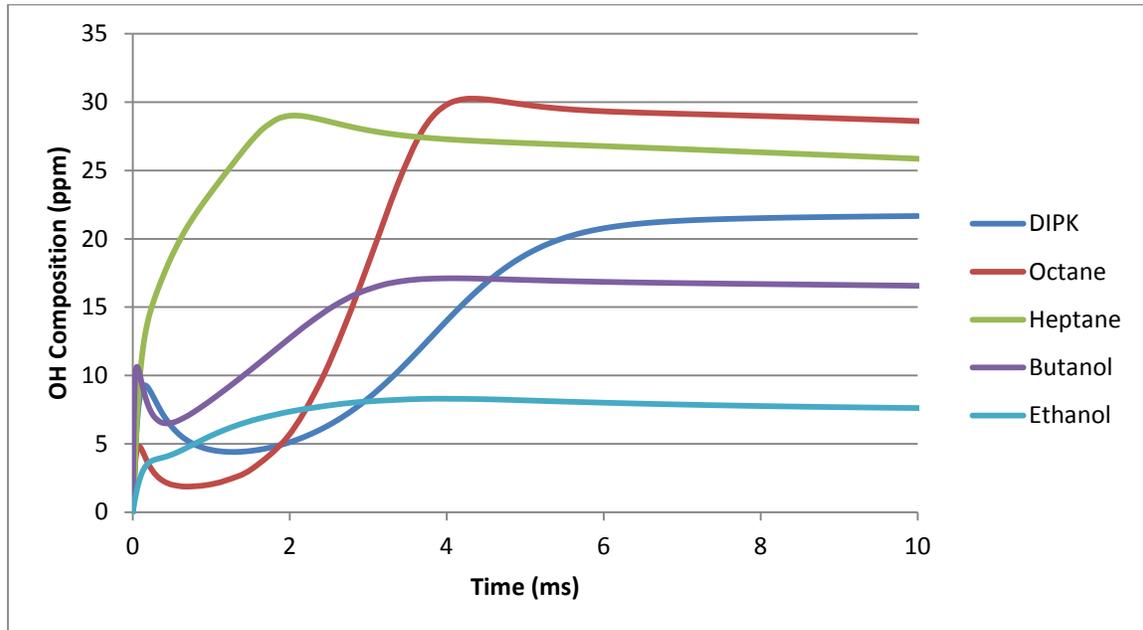


Figure 9: Comparison of the OH Production for DIPK with four common fuels

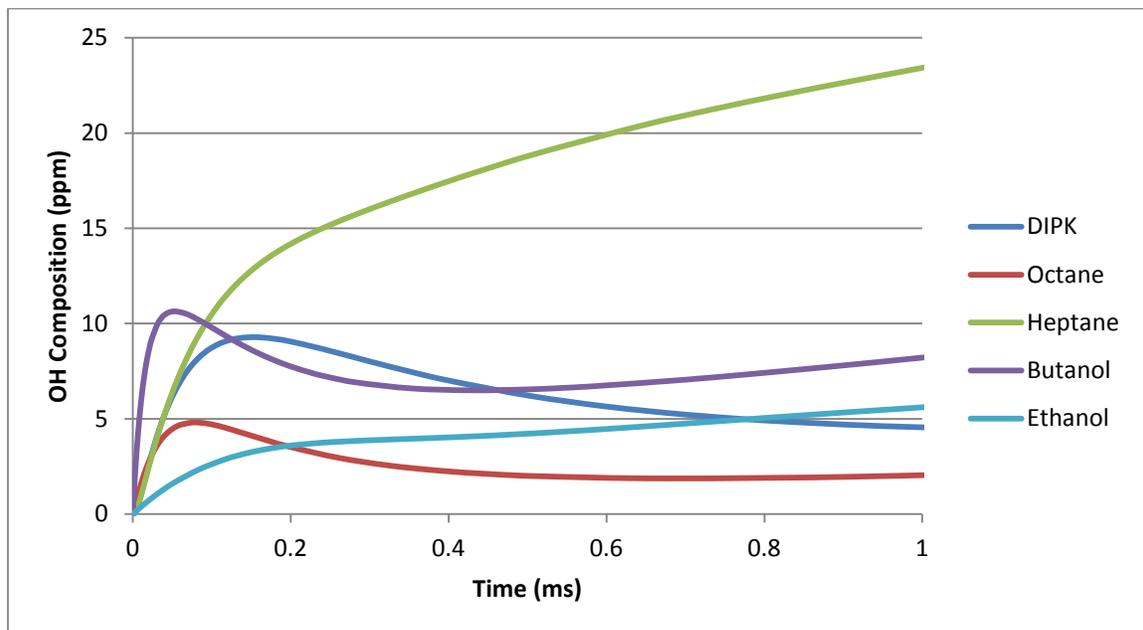


Figure 10: Comparison of OH Production - Initial OH Peak

Effect of Temperature on OH Production

To understand how DIPK will perform in engine-like environments, the effect of temperature on the production of OH was examined. Figure 11 displays the different amounts of OH produced for varying temperatures at 1 atm. OH production shows a strong positive dependence temperature. This dependence is a result of an increase in the generation of OH that occurs at higher temperatures. Another aspect of this increase is the weakening of the well as temperature increases. OH settles at a higher value not as a result of decrease in the consumption but because of increased generation. The generation of OH increases so dramatically that the well that is quite prevalent at lower temperatures becomes almost non-existent at higher temperatures, with only a slight change in the slope at 2000K. The well also slows the creation of the plateau. The plateau is reached much faster for higher temperatures as it is produced at a greater amount at the higher temperatures.

One of the main reasons for the confidence in the increased OH generation is that at the two highest temperatures, the concentration of OH is greater than the initial fuel concentration. This shows that these temperatures there must be a second source for OH as DIPK only has one oxygen atom.

The consumption of OH itself remains relatively unchanged with temperature. The difference between each plateau remains unchanged for any 100 K increase in temperature. This trend shows that farther in the combustion process, the generation of OH slows to match the speed at which OH is consumed. The difference between each temperature follows the strength of the well with little variation occurring after recovering from it.

