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DATA-DRIVEN CHEMICAL KINETIC MODELS OF OPERATIONALLY RELEVANT JET
FUELS

BY

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DISSERTATION

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ABSTRACT

This dissertation assesses the autoignition characteristics of operationally relevant fuels and develops chemical kinetic mechanisms based on a data-driven approach. Recent interest in sustainable aviation fuels (civilian) and single-fuel policies (military) in the US necessitates a detailed understanding of the effect of various jet fuels' properties on auto-ignition behavior. Fuels can dramatically differ in combustion and emissions characteristics due to fuel properties and chemical composition differences. This variation can come from differences in geographical locations or even the introduction of new alternative fuel blends into the common pipeline and just being different fuels. It is common knowledge that the Cetane number is a representative metric that summarizes combustion characteristics across a range of fuel relevant properties. However, there is no concrete relationship between cetane number and chemical reactivity.

To investigate the impact of various fuels on combustion characteristics, two different sets of cetane number (CN) varied fuels: F-24/ATJ blended fuels and varied CN controlled fuels, are evaluated. These two experiments can explore the effect of CN and chemistry on autoignition properties with minimized atomization and physical properties, respectively. Assessing the ignition behavior of fuels is done by analyzing zero-dimensional chemical ignition delay data for subsequent analysis of gas-phase reactivity from rapid compression machine (RCM) and shock tube experiments at a compressed pressure of $P_C = 2$ MPa and three different equivalence ratios in synthetic dry air, between 700 K and 1250 K. These conditions are of interest because they can cover a wide range of practical combustion operations, including internal combustion engines and gas turbines. Typically, the reactivity is linearly proportional to the cetane number. However, the results showed that derived cetane number (DCN) could not be used as the sole predictor of

ignition delay across the range of thermodynamic conditions relevant to propulsion systems. This dissertation will directly and with more detail show the connection between DCN and chemical composition effects on ignition. Combustion and reaction pathways are affected mainly by the structure of chemical components through fuel breakdown, hydrogen abstraction, and isomerization. The main components of jet fuels can be divided into three groups: normal-alkane, cyclo-alkane, and iso-alkane. In the high-temperature regime, the branched structure of iso-alkanes results in the decomposition of fuel into tertiary radicals easily, but its stable states hinder oxidization. In the intermediate and low-temperature regimes, H-abstraction and radical isomerization in branched structures retards the ignition delay due to its high number of primary C-H bonds. With regard to blending ratio, a non-linear relationship between blending ratio and ignition characteristics has been observed. The reactivity of blends likely tends to follow the component of the blended fuel with higher reactivity. When the more reactive fuel undergoes the chain branching step in the mixture system, it will sufficiently provide OH radicals and heat to the system. The variation and/or similarities in ignition behavior observed amongst fuels arises from the inherent chemical structure of fuel components.

To obtain chemical kinetic mechanisms for the fuels in this study, data-driven optimization methodology is employed, and ARLMech-HC-F24ATJ and ARLMech-HC-VariedCN were introduced for numerical simulation of the ignition process herein. The mechanisms follow the HyChem approach, which includes fuel-dependent lumped reactions and detailed C0-C4 chemistry based on combustion chemistry. Rather than modifying detailed small hydrocarbon chemistry, fuel-dependent lumped reactions are optimized toward empirical ignition delay data by genetic algorithm optimization of reaction coefficients. To express the non-linearity blending effects under intermediate and low-temperature chemistry, an alkylation (also known as co-

oxidation) reaction was considered for the F-24/ATJ blend mechanism. Unlike F-24 and ATJ mechanisms, mechanisms for varied CN fuels were started from scratch. The lumped chemical equations were formulated to satisfy the HyChem theory and chemical composition analysis from GCxGC results. This approach can be used as the mechanism development methodology for next-generation 'drop-in' fuels. The newly introduced data-driven mechanisms based on these techniques show a good performance and more accurately represent the ignition behavior than mechanisms created without using these techniques. The developed mechanisms were also used for solving practical combustion problems to examine the fuels' effects on combustion characteristics. The results provided a qualitative understanding and overall prediction of ignition behaviors and were able to validate other published experimental results.

The experimental data in this dissertation will provide a guideline and insight regarding the autoignition characteristics of various fuels: conventional hydrocarbon fuels and alternative fuels. Moreover, the suggested data-driven based chemical kinetic mechanisms and development methodology can be applied to real combustion problems with computational fluid dynamic simulations to evaluate the combustion appropriateness of newly introduced fuels.

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To my family

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Chapter 1 Introduction

1.1 Background and Motivation for Research

Hydrocarbons have always contributed as a major energy source and now account for 85% of global energy consumption. Petroleum fuels are mixtures of hydrocarbons and organic matter refined from crude oil [1]. Between 2009 and 2019, before COVID, end-use energy consumption in the transportation sector has been increased by about 25 %. Remarkably, air traffic passengers nearly doubled, and the number of flights increased about 60 % [2]. According to the US Energy Information Administration, global energy use in transportation will be increased by nearly 50% compared with 2020, resulting from non-OECD economic growth and population [3]. The growth of the world's population will increase demand for passenger and freight travel. Although electricity usage grows faster than petroleum use, hydrocarbon-based petroleum liquids, including motor gasoline, distillate, and jet fuel, continue to grow and take a large portion of the demand for transportation energy over the next 30 years.

Due to refinement, storage, and transportation advantages, petroleum-derived liquid fuels have widely been integrated into the global energy infrastructure. Petroleum liquid fuels are derived by refining crude oil. Since the compositions of crude oil feedstocks vary depending on region, well type, and time of year, variations in the final refined fuel compositions are common. Due to restrictions of refining processes: separation, conversion, and treatment process, the most prevalent components found in petroleum fuels are paraffin (alkanes), olefins (alkenes), naphthene (cycloalkanes), and aromatics [4,5]. Different refining processes result in various petroleum-based fuels such as gasoline, kerosene, and diesel. Each type of fuel usually contains numerous chemical compounds and attributes to different energy density, combustion, and emission characteristics.

Conventionally, longer carbon chains (e.g., diesel) and higher bond orders (e.g., a high portion of alkene) contain greater amounts of stored energy [6].

On the other hand, there are two representative drawbacks of using petroleum-based fuels: environmental and economic issues. The products of hydrocarbon-based fuel combustion have a harmful influence on the environment contributing to global warming and potential hazards to people. The major harmful pollutants resulting from combustion are sulfur oxides (SO_x), nitrogen oxides (NO_x), carbon monoxide, and unburned hydrocarbons (UHCs). The accumulation of harmful gases in the Earth's atmosphere causes rising temperatures, which is believed to be a major contribution to global climate change [7–9]. In addition to environmental issues, petroleum-based fuels are at risk of depletion due to the specific timeframe for Peak Oil and anticipation of the limited resource of fossil fuels globally [10]. Although new strategies such as improved fracking techniques and the introduction of non-conventional petroleum resources [11], specifically oil sands and oil shale have increased conventional oil production in recent years, global demand for petroleum liquid fuels continues to rise as the world population and developing countries grow. As crude oil becomes more limited, prices will be expected to rise with the potential risk of political and economic turmoil globally.

In response to hydrocarbon issues, current hydrocarbon-based energy systems need to undergo an epochal evolution either gradually or radically to improve power density and efficiency and resolve environmental issues. One of the solutions is a surge in the development of alternative fuels, which will alleviate the current dependence on crude oil.

The National Jet Fuels Combustion Program (NJFCP) was established to assess the relationship between composition and combustion characteristics for 'drop-in' fuel development [12]. The US Department of Energy investigates fuels and engines as dynamic design variables

that can work together to boost efficiency and performance while minimizing emissions in their co-optimization of fuels & engines (Co-optima) program [13]. To implement the integration of drop-in fuels with existing infrastructure while minimizing changes to existing propulsion systems, it is imperative to understand the characteristics of the autoignition behavior of hydrocarbons. Fuel properties and chemical compositions can differ depending on extraction and refining locations or even introducing new alternative fuels into the existing fuel stock. Varied properties of fuels can result in dramatically different combustion and emissions characteristics.

To streamline the testing/approval process [12], chemical kinetic models can predict overall fuel reactivity at a particular condition and calculate the chemistry parts of numerical simulations. Developing surrogate-based chemical kinetic models for real fuels also requires considerable effort to validate the surrogate components' multiple physicochemical properties and combustion kinetic models. Moreover, a blend of several well-known chemicals in low-temperature chemistry may not work well due to the non-linear blending effect which has not been systematically studied yet.

1.1.1 Sustainable Aviation Fuels (SAFs) and Alternative Fuels

Due to environmental concerns, sustainable aviation fuels (SAFs) have recently been proposed to unlock the potential for zero-carbon emission for commercial aviation [14]. In September 2021, the White House announced a new Sustainable Aviation Fuel Grand Challenge to increase annual sustainable aviation fuel (SAF) production to at least 3 billion gallons by 2030 [15]. This plan results from several key drivers: economic incentives, energy security, and environmental considerations. Not only high price volatility is occurring in the global fuel market, but the fuel price has also skyrocketed more than 70% in 2021 alone [16]. It is anticipated that the price will fluctuate and soar due to current concern about economic inflation after COVID and the 2022

Russian invasion of Ukraine [17,18]. The second key driver for AJF development is energy security in combat operations. The US government wants the advantage in having secure domestic energy resources not subject to political conflicts [19,20]. Finally, SAF may have the potential solution to environmental issues caused by the usage of petroleum-based fuels.

The International Civil Aviation Organization (ICAO) defines Alternative Jet Fuel (AJF) as any fuel derived from an unconventional (non-petroleum-based) feedstock [21]. Among various feedstocks, the most suitable sources to produce AJFs are biofuels. Firstly, domestically produced biofuels can improve energy independence and energy security. Secondly, the net emissions from biofuel production have been reported to be significantly lower than that of petroleum-based fuels [22]. Finally, biofuels can help rural economic development by implementing biorefineries [23]. Biofuels are energy sources derived from living matter or biomass products. AJFs can be broadly categorized as Fischer-Tropsch (FT), Hydroprocessed Esters and Fatty Acids (HEFA), Synthesized Iso-Paraffins (SIP), Synthetic Kerosene with Aromatics (SKA), Alcohol to Jet (ATJ), Catalytic Hydrothermolysis (CHJ), and Hydrocarbon Hydroprocessed Esters and Fatty Acids (HC-HEFA) according to the processing method [24].

Like the properties of petroleum-liquid fuels arising from the refining process, each biofuel possesses its own properties. Strong candidates to be used as an alternative fuel are synthetic fuels, hydrocarbon end products through thermochemical processing of biofuels. The first advantage is the compatibility of synthetic fuel with current energy infrastructure. Oxygen-containing fuels can contribute to corrosive properties that can ruin the combustion system and shorten the storage period [25]. Moreover, the produced fuels can easily be tailored and applied to current infrastructure due to the similar structures between petroleum-based and synthetic fuels. Finally,

synthetic fuels can be purified through cleaning technologies built into the thermochemical production process removing harmful contents such as sulfur and nitrogen.

Although the production of synthetic fuels is not currently competitive in terms of price, it will be economically feasible under high oil prices ($\sim \$100/\text{bbl}$) [26]. The production process costs and the mass production infrastructure should also be considered. On this point, biofuels can be a means to offset some crude oil fuels.

1.1.2 United States Military Goals

Before recently introduced SAFs, there have been several similar policies and programs to achieve either single-fuel or multi-fuel concepts. The purpose of the single-fuel concept (SFC), introduced after WWII is to simplify fuel supply logistics by using only JP-8 (F-34 NATO designation) jet fuel, produced from civilian Jet A-1 fuel [20,27,28]. When the US forces were in Germany in 1981, M1 and other gasoline turbine-powered engines could not be appropriately operated due to waxing and fuel filterability problems with the NATO's standard diesel fuel (F-54). During the war, the problem was solved by blending F-54 with aviation kerosene fuels to lower the viscosity of the F-54 fuels. The United States Department of Defense (DOD) issued a directive on fuel standardization, as the purpose of the single-fuel concept, by adapting JP-8 as a primary fuel to resolve potential issues during combat operations. However, the "uniform" fuels used by the DoD still exhibit significant fuel property variation with respect to geographical issues [12].

To resolve handling existing fuel variation even with the single fuel and incorporate SAF's into the fuel supply, several recent efforts have investigated fuel property effects on combustion phenomena. Since the introduction of their "green" initiatives program in 2009 [29], the US Navy

has made great strides in pursuing alternative fuels for drop-in use in tactical systems. As part of this energy plan, demonstrations of tactical systems using conventional fuels blended with alternative renewable fuels will provide benchmarks towards the 2020 goal [30,31]. Reducing petroleum consumption increases energy security and independence and decreases the US Navy's reliance on vulnerable foreign fuel supplies, which can be prone to intentional, accidental, or market disruptions [29].

Finding suitable drop-in replacements for US military fuels could serve as a vital component in decreasing petroleum utilization nationally. However, current alternative fuel production is limited, expensive, and the fuels lack data for comparability and assessment relative to conventional fuels

1.2 Research Objectives

This dissertation aims to investigate the autoignition characteristics of various operationally relevant fuels and develop chemical kinetic mechanisms of fuels based on a data-driven approach by using a HyChem (Hybrid Chemistry) approach.

Two combustion facilities at the University of Illinois Urbana-Champaign – rapid compression machine (RCM) and shock tube – were employed to study fuels' ignition and oxidation chemistry over a wide range of experimental conditions. The experimental apparatuses were refined to expand the experimental conditions. To increase the testing time of shock tube, driver gas composition was tailored, and the driver end wall was modified to deviate expansion waves. Moreover, the compression ratio and initial temperature of charged gas was increased to

study ignition under higher compressed temperatures. The refined combustion facilities enabled the integration of chemical ignition delay data from both devices.

The ignition characteristics of two different sets of fuels are examined empirically. The objective of these tests was to identify fuel sensitivity to combustion chemistry and to evaluate how well cetane numbers can predict combustion characteristics. Moreover, gathered experimental data was used to develop chemical kinetic models using a data-driven approach. Then, chemical kinetic mechanisms of fuels were introduced to simulate ignition behaviors under various operating conditions.

Reporting the data and introducing mechanisms will support the possible adoption of alternative fuels in the combustion community.

1.3 Outline of Dissertation

This dissertation consists of ten chapters, and the chapters are organized as follows: Chapter 1 illustrates the background, motivation, and objective of this dissertation. Chapter 2 presents the detailed description of experimental devices used to acquire chemical ignition delay data, including test protocols, calculations of pertinent data, and uncertainty analysis. Theoretical backgrounds are explained in Chapters 3 and 4. Chapter 3 examines the chemistry of hydrocarbon oxidation and the chemical kinetic modeling used in this study. Chapter 4 explores optimization techniques and implements the methodology applied to chemical kinetic problems. Chapters 5 and 6 present empirical chemical ignition delay data regarding two different sets of fuels: F-24/ATJ blends and specially formulated CN fuels. Two experiments were conducted and compared to examine the influence of various fuels on the autoignition characteristics. By acquiring data from

Chapters 5 and 6 and the optimization techniques in Chapter 4, a data-driven approach will be utilized to develop chemical kinetic mechanisms of fuels in Chapters 7 and 8. The developed mechanism is used to solve practical combustion problems in chapter 9 to give guidance on how the results from this dissertation can be used in the real world. Chapter 10 summarizes this dissertation and provides future work related to this research.

This dissertation includes and reuses a compilation of my previous published articles and manuscripts currently in preparation. For the reference of the reader, these articles are:

Journal articles

- Min, K., Valco, D. J., Oldani, A., **Kim, K.**, Temme, J., Kweon, C. B. M., & Lee, T. (2019). Autoignition of varied cetane number fuels at low temperatures. *Proceedings of the Combustion Institute*, 37(4), 5003-5011.
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(In preparation)

- **Kim, K.**, Lee, W., Wiersema, P. W., Mayhew, E., Temme, J., Kweon, C. B., & Lee, T. Effects of the Cetane Number on Chemical Ignition Delay
- **Kim, K.**, Ryu, J. I., Lee, W., Wiersema, P. W., Mayhew, E., Temme, J., Kweon, C. B., & Lee, T. Chemical ignition behavior and data-driven modeling of alternative alcohol-to-jet (ATJ) fuel
- **Kim, K.**, Wiersema, P. W., Lee, W., Ryu, J. I., Mayhew, E., Temme, J., Kweon, C. B., & Lee, T. The assessment of F-24/ATJ blend composition on autoignition characteristics and data-driven modeling
- **Kim, K.**, Lee, G., Li, C., Wang, H., & Lee, T., Impact of NO and O Chemistry in High-Enthalpy High-Speed Reacting Flows in Ground Test Facilities
- **Kim, K.**, Wiersema, P. W., Ryu, J. I., Mayhew, E., Temme, J., Kweon, C. B., & Lee, T. HyChem based data-driven modeling of Varied CN fuels

Conference articles

- **Kim, K.**, Min, K., Temme, J., Kweon, C. B., & Lee, T. (2020). Effects of F-24/ATJ blend composition on ignition kinetics at low-temperatures. In AIAA Scitech 2020 Forum (p. 0178).
- Wood, E. J., McGann, B., Motily, A., Min, K., **Kim, K.**, Lee, T., ... & Kastengren, A. (2020). Impact of Fuel Properties on Combusting Jet Fuel Spray Breakup, Analyzed using High-Speed Phase Contrast Imaging. In AIAA Scitech 2020 Forum (p. 0522).
- **Kim, K.**, Ryu, J. I., McGann, B., Min, K., Temme, J., Kweon, C. B., & Lee, T. (2021). Data-driven combustion kinetic modeling concept of alternative alcohol-to-jet (ATJ) fuel. In AIAA Scitech 2021 Forum (p. 1245).
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- Wiersema, P. W., **Kim, K.**, Lee, T., Mayhew, E., Temme, J., & Kweon, C. B. (2022). Relation between Cetane Number and the Ignition Delay of Jet Fuels. In AIAA SCITECH 2022 Forum (p. 1255).

Chapter 2 Experimental Devices and Testing Protocols

To study the autoignition properties of various operationally relevant fuels for military applications, it is imperative to investigate their physicochemical properties and combustion evaluation through testing facilities. The newly introduced alternative fuels or blends can differ significantly in their physiochemical properties. The assessment of fuels and their components enables understanding and laying the groundwork of combustion dynamics. The chemical composition of fuels ultimately determines fuels' important physical properties, including density, lubricity, volatility, and distillation. These physicochemical properties are significant when considering combustion performance, equivalence ratio, combustion emissions, and their chemical combustion process. The most important step, combustion evaluation, is truly assessing the fuels' performance, operability, and ignitability in actual combustion devices. Among various apparatuses for evaluating autoignition characteristics of fuels, a rapid compression machine (RCM) and a shock tube at the University of Illinois Urbana-Champaign measures chemical ignition delay times of fuels. In this chapter, the experimental devices used to assess fuels are discussed.