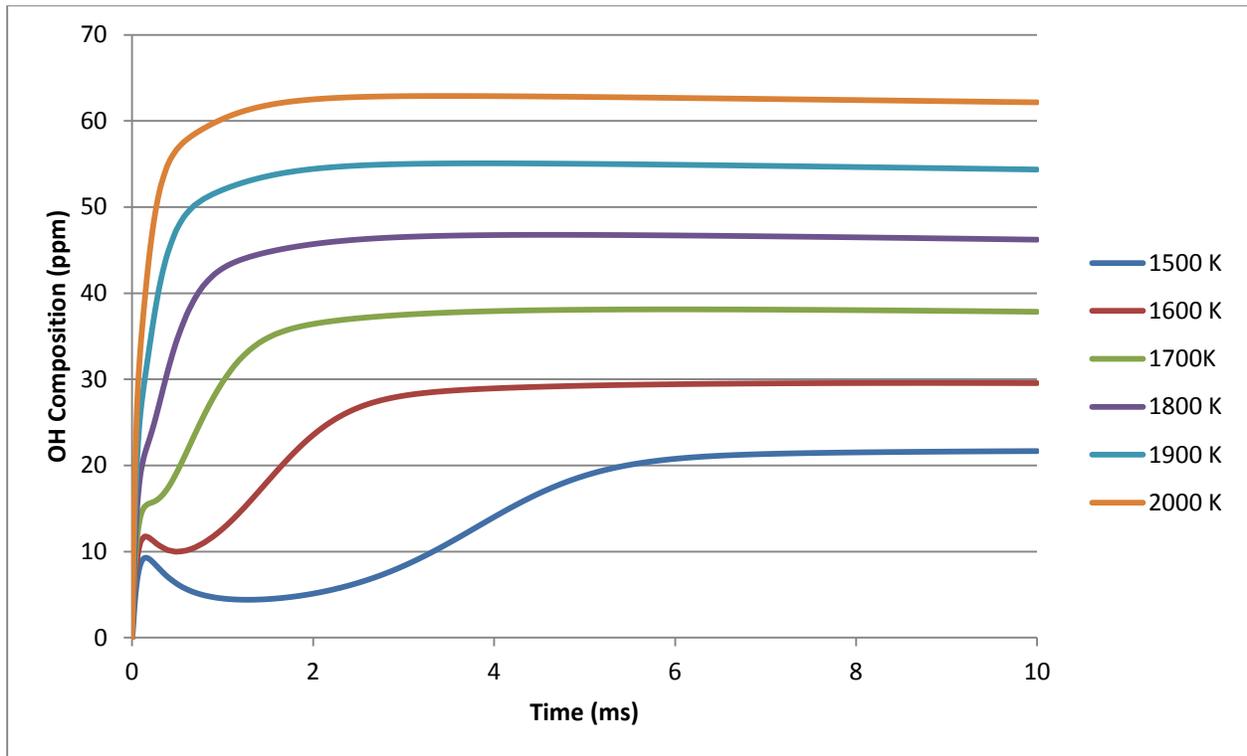


Figure 11: Effect of Temperature on the Production of OH

Effect of Pressure on OH Production

The effect of pressure on OH production was also considered. Holding the temperature at a constant 1500 K, the pressure was varied between 1 and 5 atm. Figure 12 shows the effect of pressure on the production of OH. Unlike temperature, pressure has little effect on the general shape of OH production. At 1500 K, the well does not weaken as it did with increasing temperature but intensifies. The consumption of OH is intensified at higher pressures, with no production of OH for the bottom of the well for 5 atm.

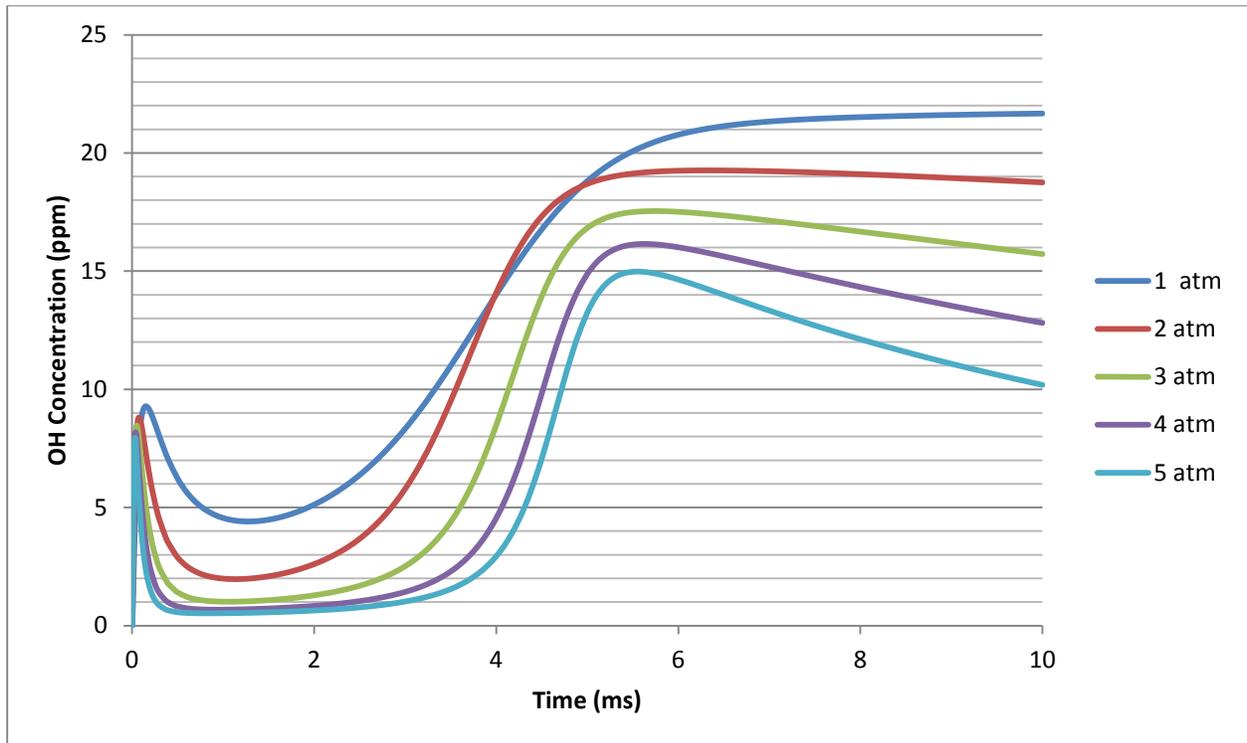


Figure 12: Effect of Pressure on the Production of OH

The well also lasts longer as the pressure increases. At one atmosphere, the well shows an immediate rebound after bottoming where at 5 atmospheres, the bottom of the well lasts for 2 ms. Another trend shown in the graph is that the OH concentration does not plateau after the well at higher pressures. These trends show that OH is consumed at a greater rate for increasing pressures. Unlike with temperature variation where the production steadied after recover, the consumption of OH does not seem to match the generation of OH. Another example of the increase in OH consumption is the larger amounts of OH at lower pressures. The peak value for OH has a significant decrease with increasing pressure. Both the initial peak, well bottom and the max OH composition are at a maximum for 1 atm.

Further investigation of the initial OH peak shows some interesting trends (Figure 13). The initial rate of production for OH is greater for higher pressures. This initial rate of production occurs before OH begins to be consumed. Although the initial rate is greater at higher pressures, the consumption of OH starts earlier and also occurs at a higher rate. This more rapid use of OH causes the initial peak in OH composition to occur both at a lower amount and earlier in the combustion process.

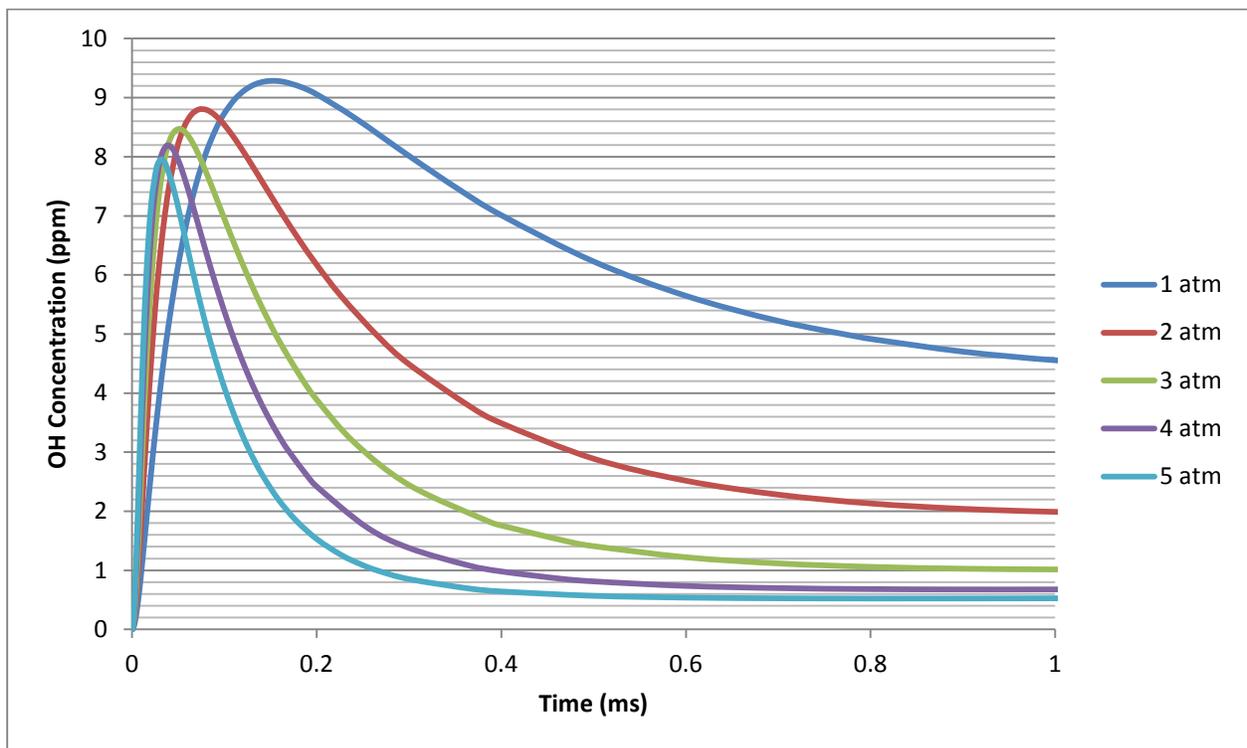


Figure 13: Effect of Pressure on Initial OH Peak

The pressure seems to affect the timing of the two peaks differently. It is clear from Figure 13 that the initial peak occurs at an earlier time for higher pressures but the second peak or plateau seems to occur at the same time. This second peak represents the tapering off of the creation of

OH. Since this occurs at the same time, it can be determined that the pressure has no effect on this incident.

4.2 Shock Tube Simulations - Kasimir 3

Kasimir 3 is a program for the simulation of shock tubes. The program was used to model two different facilities. The first facility modeled was the shock tube currently in construction at the University of Central Florida. This facility focuses on low-pressure combustion experiments and features several features to facilitate optical measurements. The second facility modeled was the high-pressure shock tube at the University of Florida. This facility was designed to look at temperatures as high as 2500 K.