2.1 Database and Gas chromatography

The Federal Aviation Administration (FAA) established a Center of Excellence for Alternative Jet Fuels and Environment (ASCENT) to study the integration of alternative jet fuels in the commercial aviation domain [12]. As a part of the National Jet Fuel Combustion Program (NJFCP), a sub-group leading research into the combustion of fuels; alternative jet fuels, and sustainable aviation fuels (SAFs), the Alternative Jet Fuel Test Database (AJFTD) was developed

and is maintained at the University of Illinois Urbana-Champaign (altjetfuels.illinois.edu) [32]. This site provides fuel test data that has been collected over recent decades. The database has been collected fuel test data from the Air Force Research Laboratory (AFRL), Metron Aviation, and the Petroleum Quality Information System (PQIS), which is managed by the Defense Logistics Agency (DLA). The Air Force Research Laboratory (ARFL) data contains pertinent approval testing and specification property results for conventional and approved alternative jet fuels. I obtained the physicochemical properties of fuels researched in this study from the Alternative Jet Fuel Test Database (AJFTD).

A gas chromatography/mass spectrometry (Agilent Technology, model 6890N/5973) was performed to examine the detailed chemical composition of each fuel. Gas chromatography is a technique for separating complex mixtures based on boiling point/vapor pressure and polarity differences. If additional fuels' chemical compositions are required, two-dimensional gas chromatography (GCxGC) analysis is requested to the University of Dayton Research Institute. The GCxGC analysis provides detailed information on fuels' chemical composition by subjecting a sample to two-dimensional separation. Analyzing both volatility and polarity of chemical components inside fuel components allows the identification of different hydrocarbon types and carbon numbers.

2.2 Rapid Compression Machine (RCM)

A rapid compression machine (RCM) implements a single compression stroke of a conventional compression-ignition engine. The charged gaseous mixture in an RCM is compressed to increase temperature and pressure within a short time (20~30 ms). The pneumatically driven

piston performs the compression process, and it stops hydraulically. RCM has widely been used for investigating autoignition and chemical reactivity studies. The main advantage of using an RCM is the low compressed temperature range around 500-750K of operation, which is an important area for low-temperature combustion processes in engine systems: lean-blow out, start-up, and homogeneous charge compression ignition (HCCI) engine. Not only focusing on low-temperature chemistry, increasing the compressed temperature by modifying the system enables studying negative temperature coefficients. Under these low-temperature conditions, ignition delays are conventionally on the order of 10 to 100's of milliseconds depending on the equivalence ratio and compressed pressure. Due to relatively longer ignition delay, RCM is also able to investigate the multistage ignition characteristics of the fuels. Not for this study, but most RCMs are also able to conduct optical diagnostics to provide insightful combustion information, including species time history analysis, temperature, and heat release measurements with the optional optically accessible windows.

However, there are some limitations of RCM systems. Because of the longer ignition delay, the system is required to reduce the heat losses and the possibility of chemical reactions during the compression process. Conventionally, the adiabatic core hypothesis, which assumes uniform temperature, is considered to calculate the chamber's temperature instead of infeasible instantaneous temperature measurements. To use the hypothesis, heat losses to the wall should occur only at a thin boundary layer which means the compression of the core occurs isentropically. Estimations made by Donovan et al. [33] show that the core region occupies approximately 70% of the compressed combustion region.

The above assumptions cause an issue in data collection. Another group reported [34–37] that the adiabatic core assumption can be broken because of a rollup vortex during the compression

stroke, which is shown in Figure 2-1.

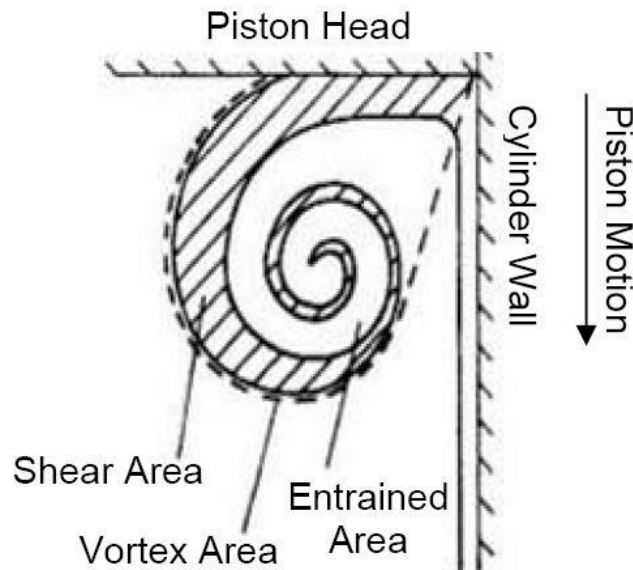


Figure 2-1 Illustration of occurring rollup vortex with a flat piston during the compression of the rapid compression machine [34]

A rollup vortex can interfere with the cool boundary layer gases, then mix with adiabatic core gas, attributing to the breakdown of the adiabatic core assumption. The penetrated vortex of fluid dynamics results in the erroneous compressed temperature of the system, causing disparities in data collected for RCMs. In order to reduce the rollup vortex boundary effects during the compression, the creviced piston is suggested [34,37,38] rather than a flat piston. The newly designed piston allows the adiabatic core assumption by eliminating the rollup vortex effects during the compression machine.

The RCM system generally uses a premixed homogeneous charge to guarantee homogeneous mixing of fuel and air. In a batch process, the vessel heats and mixes a homogenous air and fuel mixture. After the proper amount of synthetic air is introduced to the vessel, the desired amount of fuel is then injected to match the specified equivalence ratio for test conditions. The

disadvantages of a pre-mixed mixing vessel system are the potential of not fully vaporization and thermal decomposition of the fuel. Another issue with mixing vessels is the risk of condensation while introducing to the combustion chamber if fuel lines are not properly insulated or heated. These factors influence combustion resulting from incorrect equivalence ratios and fuel compositions. Instead of an available premixed charging system, the RCM used in this study utilized the direct test chamber (DTC) method [39,40]. DTC method preloads the air and fuel mixture gases directly into the preheated combustion chamber.

Moreover, the RCM has a systemic problem with measurement. Due to a relatively longer compression time, it cannot perform high reactive fuels properly. Since mechanically driven compression usually takes about 20~30 ms and can overlap with highly reactive fuels' chemical kinetic reactions, it is hard to decouple between the fuels' compression and chemical kinetic processes. Also, the highest compressed temperature condition of the system is limited by the system's highest configurable compression ratio and the initial charging temperature. In summary, RCM is the proper device to investigate lower compressed temperature and relatively low reactive fuels.

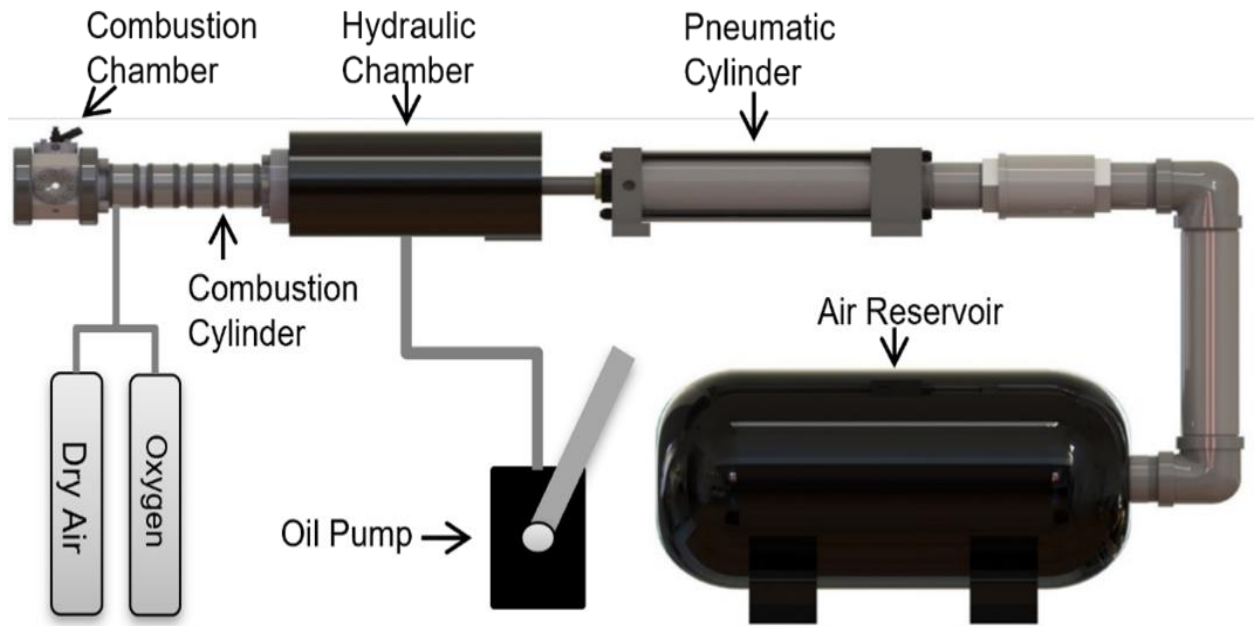


Figure 2-2 Schematics of the Rapid Compression Machine (RCM) at the University of Illinois Urbana-Champaign

Figure 2-2 indicates a schematic configuration of the RCM at the University of Illinois Urbana-Champaign. The experimental facility consists of three main parts: a pneumatic driver section, a hydraulic stopping section, and a combustion section.

A pneumatic driver section compresses the charged gas by moving a piston. The external air compressor, C-Aire 5HP (model number: A050V080-1230), constantly charges 140 psi of air to the air reservoir tank (20 gallons). The compressed air in the reservoir drives the pneumatic cylinder's 5" diameter piston assembly.

A hydraulic chamber enables control of the piston's movement and changes the compression ratio of the system. The chamber is connected to an oil pump (Star Hydraulics, CP13-250-2000) and filled with heavy, viscous mineral oil (309 SSU) to hold the piston. A solenoid valve (Parker, 71216SN2BL00N0C111P3) lets the oil out to the oil reservoir in the chamber. Once the valve

instantaneously drains the oil, pressurized air drives the piston to compress the combustion chamber. The hydraulic chamber also allows for the variation of compressed conditions. The overall stroke length of the RCM can be extended by adding up to two 1" shims to the rear (in front of the pneumatic section) of the assembly. Moreover, adding shims to the front (between the hydraulic and combustion sections) of the assembly differs the clearance volume at the top dead center.

A combustion chamber consists of a combustion cylinder and test section. The entire chamber is insulated and heated with band heaters to control the initial temperature and vaporize the fuel, achieving the DTC method. Six thermocouples (Omega, TMQSS-125U-4) and six-band heaters are attached and controlled the chamber temperature using a PID controller.

The combustion cylinder also has an inlet/outlet for the inlet of oxidizing gases and an outlet for combustion products. The anodized aluminum piston inside the combustion cylinder has a crevice to eliminate boundary roll-up issues to guarantee the adiabatic core assumption. An automotive gasoline injector (Bosch, 13537591623) injects the exact amount of fuel into the system. The fuel is fed from a fuel accumulator (Parker ACP05AA050E1ETD), constantly pressurized at 30 bar. Inside of the combustion cylinder is an aluminum piston rod with an anodized aluminum creviced piston, based on the design of Mittal et al. [34], attached to eliminate significant boundary roll-up issues, thereby achieving an adiabatic core post-compression, allowing the calculation of compressed temperatures by the adiabatic core assumption.

An ignition delay experiment of RCM starts with heating up the RCM to the desired initial temperatures, typically greater than 120°C. The heating-up process usually takes several hours to minimize a chamber's temperature fluctuations. The initial set temperature retained at 125 °C usually, but it varies depending on the target compressed temperature and volatility of fuels. Then,

the heated chamber is vacuumed to charge fuel-air mixtures from the evacuated status.

Once synthetic dry air is filled to a specified pressure to reach the desired compressed pressure, the combustion cylinder valve is closed to seal the testing section, considered a thermodynamically closed system. The injector introduces the specified amount of fuel to the system to attain a specific equivalence ratio. I allow sufficient time (~4 min) for ensuring homogeneous charging after the injection. Finally, the charged test gas is compressed to the top dead center (TDC) in less than 30 ms, resulting in autoignition. A piezoelectric pressure transducer (Kistler 6125B), amplified through a dual-mode signal amplifier (Kistler, type 5010), records the pressure history during compression and ignition with respect to the time.

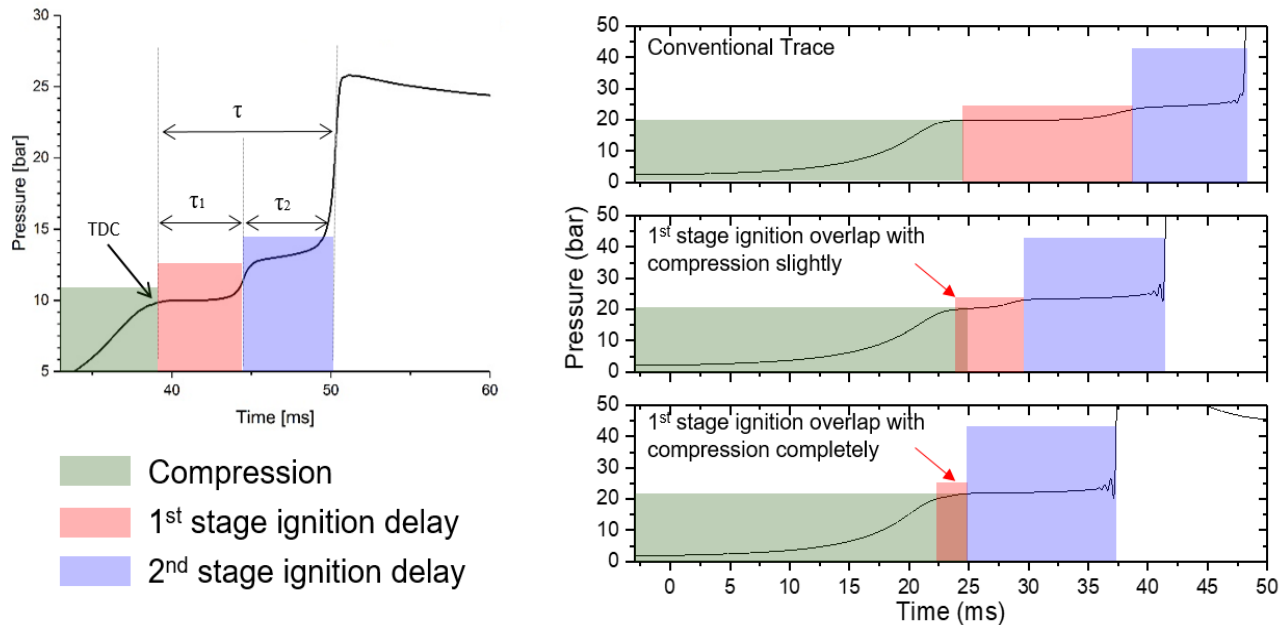


Figure 2-3 Sample ignition pressure history data measured by RCM illustrating the ignition delay definitions. A graphical description of first-stage ignition delay (τ_1), second-stage ignition delay (τ_2) and the overall ignition delay (τ) is also provided.

The ignition delay can be defined as the amount of time required for fuel to be autoignited after compressed conditions have been reached. The start time of the ignition delay is when the piston

is at the top dead center (TDC) and can be defined as the first zero-crossing inflection point of the pressure derivative. The end time of the ignition delay is designated to be the point of maximum pressure rise. The overall ignition delay (τ) is defined as the time between the start and end of the ignition delay. Ignition can be achieved with a single pressure rise or multiple distinct pressure rises, i.e., multistage ignition in the low-temperature regime. Multistage ignition has several local maxima of the pressure rise derivative. In this study, mostly one-stage and two-stage ignition cases are observed regarding test conditions. When two-stage ignition occurs, the overall ignition delay (τ) can be divided into the first-stage ignition delay (τ_1) and the second-stage ignition delay (τ_2), where $\tau = \tau_1 + \tau_2$. First-stage ignition delay (τ_1) is the time from the end of compression to the first local maximum of the pressure trace, which results from the initial formation of a cool flame [41–43]. Second-stage ignition delay (τ_2) is the time elapsed from the end of first-stage ignition until the global maximum of the pressure trace. Figure 2-3 shows an example of two-stage ignition: blue region for τ_1 and red region for τ_2 . The test was continued until early ignition, where compression and ignition are indistinguishable.

Compressed temperatures (T_C) of fuel/air mixture at TDC are the reference parameter for comparing the ignition delay of the fuel. According to Mittal et al. [36], a creviced piston performs an adiabatic core post-compression by eliminating boundary roll-up vortex issues. Under an adiabatic core condition, T_C is calculated from the pressure trace using the following relationship:

$$\int_{T_0}^{T_C} \frac{\gamma}{\gamma - 1} \frac{dT}{T} = \ln \frac{P_C}{P_0} \quad (2-1)$$

where T is temperature, P is pressure, γ is specific heat ratio, subscript 0 indicates initial conditions, and subscript C indicates the compressed condition.

The equation illustrates that lower initial temperature and smaller compression ratio will provide lower compressed temperature under identical fuel/air mixture and vice versa. Specific ratio (γ) is a temperature-dependent value and is necessary to solve for T_C . The thermodynamic data were calculated using NASA polynomials [5]. The NIST webbook [44] and Burcat's thermodynamic data [45] provide the necessary coefficients for calculations. In the case of the absence of the data, the approximated properties based on fuel surrogates were used. Surrogates were mimicked by incorporating data for available species based on chemical structure and molecular weight by analyzing GC/MS data with The Navy Fuel Composition and Screening Tool (FCAST) [46].

2.3 Shock tube

The combustion research field has widely used shock tubes and RCMs to investigate autoignition. A shock tube generates a shock wave to compress and heat the test gas (generally a low-pressure fuel-air mixture) using a driven gas (a high-pressure inert gas). A thin diaphragm divides the system into two parts: driver gas and driven gas. Puncturing the diaphragm creates a normal shock wave resulting in an instantaneous test gas pressure and temperature increment. After the shock wave hits the end wall of the driven section, it reflects the shock wave to travel again through the driven section to the end wall of the driver section, contributing to the final compression status. The main advantage of the shock tube is heating the test gas “instantaneously” by using a shock wave. In addition, a zero-dimensional model can be used to calculate the experimental condition of the shock tube system. The compressed pressure and temperature can be calculated from the normal shock equations.