The Kasimir 3 program requires little information for modeling of shock tubes relying on the 1-D shock equations to determine the pressure and temperature behind the reflected shock waves. After inputting the length of both the driver and driven sections, selecting the gases, and the driven pressure, one must only select the desired shock velocity or the driver pressure. Once the four parameters have been selected, the wave diagram is produced. The wave diagram is a graph that shows the time versus the length of the shock tube, where the lines represent various parts of the experiment including the shock wave, contact surface and expansion waves. An example of a wave diagram created for the UCF shock tube is presented below (Figure 14). Simulations for Kasimir allow a user to plan for many variables before starting experiments in a shock tube. Information such as the initial temperature and pressure that were inputs for Chemkin Pro are easily obtainable from Region 5. This simulation allows the researcher to be able to gain more accurate and more repeatable results. The simulations ran in the Kasimir 3 program included

pressure and temperature variations and the effects of various driver gases. In order to compare the results from chemical kinetic modeling and improve the models, experimentation must be conducted. See the Appendix for Tables showing the various simulations and there results.

The effect of the initial temperatures of both the driver and driven sides was considered using Kasimir. Both sides showed a positive correlation between performance of the shock tube and temperature. The result is understandable as the energy of the system would allow for greater shock strength. One means for the increase in shock strength would be the increase in the speed of sound with increasing temperatures. As the ratio of temperatures between the test region T_5 and the initial driven temperature T_1 is dependent on the Mach speed, the increase in temperature causes a rise in test temperature allowing for a greater amount of variation in the testable conditions. The same effect can be seen with an increase in the driver temperature. This increase results in the particles having a larger amount of energy and thus the need for a smaller pressure ratio between the driver and the driven sections to reach the same temperature.

The variation of pressure on shock tube performance was also examined using the Kasimir 3 program. The pressure ratio between the driver and driven sections of the shock tube determines the Mach number. As a result temperature can be held constant in the test section by holding the pressure ratio, P_4/P_1 , constant. This allows the actual pressures to increase causing the pressure in the test section to vary independently with the pressure.

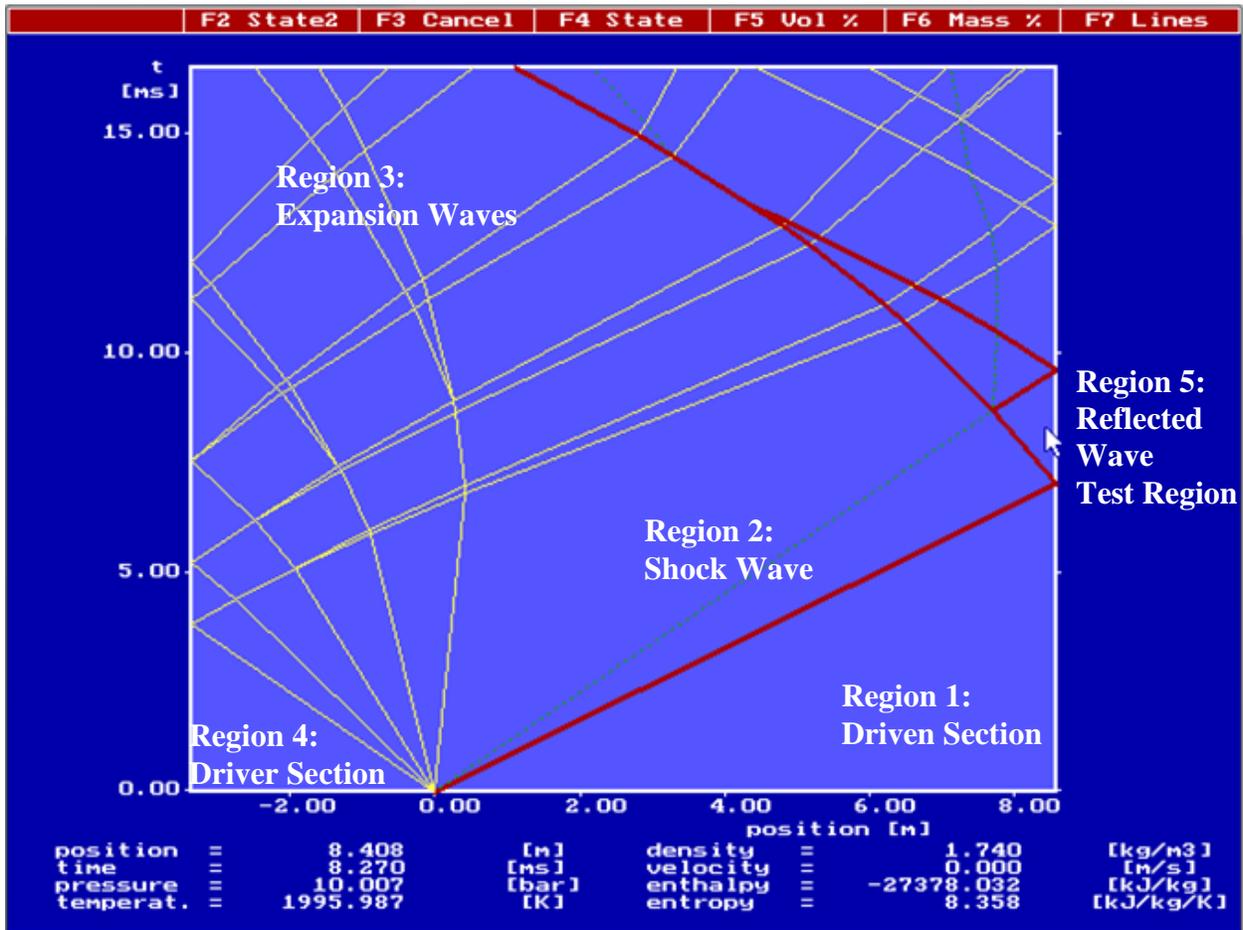


Figure 14: Typical Wave Diagram from Kasimir

One final variable was considered using the program; the effect of various driver gases. It was determined that the molecular weight played a crucial role in the performance of shock tubes. Molecules that are small such as helium were capable of reaching much higher temperatures at smaller pressure ratios. It only took a pressure ratio of $P_4/P_1 = 64.775$, to reach a temperature of 2200 K for helium, while it took a pressure ratio of $P_4/P_1 = 2370.465$ to reach the same value for Nitrogen. At the same time, the test time, the time between the initial shock wave reflection and its return, is much greater for larger molecules. The test time for helium at a temperature of 1000 K was 3.54 ms. At the same conditions nitrogen had a test time of 7.047 ms. Another issue with

the smaller gases is the contact surface. Represented as dashed line on the wave diagram, the contact surface is the separation between driver and driven gases. At lower Mach numbers, the contact surface is overtaken by the expansion waves, reducing the test times. This is a result of the expansion waves moving at a greater rate for the smaller molecules. Because of the dual nature of the driver gas, careful consideration must be paid to the nature of the experiments.