Getting identical compressed conditions and short testing time are well-known drawbacks of shock tube experiments. Puncturing a diaphragm determines the normal shock, resulting in compressed temperature and pressure. Unwanted chemical reactions between diaphragms and air-fuel gaseous mixture, uneven surface conditions of the tube, and non-uniform rupturing causes bad normal shock development, contributing to low reproducibility. When it comes to testing time, the compressed condition can no longer be sustained as the expansion wave of inter gas interferes with the compressed test gas mixture resulting from the reflected shock wave. A shock tube is a proper device to investigate high compressed temperature and relatively high reactive fuels. Therefore, shock tube and RCM complement each other to study fuel reactivity.

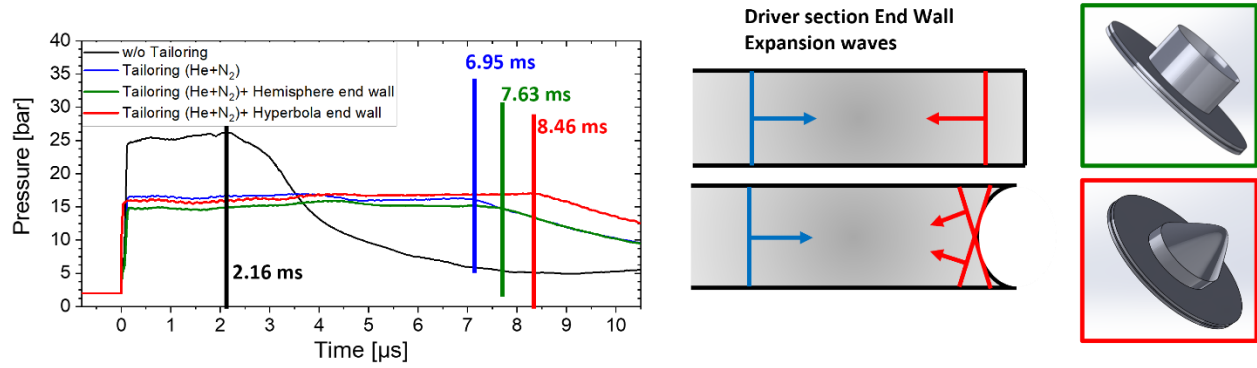


Figure 2-4 Plot of sample shock tube pressure trace with non-reactive air condition. The effects of tailoring driver gas and end wall modifications are described.

To lower temperatures with extended testing times of shock tube, a tailored He and N₂ mixture was used as the driver gas to control the incident shock condition, and driver-section inserts were added to the driver section end wall. A tailored driver mixture minimizes the interaction between the reflected shock wave and the contact surface [47]. Dumitrescu [48] firstly proposed a cone-shaped obstacle into the driver section to persist constant reflected shock conditions as far as I know. Reflected expansion waves from the driver section end wall propagate downstream into the driven section, decreasing compressed pressure finally. Whalley et al. [49] showed that different cavity geometries of the driver section end wall induce changing the directions of expansion wave experimentally and numerically. To achieve a more-constant reflected expansion wave and change the direction, I have tested the hyperbola cone and hemisphere cavity-shaped driver section insert, as shown in Figure 2-4. Applying the tailoring method and adding a specially designed driver section expanded test conditions under a shock tube.

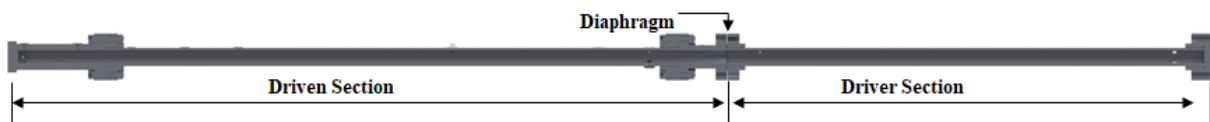


Figure 2-5 Schematics of the Shock tube at the University of Illinois Urbana-Champaign

Figure 2-5 indicates a schematic configuration of the shock tube at the University of Illinois Urbana-Champaign. The inner diameter of the shock tube is 6.35 cm. All parts are made of honed 316 stainless steel. The experimental facility consists of four main parts: a driven section, a driver section, a diaphragm section, and a fuel-supplying system.

The driven section is the test section that ignites the fuel and oxidizer mixture, requiring a sufficient length to guarantee enough testing time. The length of the driven section is 4.23 m. The entire driven section is insulated and heated with band heaters to both control the initial temperature and vaporize the fuel using a PID controller. The driven section contains 3 ports near the diaphragm section: loading air-fuel mixture, evacuating combustion product gas, and vacuuming. The five shock counter signals (PCB 111A22 pressure transducers) with known spacing are used to calculate the incident shock speed near the end wall. To investigate autoignition characteristics, an additional Kistler 6031B pressure transducer allows recording the pressure history with respect to time and calculating the ignition delay times.

The driver section is 2.74 m in length and contains 3 ports near the end wall allowing for the inlet of the driving gas, vacuuming of the driver section, and outlet of combustion product gases post-test. There is a pressure transducer near the diaphragm section to monitor the driving pressure, which helps to calculate the tailor condition, which will be explained later.

The unique feature of the diaphragm section is that the inner dimension transfers from a square on the driver side to the 6.35 cm ID circle on the driven side. The square design of holding the diaphragm was used to allow for increased stresses on the diaphragm to allow for a more instantaneous rupture. A polycarbonate sheet is used as the diaphragm, and a cross-shaped stainless-steel cutter on the end of the diaphragm section guides the proper rupture of the

diaphragm. The diaphragm section also has a pressure transducer (PCB 111A22) to trigger the data acquisition system.

Since the DTC method cannot be implemented in the shock tube system, a mixing vessel (33.7L) is used to charge the driven section through heated and insulated tubing to minimize any potential problems with the external feeding system.

An ignition delay experiment of shock tube also starts with heating the system to the desired initial temperatures, typically 125°C. The heating up process usually takes about several hours until minimizing temperature fluctuations. At the same time, the homogeneous air-fuel mixture is prepared in the heated mixing vessel. Like filling an RCM system, the vessel is charged with dry air to the specified pressure, then the desired amount of fuel to attain an equivalence ratio is injected into the vessel. An aluminum stirrer inside the vessel rotates continuously at 200 rpm to ensure mixing between air and fuel. Enough time (typically ~180 min) is allowed for complete vaporization of the fuel and homogenous mixing of the mixture.

Depending on the targeted compressed pressure conditions, the diaphragm's thickness varies. The ignition delay experiments mainly were performed under 2 MPa of compressed pressure, which requires 1.5 mm of polycarbonate diaphragm. Once the air-fuel mixture in the vessel is ready, the shock tube is evacuated and vacuumed to $10^{-5} \sim 10^{-7}$ torr to minimize the influence of impurities. The air-fuel mixture from the mixing vessel introduces to the driven section, while the driver section is pressurized with the driver gas. Driver gas is charged until the diaphragm ruptures.

Instantaneous pressure rise arising from rupturing the diaphragm triggers the data acquisition process. The Frozen Shock Wave Calculator (FROSH) code, written by Hanson et al. [50], calculates the incident and reflected shock conditions using the normal shock relations and thermodynamic data. The ignition delay can be defined as the time between the moment when the

incident shock reaches the end wall and the moment when fuel starts autoignition. The obtained ignition delay was compensated using a power-law dependency, $\tau \sim P^{-1}$ [51–53].

2.4 Uncertainty

An ignition delay measurement contains several factors affecting uncertainty. Many shock tube systems and measurement techniques have been developed to obtain more accurate data, but efforts to establish standard tools for evaluating the associated uncertainties have been limited. Therefore, this section briefly describes a procedure to explain the practical method for analyzing the accuracy of the ignition delay time and ignition temperature acquired from the shock tube. However, it may not be complete for some applications and may require additional sources of uncertainty for evaluation, while this uncertainty analysis should be sufficient for most experiments

The absolute uncertainty requires considering the accuracy of each measuring component and the relation among them. The overall uncertainty is a combination of acquisition, sampling, analysis methodology, and processing. Therefore, factors including sampling, reliability of the equipment used, and computational algorithms can be considered for the uncertainty analysis.

Each sampled data point is recorded as an independent instance, and the data can be assumed in the form of a normal distribution. Using statistical sampling theory, a confidence level (Z_c) for the uncertainty estimate depends on the purpose of analysis. If you obtain the standard deviation of a sample with a normal distribution, the sample falls within one standard deviation from the mean with 68%. This confidence level increases to 95% for the range of two standard deviations from the mean. Then, the probability of sampling the data (y) (either ignition delay time or temperature)

at a certain confidence level (Z_c) around the mean ($\bar{y}$) for the total number (n) and standard deviation ($\sigma_{y,s}$) of samples can be expressed as

$$\bar{y} \pm Z_c \sigma_{y,s} \quad \sigma_{y,s} = \sqrt{\frac{\sum_{i=1}^n (y_i - \bar{y})^2}{n(n-1)}} \quad (2-2)$$

The standard deviation or standard error can be expressed by setting the range within which the actual mean or future mean of samples belongs to a given confidence level or possibility. We can use this equation to assess the uncertainty of the averaged ignition delay time and ignition temperature due to sampling.

The ignition delay time and ignition temperature are calculated based on the changes in the pressure and temperature signals measured for a short time interval. The signals are obtained from several types of equipment, such as a pressure transducer and thermocouples, which can be sources of those uncertainties. However, if the experimental conditions are well controlled, only a few need to be considered in estimating the uncertainty. The factors include the thermal-fluidic properties of the sample fuel and the physical quantity measurements according to the position over time. In the case of the ignition delay measurements, the temperature and pressure changes of the gaseous mixture between fuel and air are the main components required to calculate the ignition delay time and compressed temperature.

The signals are obtained from equipment such as a pressure transducer and thermocouples, which are sources of equipment uncertainties. Measurement uncertainty can be mathematically estimated based on the uncertainty of the variables that make up the measurement. According to general uncertainty analysis, a measurement ($\mathcal{F}$) is expressed as a function of the independent variables $x_1, x_2, x_3, \dots, x_n$, described as

$$\mathcal{F} = \mathcal{F}(x_1, x_2, x_3, \dots, x_n) \quad (2-3)$$

where $\sigma_{\mathcal{F}}$ and $\sigma_{x1}, \sigma_{x2}, \sigma_{x3}, \dots, \sigma_{xn}$ are the uncertainties of the measurement ($\mathcal{F}$) and variables (x_i) respectively. If we assume that the variable's uncertainties are independent, the uncertainty of the measurement becomes

$$\sigma_{\mathcal{F}} = \sqrt{\left(\frac{\partial \mathcal{F}}{\partial x_1} \sigma_{x1}\right)^2 + \dots + \left(\frac{\partial \mathcal{F}}{\partial x_n} \sigma_{xn}\right)^2} \quad (2-4)$$

Equation (2-4) estimates the overall uncertainty of the measurement ($\mathcal{F}$) based on the uncertainties resulting from multiple sources. From this point, calculating the uncertainty of the shock tube system is explained. The same approach can be applied to RCM. The uncertainty analysis of an ignition delay time and compressed temperature of a sample fuel begins with the compensation of compressed pressure as follows:

$$\tau_c = f(\tau_{5f}, P_{5f}, P_c) = \tau_{5f} \times \frac{P_{5f}}{P_c} \quad (2-5)$$

where τ_{5f} is the ignition delay time measured at the compressed pressure (P_{5f}) (with the subscript “5f” signifying “final value at position 5) behind the reflected shock wave. The ignition delay time is calibrated to the reference pressure (P_c) leading to the calibrated ignition delay time (τ_c). In the below, the ignition pressure (P_{5f}) can be derived from the shock equation:

$$P_{5f} = P_{2i} \times \frac{\alpha_{2i} + 2 - \frac{P_1}{P_i}}{1 + \alpha_{2i} \frac{P_1}{P_i}} \quad (2-6)$$

where P_{2i} and α_{2i} (with the subscript “2i” signifying “ideal value at position 2) correspond to the ideal pressure and speed of sounds at position 2 before the incident shock wave. P_1 is the initial pressure in the driving section of the shock tube before the shock wave is developed (with the subscript “1” signifying “initial value at position 1) and is formed by a homogeneous mixture of air and sample fuel at a specified equivalence ratio.

P_{2i} can be calculated using the normal shock relation using a heat capacity ratio ($\gamma_1 = C_{P_1}/C_{V_1}$) of the mixture and Mach number (M_{2i}) of the shock wave at position 2.

$$P_{2i} = P_1 \times \frac{2\gamma_1 M_{2i}^2 - \gamma_1 + 1}{\gamma_1 + 1} \quad (2-7)$$

$$M_{2i} = \frac{V_{2i}}{\sqrt{\gamma_1 \frac{P_1}{\rho_1}}} \quad (2-8)$$

where V_{2i} is the average velocity of the shock wave pass from position 2 to position 5 and ρ_1 is the initial density of the mixture in the driven section. Furthermore, α_{2i} can be determined by the heat capacity ratio ($\gamma_{2i} = C_{P_{2i}}/C_{V_{2i}}$) as follows:

$$\alpha_{2i} = \frac{\gamma_{2i} + 1}{\gamma_{2i} - 1} = \frac{C_{P_{2i}} + C_{V_{2i}}}{C_{P_{2i}} - C_{V_{2i}}} \quad (2-9)$$

where

$$C_{V_{2i}} = C_{P_{2i}} - R \quad (2-10)$$

and

$$C_{P_{2i}} = a_1 + a_2 T_{2i} + a_3 T_{2i}^2 + a_4 T_{2i}^3 + a_5 T_{2i}^4 \quad (2-11)$$

Coefficients ($a_1 \sim a_5$) are NASA polynomial coefficient to estimate the heat capacity at constant pressure under the ideal temperature T_{2i} of position 2 defined as

$$T_{2i} = T_1 \times \frac{\left\{ \gamma_1 M_{2i}^2 - \left(\frac{\gamma_1 - 1}{2} \right) \right\} \left\{ \left(\frac{\gamma_1 - 1}{2} \right) M_{2i}^2 + 1 \right\}}{\left(\frac{\gamma_1 + 1}{2} \right)^2 M_{2i}^2} \quad (2-12)$$

where T_1 is the initial temperature of the mixture at position 1 in the driven section.

Finally, the calibrated ignition delay time (τ_c) is a function of independent variables as follows:

$$\tau_c = f(\tau_{5f}, P_1, T_1, \rho_1, \gamma_1, V_{2i}, a_1, a_2, a_3, a_4, a_5) \quad (2-13)$$

We can determine the uncertainty ($\sigma_{\tau_{c,E}}$) of the calibrated ignition delay time due to equipment by applying equation (2-13) into equation (2-3), expressed as

$$\sigma_{\tau_{c,E}} = \sqrt{\left(\frac{\partial f}{\partial \tau_{5f}} \cdot \sigma_{\tau_{5f}} \right)^2 + \left(\frac{\partial f}{\partial \rho_1} \cdot \sigma_{\rho_1} \right)^2 + \left(\frac{\partial f}{\partial \gamma_1} \cdot \sigma_{\gamma_1} \right)^2 + \left(\frac{\partial f}{\partial P_1} \cdot \sigma_{P_1} \right)^2 + \left(\frac{\partial f}{\partial T_1} \cdot \sigma_{T_1} \right)^2 + \left(\frac{\partial f}{\partial V_{2i}} \cdot \sigma_{V_{2i}} \right)^2 + \left(\frac{\partial f}{\partial a_1} \cdot \sigma_{a_1} \right)^2 + \left(\frac{\partial f}{\partial a_2} \cdot \sigma_{a_2} \right)^2 + \left(\frac{\partial f}{\partial a_3} \cdot \sigma_{a_3} \right)^2 + \left(\frac{\partial f}{\partial a_4} \cdot \sigma_{a_4} \right)^2 + \left(\frac{\partial f}{\partial a_5} \cdot \sigma_{a_5} \right)^2} \quad (2-14)$$

where σ is the uncertainty of each independent variable.

The uncertainty due to the equipment is determined based on the independent variables and the uncertainties associated with these independent variables. The experimental method section discusses that the sample fuel is injected into a mixing vessel under a well-controlled temperature. The sample fuel is mixed with pure air at a given volume fraction (χ) and heated in the mixing

vessel. The accuracy of mixed fuel's properties, such as the density ρ_1 and the heat capacity ratio γ_1 of equation (2-10) at position 1, depends on several errors. For convenience, if we assume that the properties of mixed fuels have a linear relationship with the volume fraction (χ_{fuel}) of sample fuel in the mixed fuel, the density (ρ_1) and heat capacity ratio (γ_1) is expressed as

$$\rho_1 = \chi_{fuel}\rho_{fuel} + (1 - \chi_{fuel})\rho_{air} \quad (2-15)$$

$$\gamma_1 = \chi_{fuel}\gamma_{fuel} + (1 - \chi_{fuel})\gamma_{air} \quad (2-16)$$

The uncertainties (σ_{ρ_1} and σ_{γ_1}) of the density and heat capacity ratio can be described as,

$$\sigma_{\rho_1} = \sqrt{\left(\frac{\partial \rho_1}{\partial \chi_{fuel}} \cdot \sigma_{\chi_{fuel}}\right)^2 + \left(\frac{\partial \rho_1}{\partial \rho_{air}} \cdot \sigma_{\rho_{air}}\right)^2 + \left(\frac{\partial \rho_1}{\partial \rho_{fuel}} \cdot \sigma_{\rho_{fuel}}\right)^2} \quad (2-17)$$

$$\sigma_{\gamma_1} = \sqrt{\left(\frac{\partial \gamma_1}{\partial \chi_{fuel}} \cdot \sigma_{\chi_{fuel}}\right)^2 + \left(\frac{\partial \gamma_1}{\partial \gamma_{air}} \cdot \sigma_{\gamma_{air}}\right)^2 + \left(\frac{\partial \gamma_1}{\partial \gamma_{fuel}} \cdot \sigma_{\gamma_{fuel}}\right)^2} \quad (2-18)$$

respectively. In this study, the volume fraction is the major cause of changes in the properties, but the cause of temperature and pressure can be ignored compared to the volume fraction. The accuracy of the volume fraction results from the pipet used to check and inject an amount of fuel. This means that the uncertainty of the volume fraction is equal to the uncertainty ($\sigma_{\chi_{fuel}}$) of the pipet. The pipet uncertainty used in this study is 0.5% for the 95% confidence level.

The changes in the pressure and temperature are measured by converting the analog signal from a commercial sensor installed at each position in the shock tube to a digital signal entered into the data acquisition system. There are three common errors in the pressure and temperature measurements. First, each sensor itself causes an error when it measures the physical quantities.