Chapter 5: Development of an OH Optical Sensor

An OH optical sensor was developed as part of this thesis to measure OH time-histories. The OH sensor is based on the design by Su et al. [45]. The system will be used to measure the ignition delay times of diisopropyl ketone and provide accurate time sensitive data for speciation studies. In this chapter, the OH sensor will be discussed in detail focusing on the need, theory, development, operation, and other uses for the device.

5.1 Current Methods for OH Optical Measurements

Currently, there are only two methods for the measurement of OH optical measurements. As OH is an intermediate species, optical measurements are the only method for measuring the production of OH during combustion. The first method for measuring OH is using laser-induced fluorescence [12]. This method uses a ring-dye laser that is shined through the test region of the test section. The other method that has been developed for OH optical measurements is through the use of a microwave discharge lamp. This method was developed by Dr. Meng-Cheh Su and Dr. Joe Michael at Argonne National Labs. Their method used a multi-pass system with a White Cell to create a long pathway for absorption. The system developed at the University of Central Florida will allow for OH time histories to be accurately recorded during the combustion of diisopropyl ketone.

5.2 Theory behind OH Optical Sensor

The microwave discharge lamp uses the principles of the Beer-Lambert Law with absorption spectroscopy to measure the OH time-histories during the combustion process. By exciting water molecules flowing through the lamp, light is emitted by OH radicals. Since light emitted by the

excitation of a molecule is capable of being absorbed by that molecule, the light is then absorbed by the OH molecules produced during combustion. The amount of OH can then be determined using the Beer-Lambert Law,

$$\frac{I}{I_0} = e^{-\sigma LN}$$

where I/I_0 is the ratio of intensity, σ , is the absorption cross-section, L is the path-length of the light and N is the number density of the molecule. The Beer-Lambert Law is applied to OH by measuring a particular wavelength of light. The wavelength in question is 308 nm. As OH is the only species in the combustion process to produce light around this wavelength, it was determined to be the optimal wavelength to measure [46].

5.3 Development of OH Optical Sensor

Two different systems were considered for the OH optical system. The first method was to redesign the multi-pass system developed by Su et al. [45]. After reviewing the system and comparing the experimental condition, it was determined that a multi-pass system was not necessary. This was determined by comparing the amount of fuel used in the planned experiments. The experiments conducted at Argonne National Labs were only measuring small amounts of fuel, around 5 to 10 ppm. A multi-pass system was necessary for Argonne National Labs because of the number density present to increase absorption. As the experiments planned are at 50 ppm of fuel, it was determined that a multi-pass system would be not be necessary.

After determining that a single pass system was all that was required for the optical sensor, other aspects of the system could be developed. The system uses two 1" Plano-convex lenses from

Newport with a 7.5 cm focal length to focus the light on either side of the shock tube. A 1" square mirror was used to after the second lens to redirect the light 90°. The mirror helps to minimize the space taken by the optical system and to remove portions of the light that were not focused. The light then shines through an interference filter from Edmund Optics with a 310 nm, 10 ± 2 nm FWHM band pass before being fed to a 203-2032 photo-detector from Newport. Figure 15 is a schematic of the optical system setup.

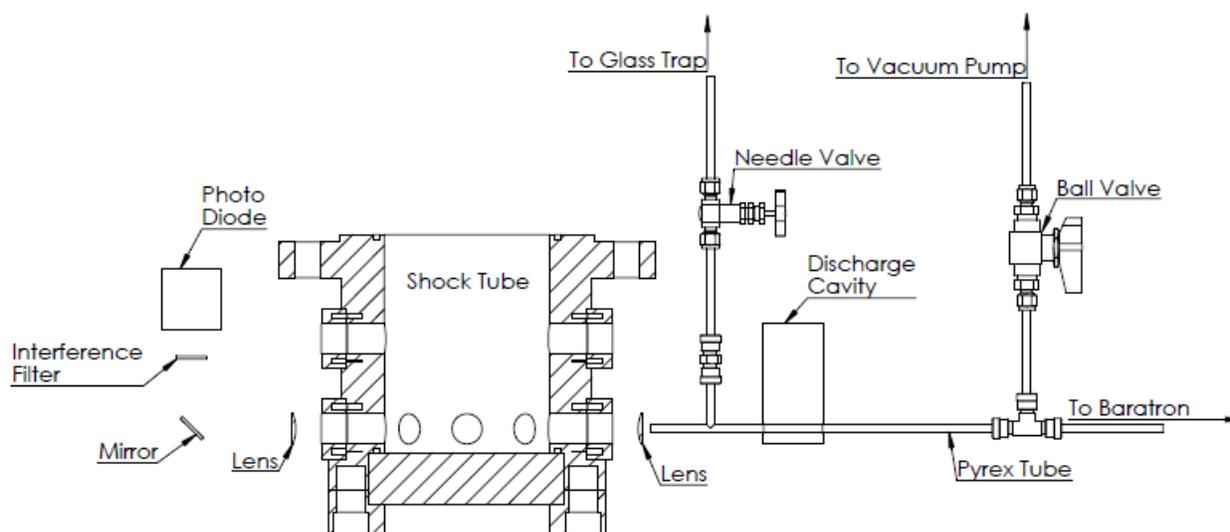


Figure 15: Optical Sensor Schematic

The resonance lamp was custom made by Chemglass. It consists of a 12" long Pyrex tube with a 1/4" o.d. The resonance lamp uses a reverse flow configuration to circulate gas through the system. A needle valve, attached to a 500 mL glass vacuum trap (CG-4529-01 from Chemglass) filled with distilled water is attached to Argon. The needle valve is used to control the pressure in the chamber for the microwave generator. At the rear of the tube, the Pyrex tube is attached to a ball valve that is then connected to a rotary vacuum pump. A baratron is used to monitor the pressure in the lamp for optimal performance of the microwave discharge.