The errors can be obtained from the data sheet of commercial products. In this study, I used the pressure sensors (Kistler 603B1 and 601B1) to measure the ignition delay time, the pressure sensors (Omega PCB 111a22) to measure the velocity of the shock wave, and T-type thermocouples (Omega KMQXL-062U-48) to measure the temperature inside the mixing vessel and shock tube. The uncertainties of these sensors are 0.5% (σ_{P_1,PT_1}), 0.5% (σ_{P_1,PT_2}), and 0.2% ($\sigma_{T_1,TC}$) for the 95% confidence level, respectively.

Second, the signals measured from these sensors are entered into the data acquisition system and processed. In this system, signal distortions can occur during signal processing. The degree of the signal distortion depends on the accuracy of the data acquisition system (LabVIEW NI-DAQ BNC2110). In this study, the uncertainties of the distortion for the pressure and temperature due to the system are 0.2% ($\sigma_{P_1,D}$) and 0.2% ($\sigma_{T_1,D}$), respectively.

Finally, the pressure (P_1) and temperature values (T_1) are measured as the initial conditions at position 1 and sampled over a given time interval. These values are averaged in an ensemble. As a result, the uncertainties are induced by the sampling and averaging over the time interval (see section A.1). Both estimated uncertainties ($\sigma_{P_1,S}$ and σ_{T_1,S_1}) due to the sampling are estimated to be 0.2% for the 95% confidence level. In addition to this, the temperature varies in each position of the shock tube. I observed the temperature changes by installing thermocouples at 12 locations in the driver section of the shock tube. The uncertainty (σ_{T_1,S_2}) due to the sampling and averaging of the temperature over the position is 0.7% for the 95% confidence level. Therefore, the uncertainties of the pressure (σ_{P_1}) and temperature (σ_{T_1}) measured at position 1 can be described as

$$\sigma_{P_1} = \sqrt{\sigma_{P_1, PT_1}^2 + \sigma_{P_1, PT_2}^2 + \sigma_{P_1, S}^2 + \sigma_{P_1, D}^2} \quad (2-19)$$

$$\sigma_{T_1} = \sqrt{\sigma_{T_1, TC}^2 + \sigma_{T_1, S_1}^2 + \sigma_{T_1, S_2}^2 + \sigma_{T_1, D}^2} \quad (2-20)$$

After the break of the diaphragm, the shock wave (V_{2i}) is developed from position 1 to position 5 on the driver section. The velocity of this shock wave is included as an independent variable in the estimation process of the ignition delay time (equation 2-14). The velocities are calculated based on the pressure signals measured from the pressure sensor installed from position 1 to position 5 and then averaged over the position as follows:

$$V_{2i} = \frac{\sum_{i=1}^n (x_{i+1} - x_i) / (t_i - t_{i+1})}{n + 1} \quad (2-21)$$

where x_i and t_i are the horizontal intervals of the pressure sensor from position 1 to position 5 and the absolute times triggered by pressure change by the shock wave. The uncertainty of velocity depends on two errors like

$$\sigma_{V_{2i}} = \sqrt{\sigma_{V_{2i,E}}^2 + \sigma_{V_{2i,S}}^2} \quad (2-22)$$

where $\sigma_{V_{2i,E}}$ and $\sigma_{V_{2i,S}}$ are corresponding to the uncertainties due to the equipment used to evaluate the shock wave velocity and the sampling over the transverse position. The equipment uncertainties result from the manufacturing for installing the pressure sensors and timing estimation based on the pressure signal measured. The timing uncertainty is caused by the pressure sensor and data acquisition system. Therefore, the equipment uncertainty can be evaluated as

$$\sigma_{V_{2i,E}} = \sqrt{\left(\frac{\partial V_{2i}}{\partial x} \cdot \sigma_x\right)^2 + \left(\frac{\partial V_{2i}}{\partial t_{PT}} \cdot \sigma_{t,PT}\right)^2 + \left(\frac{\partial V_{2i}}{\partial t_D} \cdot \sigma_{t,D}\right)^2} \quad (2-23)$$

where σ_x is the manufacturing uncertainty, which is assumed to be 0.5 mm. Furthermore, $\sigma_{t,PT}$ and $\sigma_{t,D}$ are timing uncertainties caused by the pressure sensor and data acquisition system, which are the same with σ_{P_1,PT_2} and $\sigma_{P_1,D}$, respectively.

Finally, NASA polynomial coefficients are used to estimate the ignition delay time in equation(2-13). Based on the previous experimental data, these coefficients are obtained from the least square fitting method. The uncertainties of the coefficients are thus dependent on the uncertainties of the method. The previous studies have shown that the uncertainties of these coefficients are 0.2% for the 95% confidence level.

Uncertainty analysis such as equation (2-14) can also be extended to the uncertainty analysis of the ignition temperature (T_f) that is the x-axis of the figures presented in the results section. The ignition temperature can be evaluated by the variables included in the ignition delay time as follows:

$$T_{5f} = g(P_{5f}, P_{2i}, T_{2i}, \alpha_{2i}) = T_{2i} \left(\frac{P_{5f}}{P_{2i}} \right) \frac{\alpha_{2i} + \left(\frac{P_{5f}}{P_{2i}} \right)}{1 + \alpha_{2i} \left(\frac{P_{5f}}{P_{2i}} \right)} \quad (2-24)$$

$\sigma_{T_{5f}}$

$$= \sqrt{\left(\frac{\partial g}{\partial P_1} \cdot \sigma_{P_1}\right)^2 + \left(\frac{\partial g}{\partial T_1} \cdot \sigma_{T_1}\right)^2 + \left(\frac{\partial g}{\partial \rho_1} \cdot \sigma_{\rho_1}\right)^2 + \left(\frac{\partial g}{\partial \gamma_1} \cdot \sigma_{\gamma_1}\right)^2 + \left(\frac{\partial g}{\partial V_{2i}} \cdot \sigma_{V_{2i}}\right)^2 + \left(\frac{\partial g}{\partial a_1} \cdot \sigma_{a_1}\right)^2 + \left(\frac{\partial g}{\partial a_2} \cdot \sigma_{a_2}\right)^2 + \left(\frac{\partial g}{\partial a_3} \cdot \sigma_{a_3}\right)^2 + \left(\frac{\partial g}{\partial a_4} \cdot \sigma_{a_4}\right)^2 + \left(\frac{\partial g}{\partial a_5} \cdot \sigma_{a_5}\right)^2} \quad (2-25)$$

The total uncertainty of the two primary sources (sampling and equipment) discussed here is obtained by processing individual components in the mean square root equation. The total uncertainties of the ignition delay time (σ_{τ_c}) and compressed temperature (σ_T) can be estimated as follows:

$$\begin{aligned}\sigma_{\tau_c} &= \sqrt{\sigma_{\tau_c,E}^2 + Z_c^2 \sigma_{\tau_c,S}^2} \\ \sigma_T &= \sqrt{\sigma_{T,E}^2 + Z_c^2 \sigma_{T,S}^2}\end{aligned}\tag{ 2-26}$$

where the subscripts E and S refer to the uncertainty resulting from the equipment and sampling, respectively.

Based on the derived equations, the uncertainty of compressed temperature in the RCM and shock tube system is about 10K ($\sim \pm 1.5\%$) and 25K ($\sim \pm 2.5\%$), respectively. The uncertainty of ignition delay times in RCM and shock tube is 3ms and 0.5 ms, respectively. The long compression time of RCM contributes to the larger error in ignition delay measurements.

Chapter 3 Combustion chemistry and chemical kinetics

A combustion reaction is a kind of chemical oxidation reaction that releases heat and new products. In addition to heat, it generally emits light and produces a flame. In a combustion reaction system, the system experiences exponential growth in both temperature and the number of chemical species by consuming a significant amount of fuel. Combustion chemistry can explain and depict the behavior of free radicals; thus, it is imperative to understand radical behavior to build kinetic models. Kinetic models consist of elementary reactions and their rates that follow Semenov's ignition theory [4,5,54,55], which provides the fundamental interpretation of hydrocarbon oxidation.

3.1 Combustion chemistry

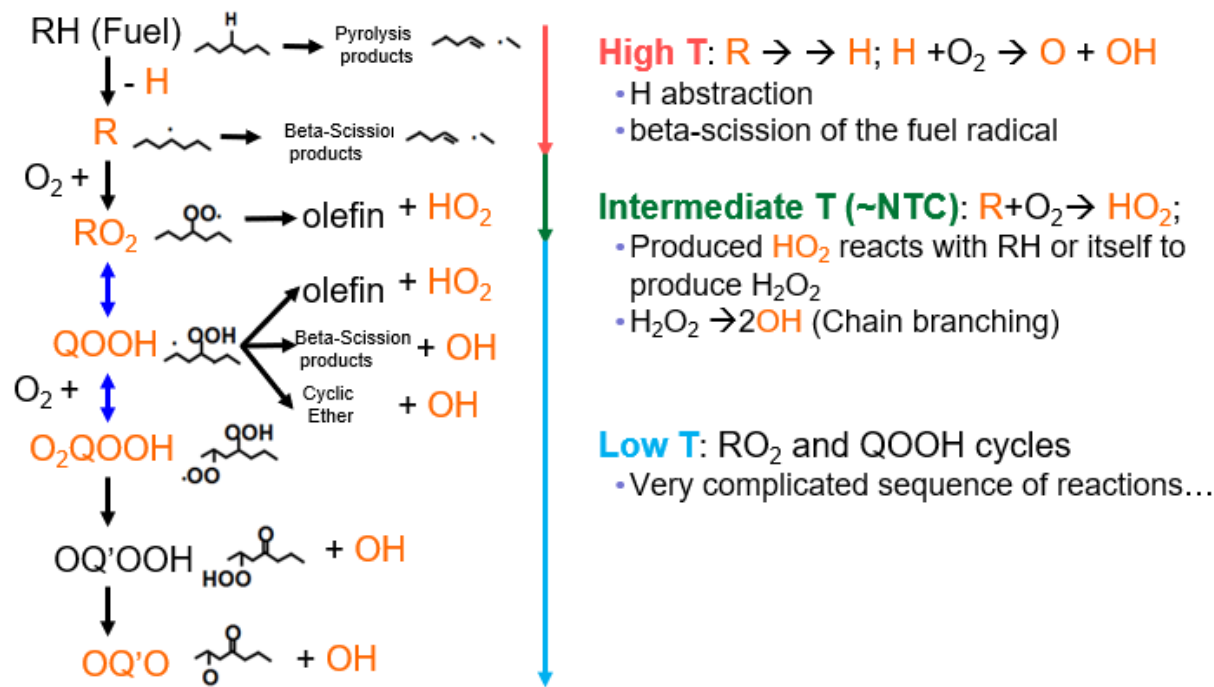


Figure 3-1 The overview of hydrocarbon combustion chemistry. High temperature (red), Intermediate temperature (green), Low temperature (skyblue)

Chemical reactions are highly sensitive to experimental conditions, including pressure, temperature, and species fraction. The combustion chemistry can be divided into two groups around 1000K: High-temperature combustion chemistry and Intermediate and Low-temperature chemistry.

Generally, over 1000 K, fuel species first undergo the pyrolysis process of alkyl radical decomposition or beta-scission, producing radicals [5]. The pyrolysis process provides "reactants" for the oxidation process, and the pyrolysis products oxidize with oxygen molecules and oxidative radicals. The pyrolysis step and the oxidation of the pyrolysis products can be separable in time, and the overall rate-limiting step of high-temperature oxidation relies on the temperature. In this aspect, the combustion properties of the real fuels are attributed to the product of thermal

decomposition in pyrolysis. Once the first H abstraction produces the fuel's alkyl radical, the C-C beta scission reaction and C-H beta scission reaction contribute to the thermal decomposition in high temperatures. It is well known that C-H beta scission reactions are slower than C-C beta scission reactions. Continuous thermal decomposition results in producing significant pyrolysis products, including C_2H_4 (ethylene), C_3H_6 (propene), $1-C_4H_8$ (1-butene), $i-C_4H_8$ (iso-butene), CH_4 (methane), C_6H_6 (benzene), C_7H_8 (toluene), H_2 (hydrogen), and usually two radical species CH_3 and H [56–58]. The produced small hydrocarbons oxidize to provide heat and radicals, leading the combustion.

Combustion chemistry of intermediate and low temperatures is much more complicated [59]. These temperature regimes are more pertinent to practical engine applications such as lean blow-out and start-up. H-abstracted fuel, “fuel radical,” with O_2 produces a peroxy radical (RO_2), and it isomerizes to a hydroperoxy radical ($QOOH$) in terms of H-atom transitioning. This isomerization reaction is the key factor of the negative temperature coefficient regime because a temperature increase results in decreased reaction rates. The hydroperoxy radical undergoes several alternative paths, which are formally chain propagation steps, beginning with one alkyl radical, and produces one HO_2 or OH radical in addition to a stable olefin or cyclic ether. In this research, I considered two chain propagation steps merged into one chain propagation step as an HO_2 radical and the alkene form (Q) of the “fuel molecule.” The hydroperoxy radical ($QOOH$) also reacts with an additional O_2 to form a hydroperoxyalkylperoxy radical (O_2QOOH), which can isomerize to an α -hydroperoxyalkylhydroperoxy radical ($HOOQ'OOH$). The decomposition of the α -hydroperoxyalkylhydroperoxy radical ($HOOQ'OOH$) yields the OH radical and a ketohydroperoxide ($OQ'OOH$). Then, the dissociation of the ketohydroperoxide ($OQ'OOH$) results in the fuel-derived alkene and the additional OH radical. The rate-determining steps of low-

temperature chemistry are a formation of an alkyl radical and an alkylperoxy radical. As alkylperoxy radical formation reactions are exothermic and reversible, this reaction is the major heat release source of low-temperature chemistry. This shift determines the chain branching of radical formation, observed as negative temperature coefficient (NTC) behavior [60].

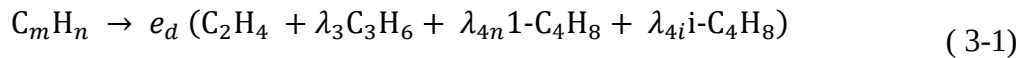
3.2 *Surrogate approach and HyChem*

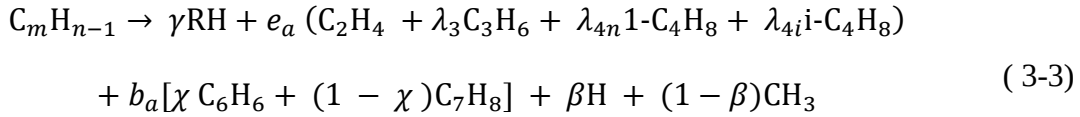
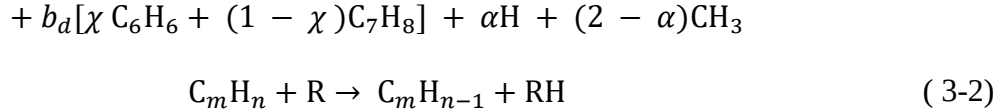
Chemical kinetic models are used to solve chemistry parts of governing equations during the numerical simulations of reactive flows (e.g., [36,37,61–63]). However, due to the complex composition and reaction network, appropriate chemical kinetic reaction mechanisms are not commonly available, especially for real fuels. Therefore, many researchers have been exploring alternative approaches to overcome the deficiency of detailed chemical kinetic models.

The perfect fidelity mechanism requires numerous chemical kinetic reactions and their thermodynamic properties during combustion. However, it is not foreseeable to thoroughly understand the kinetics and properties associated with the components and the possible reactions. Over the last few decades, the surrogate-fuel approach has focused on many studies and significant progress (e.g., [64–66]). Instead of developing a detailed reaction mechanism of a real fuel, the combustion behavior is predicted using a blend of several well-known chemicals. While considerable effort is needed to match the multiple physicochemical properties of the surrogates with that of the target fuel, such an approach has shown to be a powerful tool for the prediction of combustion behavior over a wide range of thermodynamic conditions, particularly when coupled with numerical simulations of the flow field. Many recent numerical simulations of combustion devices with real fuels have been achieved using the surrogate-fuel approach (e.g.,[61,67,68]).

Recently, a hybrid chemistry (HyChem) approach [56–58] was introduced. In this approach, the pyrolysis of the fuel is described by lumped reaction steps derived from experiments and estimations, and the oxidation process of pyrolysis fragments is modeled using a detailed reaction mechanism, USC Mech II [69]. This hybrid approach is based on the physics of the primary reaction pathways, so the reaction mechanisms produced from the approach are more reliable and preferred to other empirical methods. However, as mentioned in their paper, the lumped reaction model for the negative temperature coefficient (NTC) chemistry in HyChem is still empirical, and additional studies are required. As of now, the experimental measurement of lumped kinetic parameters requires significant effort with reasonable initial estimations. It is also highly dependent on changes in fuel composition. The current study suggests a feasible approach to utilize the HyChem model in practical environments, especially where the NTC and low-temperature regions of lean, stoichiometric, and rich mixtures.

The HyChem model comprises a lumped fuel pyrolysis model for parental fuels and a foundational, detailed fuel chemistry model for the pyrolysis and oxidation of small hydrocarbons. HyChem treated real fuels as a single lumped species, C_mH_n . Because of the limitation of common chemical kinetic solvers, m and n are positive integers. This lumped fuel species firstly breakdown into small numbers of pyrolysis products even with oxygen presence. Based on flow reactor experiments of jet fuels, the key pyrolysis products are C_2H_4 (ethylene), C_3H_6 (propene), 1- C_4H_8 (1-butene), i- C_4H_8 (iso-butene), CH_4 (methane), C_6H_6 (benzene), C_7H_8 (toluene), H_2 (hydrogen), and usually two radical species CH_3 and H . The nomenclature of Wang et al. [56–58] is used to express the thermal or oxidative thermal decomposition in high temperatures.





where R=H, CH₃, O, OH, O₂ and HO₂ and Table 3-1 explains the parameters in the equations.

Table 3-1 Description of independent stoichiometric parameters in HyChem formulation

Parameter	Description
α	Number of H atoms produced in the C-C fission reaction per fuel molecule
β	Number of abstracted H atoms per fuel molecule
γ	Yields of CH ₄ per fuel molecule in addition to H abstraction by CH ₃
λ_3	the ratio of C ₃ H ₆ to C ₂ H ₄
λ_{4n}	the ratio of 1-C ₄ H ₈ to C ₂ H ₄
λ_{4i}	the ratio of i-C ₄ H ₈ to C ₂ H ₄
χ	the ratio of C ₆ H ₆ to the sum of C ₆ H ₆ and C ₆ H ₅ CH ₃

The first reaction expresses parental fuels' thermal decomposition resulting from the C-C fission in the above chemical reactions. The reactive radicals, including H, CH₃ produced from the thermal decomposition and O, OH, O₂, and HO₂ produced through high temperature can further react with the fuel molecule as described in the second reaction. The second reaction represents that the readily reactive radicals attack the surrounding hydrogen atoms of fuel molecules resulting in the H abstraction. After the hydrogen atom is abstracted from the fuel molecule, the subsequent beta scission reaction converts the fuel radical into small hydrocarbon intermediates.

By the elemental conservation of the C and H elements, stoichiometric parameters can be expressed as:

$$e_d = \frac{[-(8 - 2\chi)m + (7 - 2\chi)n + 6\alpha + 2\chi - 26]}{6(2 + 3\lambda_3 + 4\lambda_{4n} + 4\lambda_{4i})} \quad (3-4)$$

$$e_a = \frac{[-(8 - 2\chi)m + (7 - 2\chi)n + 6\beta - (20 - 2\chi)(\gamma + 1)]}{6(2 + 3\lambda_3 + 4\lambda_{4n} + 4\lambda_{4i})} \quad (3-5)$$

$$b_d = \frac{(2m - n + 2)}{6} \quad (3-6)$$

$$b_a = \frac{(2m - n + 2\gamma + 2)}{6} \quad (3-7)$$

Four parameters of species yield (λ_3 , λ_{4n} , λ_{4i} , and χ) can be measured directly from the flow reactor experiments. Shock-tube time history experiments determine the values of α , β , and γ as they are involved in the rate coefficients. The values can be inversely estimated by comparing yields of C_2H_4 and CH_4 with respect to time.

This approach can significantly reduce the complexity of the chemical kinetic models in high temperatures as the representative reactions are lumped to express into detailed small hydrocarbon-dependent reactions. Since the approach is based on both physics of the reaction pathways and empirical pyrolysis results, it is reliable to model high-temperature chemistry.

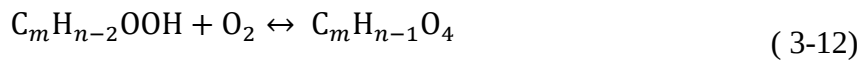
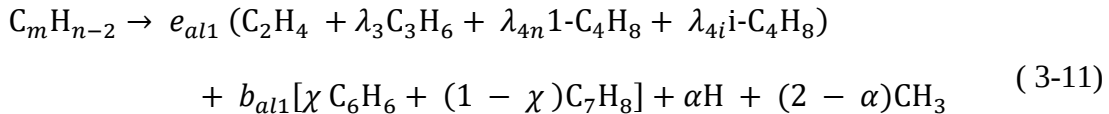
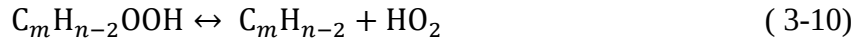
A lumped reaction model can be a simple solution to cover the NTC chemistry because of the complexity of chemical kinetics. This study focuses on the competition between a peroxy radical (RO_2) and a hydroperoxy radical ($QOOH$). I employ the same approach as the HyChem NTC model for Jet A [57] and Bikas and Peters [70]. HyChem Jet A mechanism proved that adding sub-mechanism does not influence validated high-temperature chemistry modeled according to the HyChem theory.

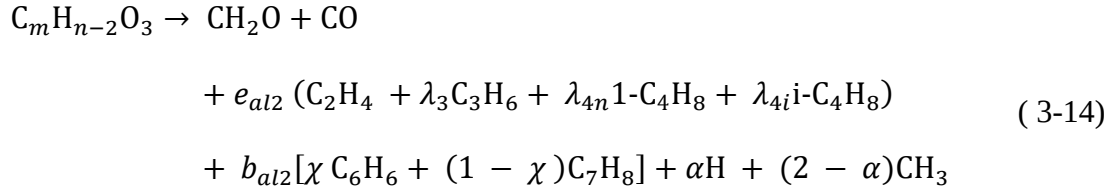
Then, the H-abstracted fuel molecule, alkyl radical, is considered to follow a generic low-temperature oxidation process. H-abstracted fuel, “fuel radical,” with O_2 produces a peroxy radical (RO_2), and it isomerizes to a hydroperoxy radical ($QOOH$) through H-atom transitioning.

This isomerization reaction is critical in the negative temperature coefficient regime because a temperature increase results in decreased reaction rates. Instead of a reversible isomerization reaction, $RO_2 - QOOH$ isomerization reaction is divided into forward and backward reactions to increase the degree of freedom. The RO_2 and $QOOH$ radicals have several chain propagating steps, including HO_2 or OH radical production. In this study, I considered chain propagation steps to merge into one dominant reaction converted into HO_2 radical and the alkene form (Q) of the parental fuel molecule [59].

Another pathway of $QOOH$ radical is a reaction with an additional O_2 to form a hydroperoxy alkyl peroxy radical (O_2QOOH), which can isomerize to a α -hydroperoxy alkyl hydroperoxy radical ($HOOQ'OOH$). The decomposition of the α -hydroperoxy alkyl hydroperoxy radical ($HOOQ'OOH$) yields the OH radical and a ketohydroperoxide ($OQ'OOH$). Then, the dissociation of the ketohydroperoxide ($OQ'OOH$) results in the fuel-derived alkene and the additional OH radical. As the accumulated radicals increase the system's temperature at this stage, the dominant reaction is the thermal decomposition of the fuel-derived alkene.

The reactions of NTC and low-temperature chemistry submodel are as follows.





The parameters (e_{al1} , e_{al2} , b_{al1} , and b_{al2}) in low-temperature chemistry can be obtained from the above parameters' equations by changing the number of elements. Because the reactions are lumped, and the fuel is originally multi-component, the radicals and species indicated above are pseudo-species and were estimated by the group additivity method [71].

Each elementary reaction is considered in the form of the Arrhenius reaction equation:

$$k = AT^b \exp\left(-\frac{E_a}{RT}\right) \quad (3-15)$$

where k is the reaction rate constant, A is the pre-exponential factor, b is the temperature exponent, E_a is the activation energy, R is the universal gas constant, and T is a reactor temperature

To sum up, the mechanism comprises three parts: the HyChem lumped for high-temperature combustion, a lumped RO_2 -QOOH cycle mechanism for low-temperature combustion, and the USC mech II for a detailed foundation chemistry model.

Chapter 4 Data-driven optimization

It is required to investigate the reaction rate coefficients of numerous reactions to develop chemical kinetic mechanisms of various operationally relevant fuels for military application. In terms of combustion chemical kinetics, the majority of reaction pathways and rates cannot be verified in the foreseeable future – a mathematically ill-defined problem. Especially, the reaction rate coefficients of lumped reaction steps should be optimized either statistically or computationally by comparing chemical species profiles and ignition delay times in well-characterized combustion devices, unlike the experimentally validated detailed reaction mechanisms of single fuel components. Many different optimization techniques could be utilized to modify the reaction rates in the base mechanism toward the experimental data set.

Optimization is a powerful tool to be applied in various engineering problems where it remains rather unknown. Optimization can be an instrument that may provide a sufficiently good solution to a complicated problem under imperfect information or limited capacity [72].

After the backbone mechanism of fuel satisfying chemical kinetic theory is built, the mechanism is optimized to develop data-driven chemical kinetic mechanisms. The sets of input parameters are reaction coefficients of lumped reaction parameters: Pre-exponential factor, temperature exponent, and activation energies. The performance measure is called the objective function, the criteria of how the optimized mechanism is similar to real experimental data. Optimization aims to find the set of input variables that minimize (or maximize) the objective function.

$$\operatorname{argmax} f(x), \quad x \in X \subseteq \mathbb{R}^n \quad (4-1)$$

where f is an objective function, x is input variables, the space X is for a domain, and $\mathbb{R}^n$ is a solution space. Since the ignition delay plot is represented as an Arrhenius plot, the value is converted into a logarithmic scale.

$$MSE = \frac{1}{n} \sum_{i=1}^n (\log_{10} y_i - \log_{10} \hat{y}_i)^2 \quad (4-2)$$

where y_i is a data point of the original mechanism, and $\hat{y}_i$ is a calculated result of the formulated mechanism.

In this chapter, three different optimization approaches: genetic algorithms, Bayesian optimization, and gradient descent method, are introduced and compared to develop data-driven chemical kinetic models of various operationally relevant fuels.

4.1 Stochastic and deterministic optimization

Optimization algorithms can be classified into several categories according to the standard. In this study, I classify it into two ways: deterministic optimization and stochastic optimization.

Deterministic optimization is an algorithm following a rigid mathematical way without random elements. This method commonly requires linear algebra and gradient calculation methods. Since the method is mathematical programming and has no random elements, the convergence to a solution is faster than stochastic-based algorithms. A rigorous mathematical formulation without stochastic elements guarantees unequivocal and replicable results from a deterministic optimization. However, mathematical calculations are required to optimize, and the optimal

solution could be a local optimum instead of the optimal global solution. When it comes to chemical kinetic problems, a series of differential equations take place in calculating thermodynamics values. Getting derivatives from such complicated equations cannot be achieved easily.

Stochastic optimization is an algorithm using and generating random variables. Stochastic optimization methods can be considered as generalized deterministic optimization tools. Giving the randomness permits less optimal local solutions within the search procedures. Many stochastic optimization techniques use statistical theories (e.g. game theory-based optimization) or mimic natural processes (e.g., genetic algorithms). Since the method is generalized to apply various optimization problems, the process is a derivative-free method, and users can easily adapt the method. On the other hand, the techniques have a slower convergence toward the optimal results, and incorrect parameter settings may lead to unwanted converged solutions.

Strategically, a rough optimization of stochastics optimization precedes a calibrated optimization of deterministic optimization to get better optimization results.

4.2 Test problem and results

The test problem is formulated to compare optimization techniques. The objective of the rate coefficient optimization is to minimize the loss between ignition delay simulation results from the original A2 NTC enabled detailed mechanism and that from the formulated mechanism. The loss will be minimized when reaction coefficients will have exactly matched each other. Two lumped reactions are chosen, and their reaction coefficients are changed into 0 values in the formulated mechanism. One lumped reaction is the high-temperature pyrolysis reaction: POSF10325 →

pyrolysis products (Reaction 1), and the other lumped reaction is the oxidation reaction of an alkyl radical: $A2C_{11}H_{21} + O_2 \leftrightarrow A2C_{11}H_{21}O_2$ (Reaction 9). Each elementary reaction is considered in the form of the Arrhenius reaction equation. From the original A2NTC enabled mechanism, ignition delay data points are calculated at $P_C = 2$ MPa and $\phi = 1.0$ and 0.5 between 0.8 to 1.4 in terms of $1000/T$ [1/K]. Mean Squared Error (also known as L2 loss) is used as a loss function for optimization. Since the ignition delay plot is represented as an Arrhenius plot, the value is converted into a logarithmic scale.

From the original A2NTC enabled mechanism, ignition delay data points are calculated at $P_C = 2$ MPa and $\phi = 1.0$ and 0.5 between 0.8 to 1.4 in terms of $1000/T$ [1/K]. Mean Squared Error (also known as L2 loss) is used as a loss function for optimization. Since the ignition delay plot is represented as an Arrhenius plot, the value is converted into a logarithmic scale.

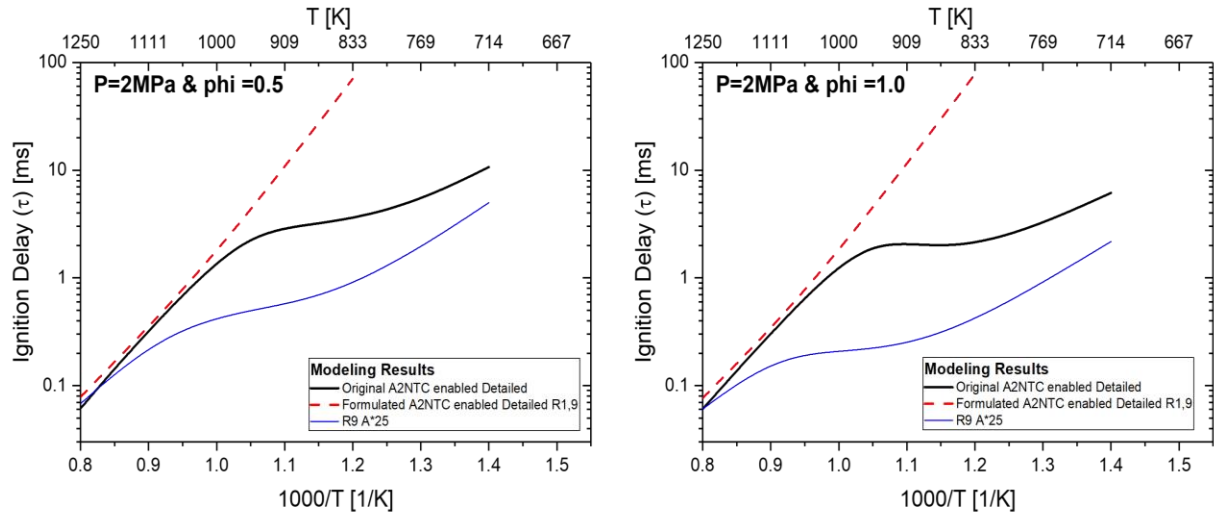


Figure 4-1 Ignition delay curve from HyChem A2 NTC enabled slow detailed mechanism (Black), R1&9 zero mechanism (Red), and R9 A*25 mechanism (Blue) under $P_C=2$ MPa and two different equivalence ratios from 1250 K to 714 K.

Figure 4-1 illustrates the ignition delay curve with respect to temperature at 2 MPa using three different mechanisms for stoichiometric and lean Jet A/air mixtures. The black line shows the results of the HyChem A2 slow NTC reaction enabled a slow detailed kinetic mechanism. The red line shows the formulated mechanism, which has R1 and R9 reaction coefficients changed to 0, and the blue line shows the mechanism, which has a pre-exponential factor of R9 that is 25 times higher than the original one. At high temperatures, some lumped reactions, fuel molecule, and radical and/or oxygen reactions provide an alternative chemical reaction pathway instead of fuel molecule beta scission and/or pyrolysis. On the other hand, reaction 9 is an important intermediate pathway to advance remaining low-temperature chemistry reactions. The red line prohibits, and the blue line accelerates the entering RO_2 -QOOH chemistry.

Optimization tool 1: Genetic Algorithm

A Genetic Algorithm (GA) is an optimization algorithm created by mimicking the process of natural selection where the better individuals are chosen for producing offspring of the next generation. Initially, the population is created within the boundaries according to the dimensions of inputs, and each individual has its own parameters. By a reproduction process, two parents are selected from the shuffled tournament by comparing merit values, but in this study, the merit value is changed into MSE in order to compare with other optimization techniques. A child is reproduced by a crossover of two parents' parameters to get better fitness. The reproduction process is repeated to create the same population size. GA proceeds over the generations until it fits well with the objectives of the problems. Previous studies showed the feasibility of GA in the chemical kinetic reaction mechanism [73–77].

Optimization tool 2: Bayesian Optimization

Bayesian optimization (BO) is a strategy for global optimization of a black-box function by constructing a posterior distribution of a surrogate model [78–80]. The Gaussian distribution is used as a surrogate model in this study. Then, acquisition functions suggest proposing sampling points in the searching space where the points show either a high objective or high uncertainty. The expected Improvement (EI) function is utilized as an acquisition function to trade-off between exploitation and exploration and determine the next sampling point. The newly added sample will be considered to expand the set of observations, and the steps are repeated until convergence or budget elapses.

$$x_t = \operatorname{argmax}_x u(x|D_{1:t-1}) \quad (4-3)$$

where x_t is the next sampling point, u is the acquisition function, and D is the dataset.

Optimization tool 3: Gradient Descent Method

Gradient descent is an optimization method based on a convex function and gradient calculation to minimize a given function to its local minimum [81]. It starts from the initial parameters, and from there, gradient descent uses the derivative of the function to find better values until convergence iteratively. A gradient represents how much the output of a function change with regard to the change of the values. Among various gradient descent methods, the stochastic gradient descent (SGD) optimizer is widely used in the machine learning communities due to its efficiency and robustness.

$$x_t = x_{t-1} - \gamma \nabla f(x_{t-1}) \quad (4-4)$$

where x_t is the next position, while x_{t-1} represents the current position. The minus sign refers to the minimization part of gradient descent, and the gamma is a learning factor.

4.3 Comparison of Optimization methods

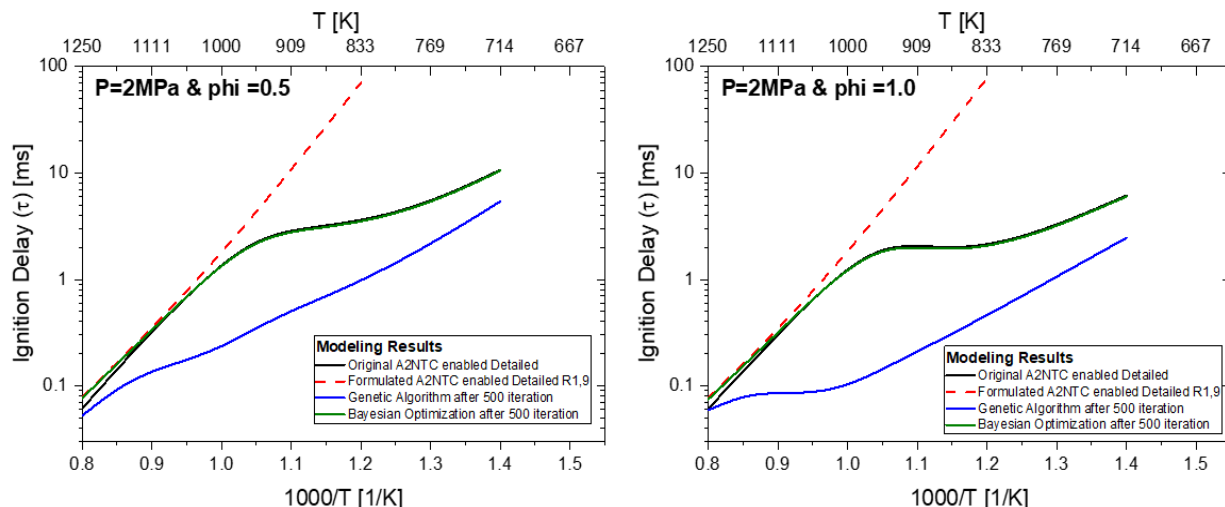


Figure 4-2 Ignition delay times calculated from the original model (Black), the test problem (Red dashed), the genetic algorithm optimized model (Blue), and Bayesian optimization optimized model (Green)

Figure 4-2 shows the comparison among the original HyChem model, the test problem model, and the stochastic optimized model using genetic algorithms (GA) and Bayesian optimization (BO). GA and BO implemented within the Python library are modified and utilized to optimize the mechanism, and Cantera kinetic solver performs thermodynamic and kinetic calculations. The number of maximum iterations was 500 for both cases. With regard to genetic algorithms (GA), the population size was 100, mutation probability and crossover probability were 0.3 and 0.7, respectively. I set the limitation on the variation of the parameters to within two orders of magnitude of the original values (both activation energy and pre-exponential factor), and the temperature exponent was bounded between -4 and 4. Both of the optimized models improve the

performance. The optimized results from genetic algorithms show large discrepancies even under minimized MSE cases. Otherwise, the results from Bayesian optimization show a better performance all over the range. Figure 4-3 shows the mean square error loss with regard to iteration numbers. Bayesian optimization is also much more accurate and efficient than genetic algorithms when it comes to computational cost.