A GMP150 microwave generator from Opthos is used to create the light. The microwave generator is attached to a Evenson Discharge Cavity. The Evenson Cavity was chosen for the system as it is capable of exciting both static and flowing gases. As there are many potential uses for the microwave discharge lamp beyond OH, it was determined that this was ideal.

5.4 Operation of OH Optical Sensor

The microwave discharge lamp must be operated at specific conditions to create light at 308 nm. The pressure must be maintained at 4-6 torr. This is accomplished by altering the flow rate using the needle valve and the ball valve. After the required pressure was maintained, the microwave generator was turned on to between 50 and 100 W. The discharge is then ignited using a high frequency igniter coil from Opthos. This igniter coil provides a sharp spike in energy to cause the initial excitation. As the discharge is created, careful consideration of the reflected power in the microwave generator had to be observed. The reflected power was minimized by using tuning forks on the discharge cavity. The discharge cavity was air-cooled using compressed air fed into the cavity. A VI was created to measure the intensity of the light.

5.5 Other Uses for the Microwave Discharge Lamp

Microwave discharge lamps produce ultraviolet light based on the substance that is flowed through the lamp. A survey done by Davidson and Hanson show a variety of uses for such a lamp over a range of wavelengths between 151 nm and 450 nm[47]. The table below shows a compilation of their survey. Microwave discharge lamps can also go to lower wavelengths. Another survey from Michael and Lifshitz found articles that used a similar discharge lamp setup

to measure species as low as 120 nm[48]. In this survey, H atoms were measured at wavelengths of 121.567 nm. O atoms and N atoms were also measured at similar wavelengths.

Table 1: Survey of Different Studies using Lamp Diagnostics [47]. (Used without permission).

Wavelength (nm)	Species	Method	Reference
151.0	CO	μ wave Discharge Lamp	(Frank <i>et al.</i> , 1986; Markus, 1995)
174.4	C ₂ H ₄	μ wave Discharge Lamp	(Saito <i>et al.</i> , 1995; Zelson <i>et al.</i> , 1994)
206.2	HN ₃	Iodine Lamp	(Kajimoto <i>et al.</i> , 1979)
213.9	CH ₃	Zinc Lamp	(Baeck <i>et al.</i> , 1995; Hwang <i>et al.</i> , 1993)
216.6	CH ₃	Xe-Hg Lamp	(Hwang <i>et al.</i> , 1988; Moller <i>et al.</i> , 1986)
226.1	HO ₂	Lamp	(Kijewski and Troe, 1971)
230.0	HO ₂	Lamp	(Hippler <i>et al.</i> , 1990b)
230.0	N ₂ O	Xe Lamp	(Endo <i>et al.</i> , 1979)
250.0	CINO	Xe Lamp	(Endo <i>et al.</i> , 1979)
250.0	O ₂	Xe Lamp	(Endo <i>et al.</i> , 1979)
254.0	O ₃	Xenon Lamp	(Takahashi <i>et al.</i> , 1995a)
260.0	NF ₂	Deuterium Lamp	(Koudriavtsev <i>et al.</i> , 1995)
260.0	Benzyl	Xe-Hg Lamp	(Hippler <i>et al.</i> , 1990a)
265.0	2-Methylbenzyl	Xe-Hg Lamp	(Hippler <i>et al.</i> , 1994)
303.4	NH	Hg Lamp	(Szekely <i>et al.</i> , 1984b)
306.5	OH	μ wave Discharge Lamp	(Bott and Cohen, 1984; Bott and Cohen, 1989; Hidaka <i>et al.</i> , 1982)
339.0	BrO	Xe Lamp	(Takahashi <i>et al.</i> , 1995a)
388.4	CN	Hg Arc Lamp	(Louge and Hanson, 1984b; Szekely <i>et al.</i> , 1983a; Szekely <i>et al.</i> , 1983b; Szekely <i>et al.</i> , 1984a; Szekely <i>et al.</i> , 1984b; Szekely <i>et al.</i> , 1984c; Szekely <i>et al.</i> , 1984d)
405.0	NO ₂	Xe Lamp	(Endo <i>et al.</i> , 1979)
415.0	Br ₂	Xe Lamp	(Takahashi <i>et al.</i> , 1995a)
421.6	CN	Xe Lamp	(Fueno <i>et al.</i> , 1973)
450.0	NO ₂	Tungsten Lamp	(Fifer and Holmes, 1982)

Another use for the microwave discharge lamp is the detection of various types of metals. Microwave discharge lamps have been used to measure lead, mercury, strontium, manganese and uranium) found in an introduction section from [49], who were investigating fluorine.)

Chapter 6: Planned Experiments

In order to improve chemical kinetic modeling, experiments must be performed and compared to the model. Experiments using two distinct shock tube facilities are currently planned for the near future. These experiments will help validate the model developed for DIPK and to point out areas that need to be improved. Shock tubes were determined to be the best method for validation as the experimental conditions are both controllable and repeatable.

6.1 Necessity of Experiments

Currently, there are only two experimental data points for the ignition delay times of DIPK [50]. These data points are for temperatures of around 1000 K. The problem with the data points is that they show much lower ignition delay times than the model. The model shows that the ignition delay for 950 K should be 24.6 ms but the measured value was only 3.5 ms. To further improve the model, experiments must be performed that can help to understand and improve the chemical kinetic model.

6.2 Experimental Conditions

The planned experiments will explore both the ignition delay times and the production of OH behind reflected shock waves. The experiments will cover a temperature range of 700 to 1500 K for the ignition delay times and up to 2000 K for OH production. The pressures at the test section will to be looked at will be vary between 1 and 10 atm. The effect of equivalence ratios will also be examined were $\Phi = 0.5, 1.0$ and 2 .