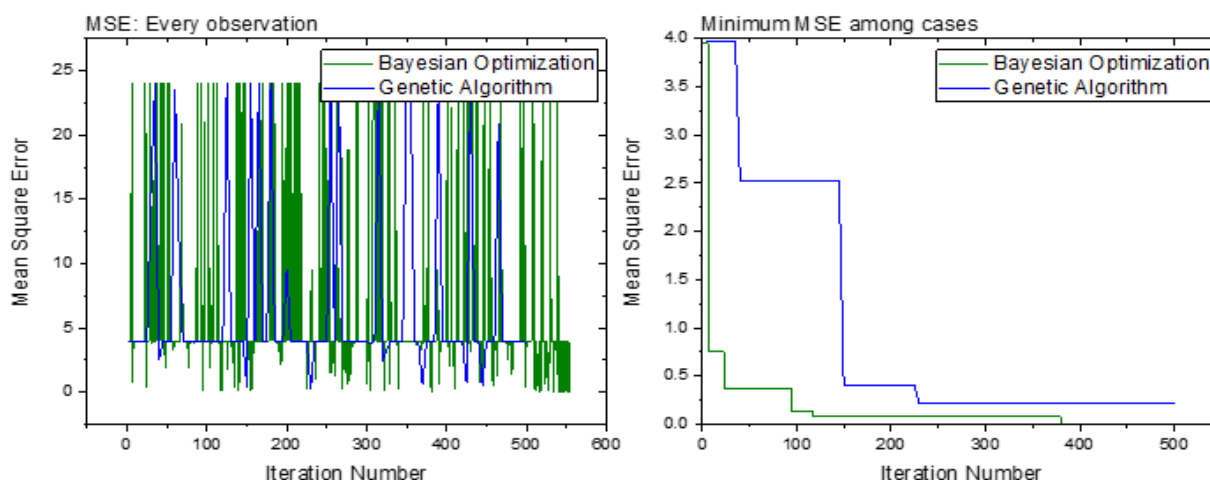


Figure 4-3 The history of the MSE loss function in terms of every observation (Left), and minimum among cases (Right)

Due to the complexity of the chemical kinetic ODE system, the gradients of ignition delay time are traditionally calculated using a brute force method where the computation is costly. Recent studies have tried to reduce the gradient calculation by using advanced algorithms [82–84]. Among different types of algorithms, this work utilizes the senBVP method, which involves reformulating the ignition delay sensitivity calculation into temperature sensitivity calculations [83]. Sensitivity is a tool to analyze how the different values of a set of independent variables affect a specific dependent variable under certain specific conditions.

$$S_{k_i}^{var} = \frac{k_i}{var} \frac{\partial(var)}{\partial k_i} \quad (4-5)$$

where var is any dependent variable, k_i is the reaction rate constant. The ignition delay sensitivity can be calculated by parameterization of temperature sensitivity according to the senBVP.

$$S_{k_i}^{\tau} = \frac{k_i}{\tau} \frac{\partial \tau}{\partial k_i} = \frac{k_i}{\tau} \frac{T}{T} \frac{\partial \tau}{\partial T} \frac{\partial T}{\partial k_i} = \left(\frac{k_i}{T} \frac{\partial T}{\partial k_i} \right) \frac{\partial \tau}{\partial T} \frac{T}{\tau} = S_{k_i}^T \frac{T}{\tau} \left(\frac{\partial T}{\partial \tau} \right)^{-1} \quad (4-6)$$

where T is a reactor temperature, and τ is an ignition delay time. Then, the following equations indicate the ignition delay gradient with respect to each reaction parameter.

$$S_{k_i}^{\tau} = \frac{k_i}{\tau} \frac{\partial \tau}{\partial k_i} \rightarrow \frac{\partial \tau}{\partial k_i} = \frac{\tau}{k_i} S_{k_i}^{\tau} \quad (4-7)$$

$$\frac{\partial \tau}{\partial A_i} = \frac{\partial \tau}{\partial k_i} \frac{\partial k_i}{\partial A_i} = \frac{\tau}{k_i} S_{k_i}^{\tau} T^{b_i} \exp\left(\frac{-E_{a_i}}{RT}\right) = \frac{\tau}{A_i} S_{k_i}^{\tau} \quad (4-8)$$

$$\frac{\partial \tau}{\partial b_i} = \frac{\partial \tau}{\partial k_i} \frac{\partial k_i}{\partial b_i} = \frac{\tau}{k_i} S_{k_i}^{\tau} A_i \exp\left(\frac{-E_{a_i}}{RT}\right) \ln(T) T^{b_i} = \tau S_{k_i}^{\tau} \ln(T) \quad (4-9)$$

$$\frac{\partial \tau}{\partial E_{a_i}} = \frac{\partial \tau}{\partial k_i} \frac{\partial k_i}{\partial E_{a_i}} = \frac{\tau}{k_i} S_{k_i}^{\tau} A_i T^{b_i} \exp\left(\frac{-E_{a_i}}{RT}\right) \frac{(-1)}{RT} = \tau S_{k_i}^{\tau} \frac{(-1)}{RT} \quad (4-10)$$

and then, derived equations are represented with respect to the MSE form.

$$MSE = \frac{1}{n} \sum_{i=1}^n (\log_{10} \tau_i - \log_{10} \hat{\tau}_i)^2 \quad (4-11)$$

For any reaction coefficients y,

$$\begin{aligned}
\frac{\partial MSE}{\partial y} &= \frac{1}{n} \sum_{i=1}^n \left[-\frac{2 \log_{10}(\tau_i)}{\hat{\tau}_i} \frac{\partial \hat{\tau}_i}{\partial y} + \frac{2 \log_{10}(\hat{\tau}_i)}{\hat{\tau}_i} \frac{\partial \hat{\tau}_i}{\partial y} \right] \frac{1}{\ln(10)} \\
&= \frac{1}{n} \sum_{i=1}^n \left[-\frac{2}{\hat{\tau}_i} \frac{\partial \hat{\tau}_i}{\partial y} [\log_{10}(\tau_i) - \log_{10}(\hat{\tau}_i)] \right] \frac{1}{\ln(10)}
\end{aligned} \tag{4-12}$$

Therefore,

$$\frac{\partial MSE}{\partial A_j} = \frac{1}{n \ln(10)} \sum_{i=1}^n \left[-\frac{2S_{kj}^\tau}{A_j} [\log_{10}(\tau_i) - \log_{10}(\hat{\tau}_i)] \right] \tag{4-13}$$

$$\frac{\partial MSE}{\partial b_j} = \frac{1}{n \ln(10)} \sum_{i=1}^n \left[-2S_{kj}^\tau \ln(T_i) [\log_{10}(\tau_i) - \log_{10}(\hat{\tau}_i)] \right] \tag{4-14}$$

$$\frac{\partial MSE}{\partial E_{aj}} = \frac{1}{n \ln(10)} \sum_{i=1}^n \left[-2S_{kj}^\tau \left(\frac{-1}{RT_i} \right) [\log_{10}(\tau_i) - \log_{10}(\hat{\tau}_i)] \right] \tag{4-15}$$

Using the above-derived gradients with respect to the reaction coefficients, MSE could be minimized. A deterministic optimization tool is built with Cantera's temperature sensitivity calculation. Derived equations are validated by using the finite-difference method (often termed the "brute-force method"). A pyrolysis reaction (R1) of POSF10325 is selected to calculate the gradients of reaction parameters under compressed pressure at 2 MPa, compressed temperature at 1100K, and stoichiometric conditions. Figure 4-4 and Table 4-1 represent the validation results, showing that the formulated equations can calculate the gradients. According to the MSE distribution with respect to reaction parameters, there could be two minimum cases (Left and right). If one reaction is slow, the alternative reaction pathway could be used to advance the chemical reaction. If the pyrolysis reaction is slow, then the reaction combining with oxygen

molecules could be dominated in terms of an alternative pathway instead of the pyrolysis reaction and advance the following combustion reactions.

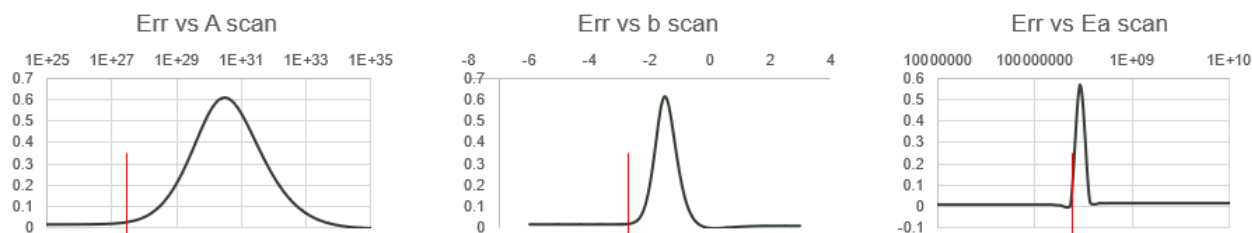


Figure 4-4 MSE errors with respect to reaction parameters (Pre-exponential factor, temperature exponent, activation energy)

Table 4-1 Gradient calculation based on Finite difference method and derived equation for utilizing sensitivity analysis regarding compressed temperature

	Finite difference method	Derived equation
$\frac{\partial MSE}{\partial A_j}$ @ $A=1.53E+27$	3.806E-30	3.809E-30
$\frac{\partial MSE}{\partial b_j}$ @ $b=-2.58$	0.0461	0.0422
$\frac{\partial MSE}{\partial Ea_j}$ @ $Ea=87969$ cal/mol	-4.945E-10	-5.005E-10

Since the gradients varied according to reaction parameters, the value should be normalized and regularized. Only the temperature exponent value will be adjusted to minimize the loss without mathematical techniques. The gradient descent method is implemented to optimize the test problems. Temperature sensitivity is calculated from CVODES [85,86], but it requires a longer time than calculating ignition delay. Table 4-2 shows the parameters of the outcome mechanism. The parameters of Bayesian optimization and the Gradient descent method are closer to the original model, but the GA's result shows a significant discrepancy.

Table 4-2 Optimized reaction parameters in models according to optimization techniques, the unit of Ea is cal/mol

	Original	GA	BO	Gradient
R1 POSF10325 => Pyrolysis products	A : 1.53e+27 b : -2.58 Ea : 87697	A : 2.59e+25 b : 0.87 Ea : 79460	A : 9.45e+25 b : -2.94 Ea : 97631	A : 1.52e+27 b : -2.58 Ea : 87702
R9 A2C11H21 + O2 <=> A2C11H21O2	A : 1.25e+10 b : 0 Ea : 0	A : 6.17e+9 b : 0 Ea : 0	A : 1.27e+10 b : 0 Ea : 0	A : 1.26e+10 b : 0 Ea : 0

Chapter 5 Autoignition of F-24/ATJ blends

This chapter investigates the autoignition characteristics of military aviation fuel (F-24), alternative alcohol to jet (ATJ) fuel, and four volumetric blends of two fuels by analyzing chemical ignition delay over a wide temperature range in the RCM and shock tube. This experiment can explore the effects of CN/chemistry with minimized changes to Atomization. Chemical kinetic data for these blended fuels can provide fundamental ignition characteristics of a commonly used army conventional jet fuel and an alternative fuel and blending effects on autoignition. Ultimately, the ignition delay data will provide to the development of chemical kinetic mechanisms of F-24 and ATJ blended fuels.

5.1 Chemical and physical properties

Two different single kerosene-based fuels were chosen as reference fuels: F-24 and ATJ (POSF 12368). F-24 is a military-purpose jet fuel composed of ASTM D910 Jet A plus the military additives: status dissipater additive (SDA), fuel system icing, inhibitor (FSII), and corrosion inhibitor/lubricity improver (CI/ LI)) [87]. F-24 is based on Jet A fuel, thus it is expected that the physicochemical properties and combustion behavior of F-24 are similar to those of Jet A.

The alternative alcohol to jet (ATJ) fuel can be produced by biomass sources such as sugars, starches, or lignocellulosic biomass. Any fermentable sugars are fermented with yeast to turn into isobutanol. The isobutanol goes through additional steps at a biorefinery to refine into ATJ. To maintain a high concentration of alcohol, the produced isobutanol is dehydrated using phase separation. Through the dehydration process, oxygen abstraction from the molecules converts into

isobutylene. Then, oligomerization allows isobutylene to form largely branched hydrocarbon structures from C8 to C16. The branched iso-paraffinic molecules have single carbon-to-carbon bond and are readily hydrogenated to hydrocarbons. ATJ fuels satisfy ASTM D7566 [88], are isobutanol- and ethanol-based fuels standard, and are used in aviation.

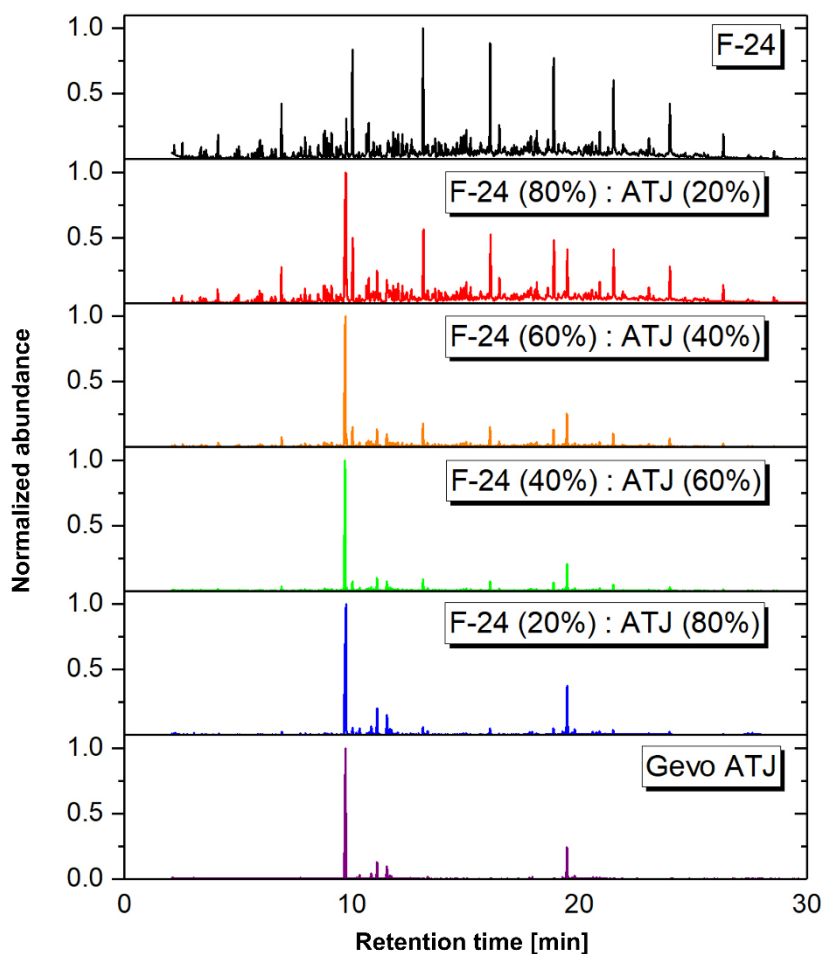
Fuels were blended at four volumetric ratios, ranging from 20% to 80%, incrementing by 20%. The chemical and physical properties of two neat fuels and their blends are listed in Table 5-1. As a wide range of CN (48.5 to 17.7) can be formulated by blending two different kinds of fuels, this experiment can explore the effects of CN/chemistry with minimized changes to Atomization. A gas chromatography/mass spectrometry (Agilent Technology, model 6890N/5973) was used to analyze the detailed chemical composition of fuels, as shown in Figure 5-1. F-24 shows a very similar structure to conventional jet fuels, which contain several normal alkanes peaks showing evenly distributed Gaussian shapes. Along with the majority of normal alkanes, F-24 also contains diverse hydrocarbon components, including branched alkanes, cyclic alkanes, and aromatics. One significant difference between F-24 and Jet A is peaks for carbon numbers lower than C8. A large portion of high carbon number alkanes in F-24 may indicate its higher freezing point and boiling point compared to conventional jet fuels. Since less energy is required to break higher n-alkanes, F-24 shows slightly higher fuel reactivity. ATJ contains the dominant peaks of two neat components. ATJ fuel mainly consists of two highly branched isoparaffins: iso-dodecane (2,2,4,4,6 or 2,2,4,4,6 pentamethyl heptane) and isocetane (2,2,4,4,6,8,8 or 2,2,4,4,6,6,8 heptamethylnonane).

Table 5-1 Selected physical and chemical properties of F-24/ATJ blends

Fuel	[vol %]	F-24	80/20	60/40	40/60	20/80	ATJ
Properties	Methods	Properties					
Cetane Number	ASTM D613	48.5	42	35.5	29.4	<21.4 ^a	<17.7 ^{a,b}
MW [g/mol]	(calculated)	160.6	164.08	167.56	171.04	174.52	178
Density [g/ml]	ASTM D4052	0.8037	0.795	0.7862	0.7774	0.7687	0.7595
Viscosity [mm ² /sec]	ASTM D445	1.377	1.395	1.415	1.446	1.479	1.528
Flash Point [°C]	ASTM D93	48.3	50.0	48.9	50.6	50.0	51.1
HCR	SAE J1829	1.97	1.98	2.02	2.11	2.11	2.16
Carbon content [wt%]	ASTM D5291	85.84	85.67	85.43	84.94	84.92	84.63
Hydrogen content [wt%]	ASTM D5291	14.16	14.22	14.48	15.06	15.01	15.37

^a Lowest cetane number that can be measured from ASTM D613 is 21.4

^b DCN 17.7 is measured from ASTM D6890

**Figure 5-1** Gas chromatography mass spectrometry results for F-24 / ATJ blended fuels

5.2 Ignition delay

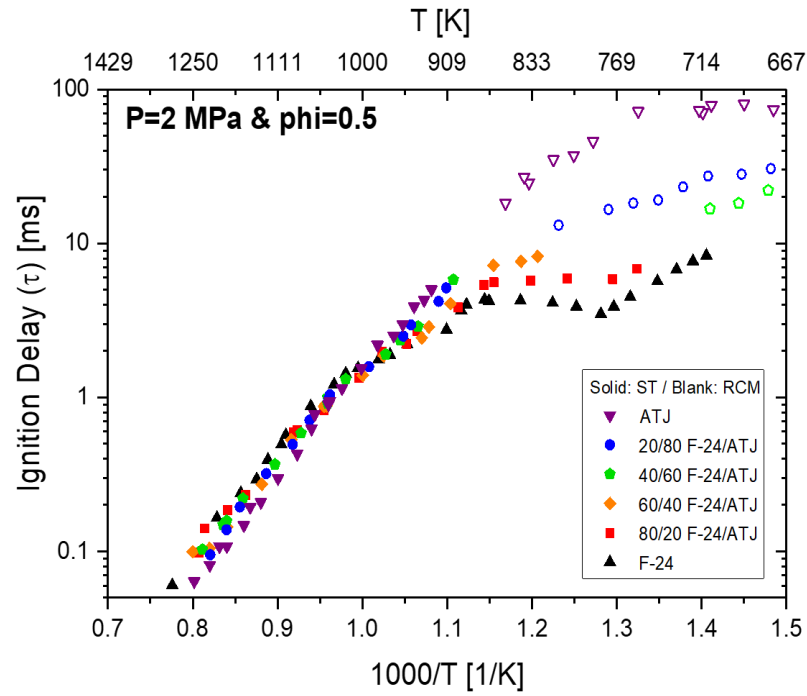


Figure 5-2 Overall chemical ignition delays for F-24/ATJ blends at $P_C = 2$ MPa and $\phi = 0.5$. Solid points and blank points from shock tube and RCM, respectively

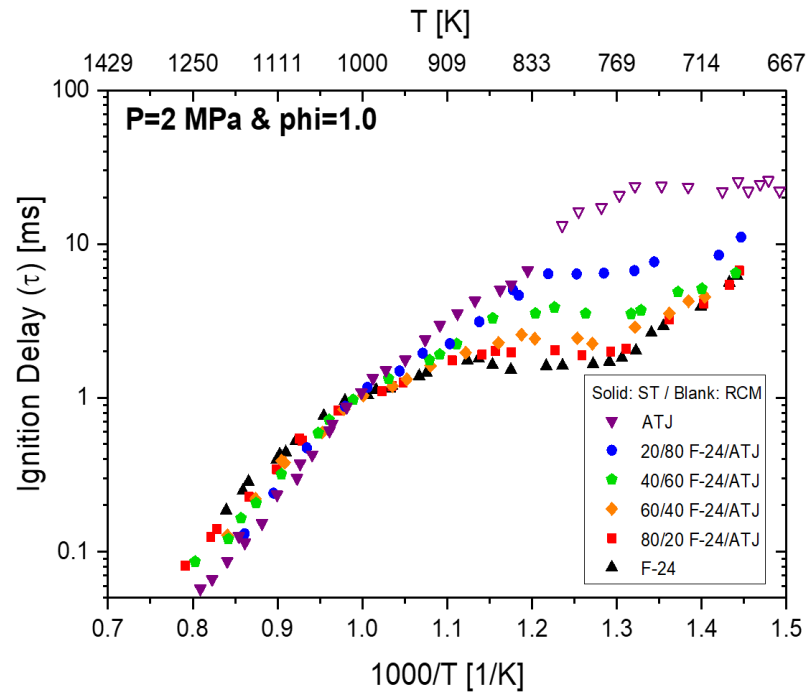


Figure 5-3 Overall chemical ignition delays for F-24/ATJ blends at $P_C = 2$ MPa and $\phi = 1.0$. Solid points and blank points from shock tube and RCM, respectively

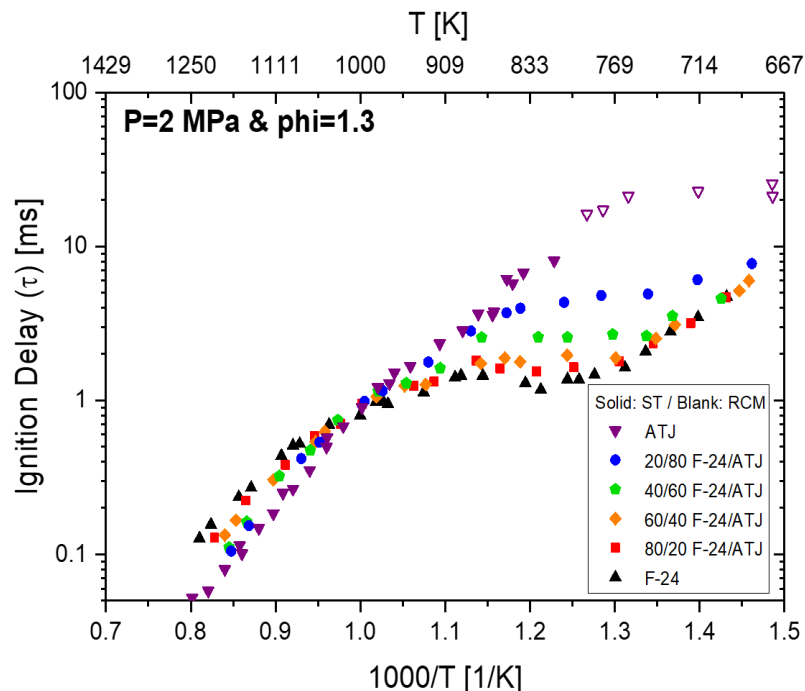


Figure 5-4 Overall chemical ignition delays for F-24/ATJ blends at $P_C = 2$ MPa and $\phi = 1.3$. Solid points and blank points from shock tube and RCM, respectively

Figures 5-2, 5-3, and 5-4 display overall ignition delay time among various fuels at 2 MPa under lean ($\phi=0.5$), stoichiometric ($\phi=1.0$), and rich ($\phi=1.3$) condition respectively. Figure A-1, A-2, and A-3 in Appendix A. show computed uncertainty values of each condition.

Unlike conventional chemical ignition delay investigation focusing on only low or high, the results indicate the entire temperature range of F-24/ATJ blends' ignition delay. Computed uncertainty values include the error of sampling, reliability of the equipment, and computation algorithms. Overall, the uncertainty values to the compressed temperature and measured ignition delay time are less than 5% in this experiment.

Generally, we can observe a conventional Arrhenius relationship, a negative dependence on temperature, and retarded ignition time of ATJ compared to Jet A. The highly branched structures

of isododecane and isocetane are attributed to the longer ignition delays. The high levels of branching result in inhibiting chemical reactions.

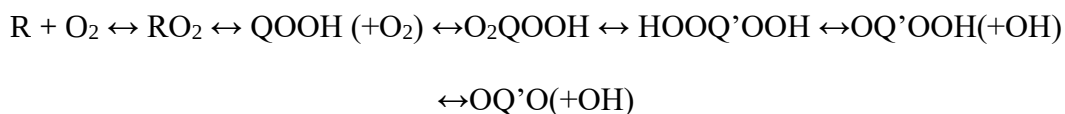
In high temperatures, the thermal decomposition of the parental fuel and oxidation of pyrolysis products are the rate-limiting combustion reaction depending on temperature. According to chemical composition analysis, ATJ mostly consists of isoalkanes, and F-24 has various kinds of hydrocarbons: normal alkanes, isoalkanes, cycloalkane, etc. Chemical structure differences between two fuels contribute to a different distribution of pyrolysis products. By hyperconjugation and inductive effect, large numbers of branched methyl groups in isoalkane structures can easily donate electrons. Empty 2p orbital of carbon can be easily overlapped with the nearby methyl group's C-H sigma orbital. Because of electron density differences, electron distribution in sigma orbital can move to P orbitals. The C-C bond energy between tertiary radical and carbon is relatively lower than other radicals. Isoalkane can easily convert into stable tertiary radicals under fuel pyrolysis reaction. Therefore, the main pyrolysis products of isoalkanes are the large portion of iso-butene and the small portion of propene. Normal alkanes and cycloalkanes easily decompose into methyl and primary radicals by C-C beta scission reactions, and their C-C bond energies are relatively higher than tertiary radicals.

Consequently, conventional jet fuels produce ethylene and methane by thermal decomposition. Regarding the reactivity of small hydrocarbons, the oxidation of isobutene is slower than that of ethylene and methane. If the temperature is high enough where the rates of fuel decomposition are similar, a high level of isobutene resulting from isoalkane decomposition as an intermediate is less reactive, attributing to the longer ignition delay.

According to the results, the thermal decomposition of the fuel is a dominant reaction above around 1000K at compressed pressure of 2 MPa. Lower CN fuel, ATJ, has a shorter ignition delay

time, and the rate of fuel decomposition can explain it. As the effect of fuel decomposition reduces as the equivalence ratio decreases, ATJ and F-24's ignition delay times show somewhat similar, short, and linear ignition delay times. Another group reported that ATJ retarded again after 1300 K [56]. Since oxygen does not affect β -scission inside the fuel molecules, the amount of oxygen present influences the overall ignition delay by affecting the small hydrocarbon oxidation.

In low-temperatures, the general chemical reaction of low-temperature combustion is as follows:



It is well known that the rate-determining steps of the above reaction pathways are the $R + O_2 \leftrightarrow RO_2$ equilibrium reaction and the $RO_2 \leftrightarrow QOOH$ isomerization reaction [55,89,90]. The heavily branched structure of isododecane and isocetane results in a retarded ignition delay. In low-temperature combustion, the structure of iso- in the isomerization reactions $RO_2 \leftrightarrow QOOH$ and $O_2QOOH \leftrightarrow HOOQ'OOH$ inhibits its isomerization. The reasoning for this is that it usually has primary bonds, which are among the most stable type of C-H bonds. Also, the transition state ring of its isomerization proceeds under 5-membered transition state rings. In addition to this, isocetane and isododecane have been reported to produce a high amount of isobutene, a stable chemical, under the combustion reaction pathway [58]. Otherwise, the structure of normal-alkanes and cyclo-

alkanes is likely to have a 6 or 7-member transition state ring and secondary bonds. Another notable aspect of ATJ is that negative-temperature-coefficient (NTC) behavior, a decrease in reaction activity with an increase in temperature, begins faster than F-24. The NTC behaviors start earlier with decreasing compressed pressure, and the ignition delay becomes longer. This is due to the fact that oxidization reactions $R + O_2 \leftrightarrow RO_2$ and $QOOH + O_2 \leftrightarrow O_2QOOH$ will be hindered.

In terms of blending ratio, ignition delay increases for blended fuels with an increasing volumetric ratio of ATJ. Increasing ATJ concentration did not show linear increments of ignition delay time. Adding F-24 up to 60% had a slight increment of ignition delay times while adding 80% F-24 showed an intermediate reactivity between F-24 and ATJ. The reactivity of blends likely tends to follow the fuel with higher reactivity. When the more reactive fuel undergoes the chain branching step in the mixture system, it will sufficiently provide OH radicals and heat to the system. The OH radical and heat release from the fuel with higher reactivity will accelerate the other fuel's reactivity. The result also shows that even a small portion of F-24 can dramatically change the ignition delay.

5.3 Chapter Summary

The autoignition characteristics of two neat fuels (F-24 and ATJ) and four volumetric blended fuels (20, 40, 60, and 80% F-24 in ATJ) have been investigated using the RCM and shock tube over a wide range of temperatures at compressed pressures of 2 MPa at various equivalence ratios (0.5, 1.0, and 1.3). Fuels with a higher amount of F-24, containing an abundance of normal alkanes and cyclo alkanes, indicate higher chemical reactivity. On the other hand, the heavily branched alkane in ATJ results in different autoignition characteristics depending on the compressed

temperature. Below 1000K, F-24 showed higher chemical reactivity. On the other hand, heavily branched alkanes of ATJ hinder isomerization reactions in low-temperature combustion chemistry. In addition to retarded ignition delay, isoparaffin enters the Negative Temperature Coefficient (NTC) regime earlier than any other conventional jet fuels. Under different air-fuel ratios, linear blending has a non-linear effect on ignition. The blended fuels show non-linear variation in ignition delay, and 20/80 F-24/ ATJ indicates the middle reactivity between two neat fuels. Chemical structures of each fuel influence ignition delay. However, fuels having lower cetane with heavily branched alkanes in high temperatures showed shorter ignition delay as they are more readily broken down into small radical species. The results of this study show the importance of chemical structure on ignition chemistry under low-temperature and the guideline of fuel blending of two different neat fuels for providing optimal utilization in advanced combustion.

Chapter 6 Autoignition of Varied CN fuels

This chapter evaluates the effects of cetane number on autoignition reactivity and chemical ignition delay. Cetane number is a representative metric that summarizes combustion characteristics across various fuels' relevant properties. However, there is no concrete relationship between cetane number and chemical reactivity. To investigate the impact of cetane number on combustion characteristics, a set of test fuels have been formulated with varying cetane numbers between 30 and 55 while maintaining other properties as constant as possible. The results provide a guideline for practical experiments to evaluate the impact of cetane number on combustion characteristics.

6.1 *Chemical and physical properties*

The four different varied CN fuels (30, 40, 50, and 55) have been formulated from commercially available Jet-A aviation fuel. The varied CN fuels are constructed by maintaining other physical and chemicals within a similar range, as shown in Table 6-1. Of the restricted properties, density, hydrogen to carbon ratios (HCRs), and their individual species content have been strictly controlled to minimize deviations among the fuels. HCR of the fuels is especially well maintained with an average of 2.001 and a standard deviation of 0.02. Although other properties are not perfectly maintained, the variations were minimized to isolate the true effects of cetane number on combustion characteristics. Chemical species are added as either cetane improvers or cetane inhibitors. The detailed Gas Chromatography/Mass Spectrometry (Agilent

Technology, model 6890N/5973) results are shown in Figure 6-1. The normalized abundance is shown relative to retention time.

The main components of the four tested fuels are n-decane, n-undecane, and n-dodecane, which are the main components of conventional jet fuels. Lower reactivity fuels (CN-30 and CN-40) are controlled by adding isododecane (2,2,4,6,6-pentamethylheptane) and 1&2-methylnaphthalene, which exhibit lower reactivity. The cetane numbers of 2,2,4,6,6-pentamethylheptane and x-methylnaphthalene are extremely low compared to conventional normal alkanes, 9 and 0, respectively. The CN-50 fuel has a normal Gaussian distribution of normal alkane like other conventional petroleum-derived jet fuels, generally having a cetane number near 50. Regarding the CN 55 fuel, Min *et al.* [91] and Meininger *et al.* [92] reported that a representative cetane improver, 2-ethylhexylnitrate (i.e., 2-EHN), has been used to increase fuel reactivity. However, the spectroscopy results do not observe the peaks of these cetane improvers. Instead, it contains a large portion of higher n-alkanes (C14-16) which can be easily broken down into smaller species in terms of fuel pyrolysis.

Table 6-1 Selected physical and chemical properties of Varied CN fuels

Properties	CN30	CN40	CN50	CN55
Cetane Number	30.0	41.0	51.0	54.0
MW [g/mol]	162.9	164.4	156.3	161.9
Density [g/cc]	0.78	0.80	0.79	0.79
Flash Point [°C]	52	59	50	57
H/C ratio	1.99	1.97	2.01	2.01
C content [wt%]	85.72	85.60	85.47	85.47
H content [wt%]	14.3	14.1	14.4	14.4

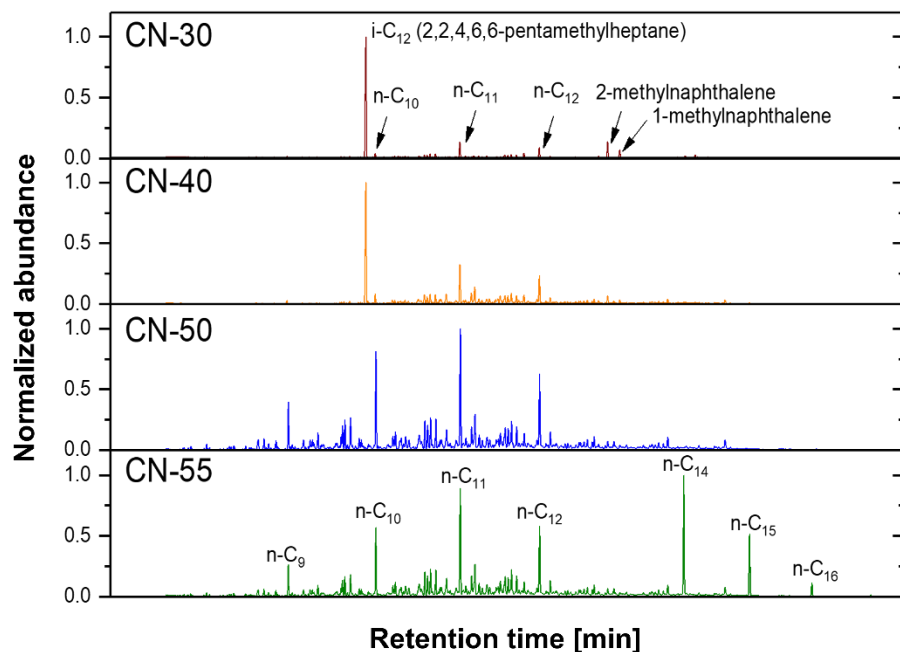


Figure 6-1 Gas chromatography mass spectrometry results for Varied CN fuels

6.2 Ignition delay

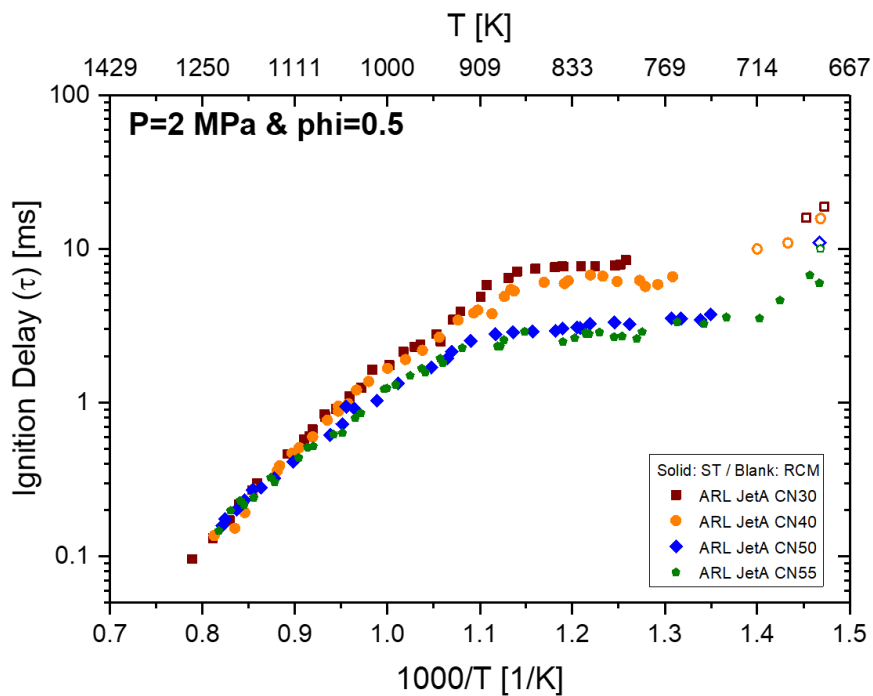


Figure 6-2 Overall chemical ignition delays for Varied CN fuels at $P_C = 2$ MPa and $\phi = 0.5$. Solid points and blank points from shock tube and RCM, respectively