6.3 Shock Tube at the University of Central Florida

The facility currently in development at the University of Central Florida is designed for low pressure experiments.

The shock tube at the University of Central Florida is made of 6" schedule 120 Pipe with an inner diameter of 5.501". The shock tube consists of a 4.88 m driver section. The driven section is 6.73 m long and the test section is an additional 1.81 m. The driven and test sections were honed and electro-polished to provide a smooth surface for minimal boundary layer effects. The shock tube will use plastic diaphragms in conjunction of a cutter located directly behind the diaphragm. As the pressure increases in the driver section, the diaphragm will bulge and eventually hit the metal blades. This will allow the pressure ratios to be controlled in the facility as well as ensure ideal rupturing of the diaphragms. The shock tube will be able to record the shock velocity and attenuation as it approaches the end wall using 5 rapid response PCB 113B26 Pressure transducers. Two Kistler pressure transducer, one mounted to the side and another in the end wall, will measure the pressure trace of P_5 . This pressure trace can then be used to measure the ignition delay times. The driven section can also be heated to 200 °C if needed. This allowed us to eliminate some of the discontinuities with the temperature and improve the performance of the shock wave as shown with Kasimir 3. A 40 L mixing chamber will be used to ensure uniformity of the test gas. The shock tube will be evacuated to approximately 6 μ torr after each run using an Agilent V301 turbo-molecular vacuum pump. The shock tube is designed with optical side access for the OH optical sensor. The sensor can be used in conjunction with the

device to record the OH time history for both the ignition delay times and to study the OH production.

The experiments that will be performed in this shock tube will be ignition delay times for the low pressures. This facility will also handle all of the OH production experiments. These experiments require low pressures and are performed with small amounts of fuel present and require the use of a turbo-molecular pump for experimentation.

6.4 Shock Tube at the University of Florida

The facility at the University of Florida will provide additional ignition delay and will be able to go beyond the pressure limits of the other facility. As shown by the model, ignition delay times can vary significantly with the initial pressure.

The shock tube consists of a 6.1 m driven section made from 4-in seamless pipe. The driver section is 1.8 m in length and made from the same 4-in seamless pipe. A separate test section, 1.24 m in length, is made of stainless steel pipe and has an inner diameter of 3.5 cm. The test section is separated by a Mylar sheet with a thickness of 0.0005 in. The driven and test sections will be vacuumed using a DS102 PH Rotary Vane Vacuum Pump from Agilent Technologies. The thin film is to prevent circulation of the fuel throughout the driven section and is considered small enough to have minimal effect on the combustion of the fuel as seen in Mikolaitus et al. [51]. The fuel is circulated through the test section using an oil-less pump for 15 minutes to establish a uniform mixture. The shock velocity will be established using three PCB 113A26 dynamic pressure transducers. The reflected temperature and pressure will then be calculated

using the shock velocity. The ignition delay times can be calculated using a Model 203-2032 photo-detector, from Newport, mounted with a 310 nm with a 10 ± 2 nm FWHM bandwidth filter from Edmund Optics on the end wall.

Chapter 7: Conclusions

The oxidation of diisopropyl ketone has been simulated using chemical kinetic modeling. The ignition delay times as well as the production of OH have been studied. Experiments have been planned at two different shock tube facilities to validate the model. The experiments were simulated using the Kasimir 3 program in order to match the conditions of the modeling with the pre-experimental shock tube conditions. The development of an OH optical sensor has also been described for the use in recording the OH time histories for both ignition delay measurements and OH time histories.

The comparison of DIPK to the other four fuels shows several important trends. The simulations from Chemkin Pro show that DIPK has a strong similarity with is-octane. At an initial pressure of 10 atm, both fuels exhibit the same behaviors at similar temperatures. This includes the start of the negative slope that begins the negative temperature coefficient region. This is different than n-heptane who undergoes the full NTC behavior at higher temperatures than the other two fuels. Another trend occurs with the production of OH. Both fuels show similar dips in OH concentration after the initial rise. Iso-octane is a surrogate fuel for gasoline and the similarities in combustion show that DIPK may be an effective alternative for gasoline based engines. DIPK also showed improved performance compared to n-butanol and ethanol at low temperatures. Both of these fuels had ignition delay times that continued to rise, approaching infeasible lengths of time for engines, which is caused by a lack of adequate chemistry modeling at these temperatures.

The effects of pressure and equivalence ratio were also explored for DIPK in regards to ignition delay. At higher pressures, more commonly associated with diesel engines, the ignition delay times begin to behave more similarly to n-heptane. The curve of the ignition delay times is shifted down and to the left, displaying the same NTC behavior as n-heptane did. This trend, a necessity for diesel engines shows that further investigation of DIPK at higher pressures is needed for comparison.

As experimental results for DIPK are scarce, the data that will be gathered from the planned experiments will be used to validate and improve the current chemical kinetic model. The improvements of the chemical kinetic model will help to better understand the combustion process of diisopropyl ketone.

Appendix

Kasimir Simulations

Independence of Pressure and Temperature in Test Region

Table 2: Pressure (P₅): 1 atm

P ₅ (Bar) Actual	T ₅ (K) Ideal	T ₅ (K) Actual	M _D	P ₁ (Bar)	P ₄ (Bar)	P ₄ /P ₁
1.056	2000	1995.990	2.80	0.025	1.240	49.600
1.055	1800	1800.911	2.63	0.030	1.117	37.233
1.023	1600	1607.127	2.45	0.036	0.982	27.278
1.004	1300	1303.735	2.14	0.054	0.842	15.593
1.002	1000	997.989	1.78	0.100	0.767	7.670
0.999	700	704.653	1.37	0.263	0.785	2.985

Table 3: Pressure (P₅): 2 atm

P ₅ (Bar) Actual	T ₅ (K) Ideal	T ₅ (K) Actual	M _D	P ₁ (Bar)	P ₄ (Bar)	P ₄ /P ₁
1.984	2000	1995.990	2.80	0.047	2.332	49.617
1.969	1800	1800.911	2.63	0.056	2.085	37.232
2.046	1600	1607.127	2.45	0.072	1.965	27.292
2.008	1300	1303.735	2.14	0.108	1.684	15.593
2.004	1000	997.989	1.78	0.200	1.534	7.670
2.002	700	704.653	1.37	0.527	1.574	2.987

Table 4: Pressure (P₅): 3 atm

P ₅ (Bar) Actual	T ₅ (K) Ideal	T ₅ (K) Actual	M _D	P ₁ (Bar)	P ₄ (Bar)	P ₄ /P ₁
2.956	2000	1995.990	2.80	0.070	3.473	49.614
2.954	1800	1800.911	2.63	0.084	3.128	37.238
2.984	1600	1607.127	2.45	0.105	2.865	27.286
2.994	1300	1303.735	2.14	0.161	2.510	15.590
3.006	1000	997.989	1.78	0.300	2.301	7.670
3.001	700	704.653	1.37	0.790	2.359	2.986

These tables show how the pressure, P₅, and the temperature, T₅, vary independently of each other. The temperature is dependent on the pressure ratio P_4/P_1 , while the pressure is a function of the actual pressures in the driver and driven sections. The simulations were modeling the shock tube at the University of Central Florida. These calculations were performed using helium as the driver gas.

Effect of Variations in Driver Temperature

Table 5: Temperature (T₅): 900 K

T ₄ (K) Actual	P ₁ (Bar)	P ₅ (Bar) Actual	T ₅ (K) Actual	u (m/s)	M _D	P ₄ (Bar)	P ₄ /P ₁
300	0.150	3.819	901.561	810	2.32	13.477	89.847
400	0.150	3.819	901.561	810	2.32	8.853	59.020
500	0.150	3.819	901.561	810	2.32	6.721	44.807
600	0.150	3.819	901.561	810	2.32	5.502	36.680

Table 6: Temperature (T₅): 1000 K

T ₄ (K) Actual	P ₁ (Bar)	P ₅ (Bar) Actual	T ₅ (K) Actual	u (m/s)	M _D	P ₄ (Bar)	P ₄ /P ₁
300	0.150	4.757	999.071	870	2.49	22.218	148.120
400	0.150	4.757	999.071	870	2.49	13.657	91.047
500	0.150	4.757	999.071	870	2.49	9.950	66.333
600	0.150	4.757	999.071	870	2.49	7.916	52.773

Table 7: Temperature (T₅): 1100 K

T ₄ (K) Actual	P ₁ (Bar)	P ₅ (Bar) Actual	T ₅ (K) Actual	u (m/s)	M _D	P ₄ (Bar)	P ₄ /P ₁
300	0.150	5.811	1101.147	930	2.67	36.734	244.893
400	0.150	5.811	1101.147	930	2.67	21.015	140.100
500	0.150	5.811	1101.147	930	2.67	14.657	97.713
600	0.150	5.811	1101.147	930	2.67	11.314	75.427

These tables show how the driver temperature affects the shock tube performance. As the driver temperature increases, the pressure ratio P_4/P_1 is reduced allowing for higher temperatures to be reached more easily. These simulations were based on the shock tube facility at the University of Florida. The driver gas for these simulations was Nitrogen.

Differences between Various Driver Gases

Table 8: Helium - Pressure (P₅): 10 atm

P ₅ (Bar) Actual	T ₅ (K) Ideal	T ₅ (K) Actual	M _D	P ₁ (Bar)	P ₄ (Bar)	P ₄ /P ₁
9.989	2200	2202.87	2.97	0.2	13.155	65.775
10.146	1900	1908.474	2.725	0.26	11.373	43.742
10.231	1600	1607.127	2.45	0.36	9.823	27.286
10.227	1300	1303.735	2.14	0.55	8.574	15.589
10.019	1000	997.989	1.78	1	7.67	7.670
10.257	700	704.653	1.37	2.7	8.062	2.986

Table 9: Helium - Pressure (P₅): 20 atm

P ₅ (Bar) Actual	T ₅ (K) Ideal	T ₅ (K) Actual	M _D	P ₁ (Bar)	P ₄ (Bar)	P ₄ /P ₁
9.989	2200	2202.87	2.97	0.2	13.155	65.775
10.146	1900	1908.474	2.725	0.26	11.373	43.742
10.231	1600	1607.127	2.45	0.36	9.823	27.286
10.227	1300	1303.735	2.14	0.55	8.574	15.589
10.019	1000	997.989	1.78	1	7.67	7.670
10.257	700	704.653	1.37	2.7	8.062	2.986

Table 10: Nitrogen - Pressure (P₅): 10 atm

P ₅ (Bar) Actual	T ₅ (K) Ideal	T ₅ (K) Actual	M _D	P ₁ (Bar)	P ₄ (Bar)	P ₄ /P ₁
9.989	2200	2202.869	2.97	0.2	474.093	2370.465
10.146	1900	1908.475	2.725	0.26	228.741	879.773
9.947	1600	1607.127	2.45	0.35	107.696	307.703
10.041	1300	1303.735	2.14	0.54	53.144	98.415
10.019	1000	997.989	1.78	1	26.386	26.386
10.067	700	704.653	1.37	2.65	14.277	5.388

Table 11: Nitrogen - Pressure (P₅): 20 atm

P ₅ (Bar) Actual	T ₅ (K) Ideal	T ₅ (K) Actual	M _D	P ₁ (Bar)	P ₄ (Bar)	P ₄ /P ₁
19.978	2200	2202.869	2.97	0.4	948.186	2370.465
19.903	1900	1908.474	2.725	0.51	448.683	879.771
19.894	1600	1607.128	2.45	0.7	215.393	307.704
20.083	1300	1303.735	2.14	1.08	106.289	98.416
20.038	1000	997.989	1.78	2	52.773	26.387
19.944	700	704.653	1.37	5.25	28.284	5.387

These tables show the greater pressure ratios needed to reach the same temperatures. This shows the infeasibility of using heavier gases for high temperature testing. These simulations were based on a theoretical high pressure shock tube.

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