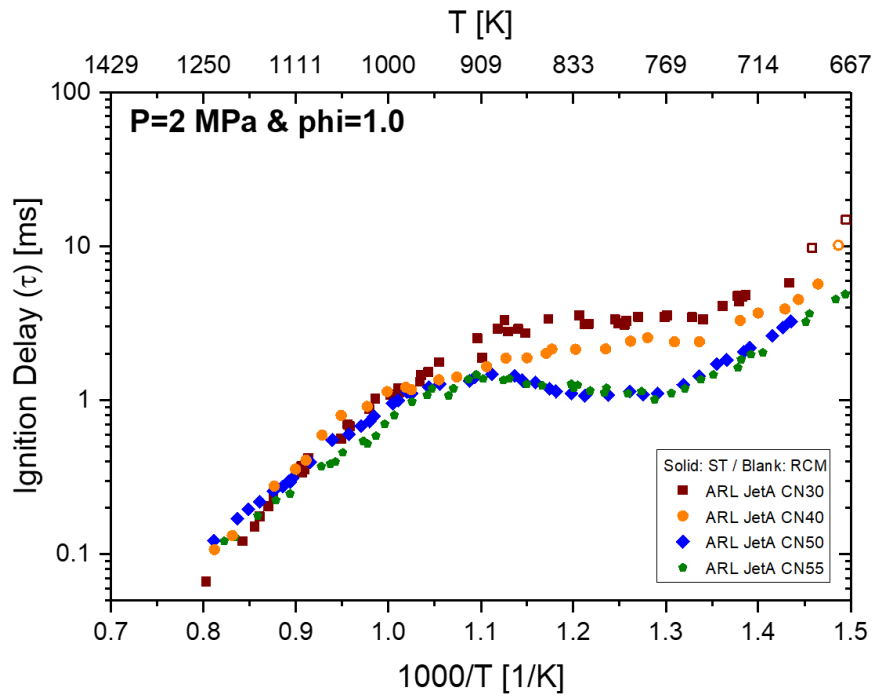


Figure 6-3 Overall chemical ignition delays for Varied CN fuels at $P_C = 2$ MPa and $\phi = 1.0$. Solid points and blank points from shock tube and RCM, respectively

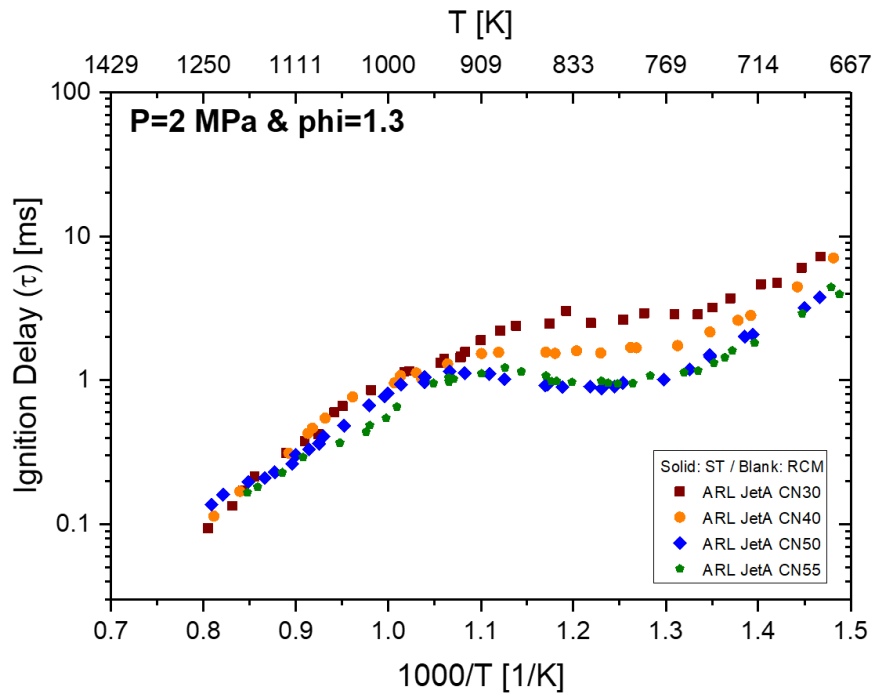


Figure 6-4 Overall chemical ignition delays for Varied CN fuels at $P_C = 2$ MPa and $\phi = 1.3$. Solid points and blank points from shock tube and RCM, respectively

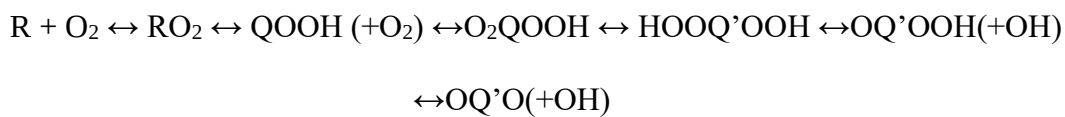
Figures 6-2, 6-3, and 6-4 show overall ignition delay time among various fuels at 2 MPa under lean ($\phi=0.5$), stoichiometric ($\phi=1.0$), and rich ($\phi=1.3$) condition respectively. Figures A-4, A-5, and A-6 in Appendix A. show computed uncertainty values of each condition.

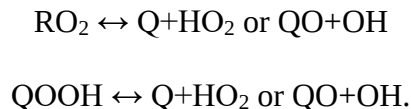
Overall, a conventional Arrhenius relationship, a negative dependence on temperature, is observed. Ignition delays between CN30, CN40, and CN 50 start to show a clear difference below 1000K, which can be considered the starting negative temperature coefficient (NTC) regime, but CN 50 and CN55 appear nearly identical to each other. As temperature decreases, the curves of CN30 and CN40 converge, and CN 50 and CN55 start to be separated slightly. The trend of CN30 and CN40 are similar, and the trend of CN 50 and CN55 are similar can be explained by the chemical composition similarity between the pairs of fuels. CN30 and CN40 contain iso-dodecane and methylnaphthalene; CN50 and CN55 mainly contain normal alkanes.

Most of the fuels show fairly similar, short, and linear ignition delay times above 1000K. CN30 has a shorter ignition delay in the high-temperature regions than CN50 and CN 55. This can be explained by which step of the combustion reaction is rate-limiting.

Above 1000 K, the overall reaction rate is determined by the thermal decomposition of the parent fuel. Since iso-alkanes have large numbers of branched methyl groups, fuels will be decomposed into stable tertiary radicals by hyperconjugation. On the other hand, the structure of normal alkanes is likely to decompose into methyl and primary radicals. If the temperature is high enough where the rates of fuel decomposition are similar, the heavily branched structure will exhibit lower reactivity due to stabilized radical species.

Below 1000 K, the general chemical reaction of low-temperature combustion is as follows:





It is well known that the rate-determining steps of the above reaction pathways are the $\text{R} + \text{O}_2 \leftrightarrow \text{RO}_2$ equilibrium reaction and the $\text{RO}_2 \leftrightarrow \text{QOOH}$ isomerization reaction [55,89,90]. The heavily branched structure results in a retarded ignition delay.

In low-temperature combustion, the structure of iso-alkane in the isomerization reactions $\text{RO}_2 \leftrightarrow \text{QOOH}$ and $\text{O}_2\text{QOOH} \leftrightarrow \text{HOOQ}'\text{OOH}$ inhibits its isomerization. This is because it usually has primary bonds, which are among the most stable type of C-H bonds. Also, the transition state ring of its isomerization proceeds under 5-membered transition state rings. In addition, heavily branched structures have been reported to produce a high amount of isobutene, a stable chemical, under the combustion reaction pathway [58]. Otherwise, the structure of n-alkanes is likely to have a 7-member transition state ring and secondary bonds.

Another notable aspect of lower CN fuels is that negative-temperature-coefficient (NTC) behavior, which decreases reaction activity with an increase in temperature, begins faster at a lower temperature than higher CN fuels. The NTC behaviors start earlier with decreasing compressed pressure, and the ignition delay becomes longer. This is since oxidation reactions $\text{R} + \text{O}_2 \leftrightarrow \text{RO}_2$, and $\text{QOOH} + \text{O}_2 \leftrightarrow \text{O}_2\text{QOOH}$ will be hindered.

Equivalence ratio minimally affects ignition delay in the high-temperature range, where fuel pyrolysis is the rate-limiting step. Since oxygen does not affect β -scission inside the fuel molecules, there is no discernible difference among the ignition delay curves in the high-temperature regime. The amount of oxygen present for the oxidation of fuel breakdown products

slightly affects the overall ignition delay. Once alkyl radicals are produced by hydrogen abstraction at low-temperatures, oxygen influences low-temperature chemistry. At lean conditions, the deficiency of alkyl radicals in $R + O_2 \leftrightarrow RO_2$ limits first-stage heat release, slowing the $RO_2 \leftrightarrow QOOH$ isomerization reaction. The first step is also limited by scarce oxygen in the mixture in rich conditions. The ignition delay time is shortest at the stoichiometric condition at a low temperature.

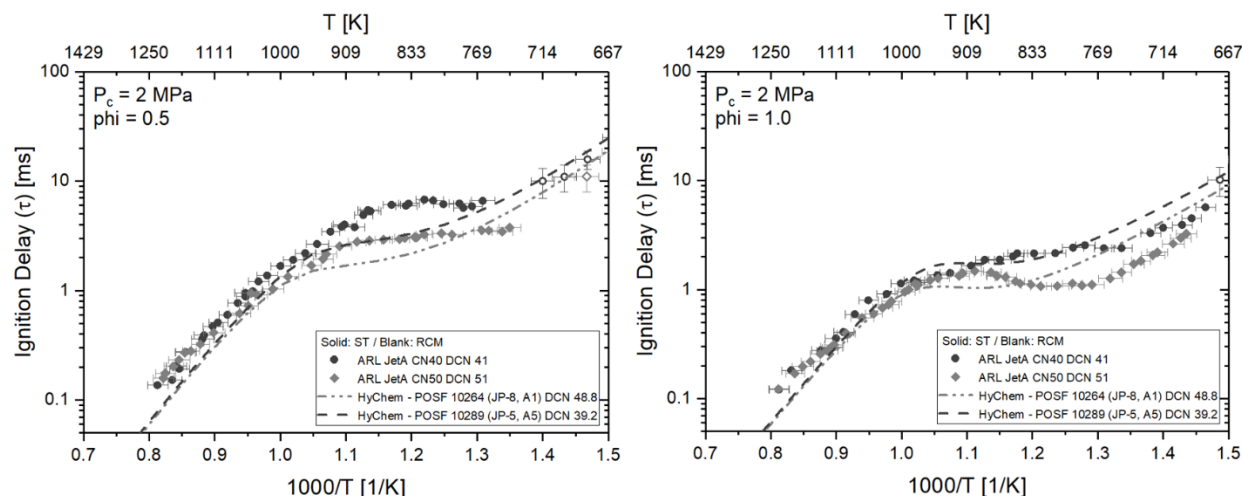


Figure 6-5 Ignition delays of fuels with a DCN of approximately 40 and 50 at 2 MPa

The ignition delay results of CN40 and CN50 are compared with conventional jet fuels, JP-5 and JP-8 measured in the National Jet Fuels Combustion Program (NJFCP), which have similar derived cetane number, respectively, as shown in Figure 6-5. Hybrid Chemistry (HyChem) JP-8 and JP-5 models [57] are employed to compare chemical ignition delay results. In this approach, the pyrolysis of the fuel is described by lumped reaction steps derived from experiments and estimations, and the oxidation process of pyrolysis fragments is modeled using a detailed reaction mechanism, USC Mech II [69]. HyChem models are validated using various experimental metrics, including ignition delay and species time history [57].

Although the derived cetane numbers of the two comparison fuels are nearly identical to CN fuel counterparts, the chemical compositions are quite different. Conventional jet fuels contain various chemical structures, including iso-alkanes, normal-alkanes, and aromatics, but formulated CN fuels in this experiment mainly contain Gaussian distributed normal-alkanes, and CN40 fuels have heavily branched alkanes to lower cetane number.

While the intermediate temperature region and NTC region under stoichiometric conditions appear to be correlated to the DCN of the fuel at least the ranking among them, but no clear relationship in the other regions. It is seen that similar cetane number fuels could show different chemical ignition delays over a wide range of temperatures. Especially, both experimental and simulated results at high temperatures appear to converge to the same ignition delay as temperature increases. The chemical ignition delay results are closely matched, starting around 830K, which is near the operating condition (~ 850 K and ~ 2.14 MPa) specified in the constant volume chamber ASTM D6890-10a ignition quality tester (IQT) method [93]. The IQT method measures the sum of physical and chemical ignition delay due to injection in the high-pressure chamber. Our group previously reported that the fuel breakdown effect is collapsed above 4 MPa, and the total ignition delay differences were reduced [43]. The portion of chemical ignition delay is larger under lower compressed pressure, which is more representative of thermodynamic conditions for small engines and turbines. Therefore, a comprehensive investigation of physical and chemical ignition delay should be performed to achieve a true understanding of the effect of fuels' properties on ignition characteristics.

6.3 Chapter summary

The autoignition characteristics of four formulated CN fuels (CN 30, 40, 50, & 55) have been investigated in an RCM and shock tube at 2 MPa under different equivalence ratios to see the effects of fuel species on cetane number on chemical ignition delay. Fuels with nominally matched CN exhibit different combustion at specific conditions. Higher CN showed faster chemical reactivity generally. Below 1000K, fuels with an abundance of normal alkanes showed a higher cetane number and faster chemical reactivity. On the other hand, heavily branched alkanes hinder isomerization reactions. Also, iso-alkane components cause the Negative Temperature Coefficient (NTC) regime to start at lower temperatures than other normal alkane components. However, a lower cetane number of fuels with heavily branched alkanes in high temperatures showed shorter ignition delay as they are more readily broken down into small radical species. The results showed that DCN could not be a sole property used to predict ignition delay except in the intermediate temperature or NTC region, where DCN shows the best correlation to ignition delay. The data and findings could provide general guidance for jet fuel reactivity across various operating conditions based on chemical compositions by conducting extensive testing of autoignition behavior. They can help inform the design and development of next-generation engines, which are less sensitive to fuel property variations.

Chapter 7 Data-driven modeling of F-24/ATJ blends

Data-driven chemical kinetic mechanisms for F-24/ATJ blends are developed for numerical simulations of the ignition process. The main purpose of this study is to obtain a practical mechanism across wide temperature and equivalence ratio ranges, with a particular focus on the negative temperature coefficient and low-temperature regions. The process requires a base mechanism of similar fuel and an experimental ignition delay data set of the target fuels. The mechanism comprises a fuel-dependent lumped mechanism and detailed C0-C4 chemistry, as indicated in Figure 7-1. Without modification of detailed small hydrocarbon chemistry, fuel-dependent lumped reactions are selected and optimized toward chemical ignition delay data in the previous chapter 5. These practical mechanisms are suitable for the numerical simulations of the F-24/ATJ blends problem, and they will provide guidance on blending alternative fuels with conventional fuels.

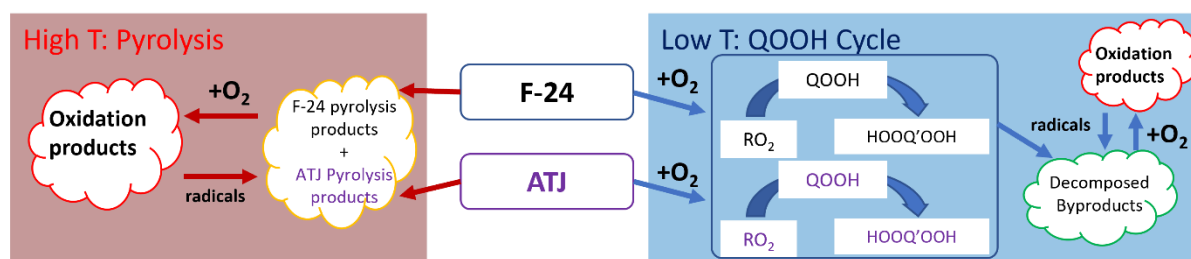


Figure 7-1 Overview of developing F-24/ATJ blends chemical kinetic models

7.1 F-24 mechanism

As mentioned earlier, F-24 is based on Jet A fuel, and it is expected that the physicochemical properties and combustion behavior of F-24 are similar to those of Jet A. As physicochemical

properties and chemical composition of F-24 are similar to those of Jet A, it is reasonable to use a Jet A kinetic mechanism as a base mechanism for F-24. In this study, a negative temperature coefficient enabled Jet A skeletal mechanism from HyChem [57] is used as a base model, and 55 reaction rates of the mechanism are modified and optimized to develop F-24 chemical kinetic models.

The HyChem models consist of two parts: pyrolysis and oxidation processes. The constants and activation energy of pyrolysis reactions were initially estimated from n-dodecane in JetSurf 2.0 [94][74] and fitted to the experimental species time history data with typical measurement uncertainties of 20% [58]. The pyrolysis process of F-24 may have different characteristics due to military additives and measurement uncertainties. The oxidation process is from the USC Mech II detailed reaction mechanism. The detailed oxidation mechanism can be used generally. Thus, the oxidation reactions of F-24 are similar to those of Jet A. The NTC-enabled model additionally includes a submodel for NTC and low-temperature regions, but [57] mentioned that the model is tentative as the submodel is not a physics-based treatment. The rate parameters of the NTC submodel in the base mechanism were simply assumed from n-dodecyl radical isomers, so these rate parameter estimations may not be valid across wide temperature and equivalence ratio ranges. Therefore, it may be adequate to modify the reaction rates of the pyrolysis and NTC submodels only. Instead of selecting a reaction set by sensitivity analysis, a manual selection of 16 reactions by the base model analysis was employed, as HyChem NTC-enabled skeletal mechanism has 7 reactions for the pyrolysis process and 9 reactions for the NTC submodel.

The cyan dashed line in Figure 7-2 shows that the GA optimization process with the manually selected reaction set has a lower merit value (~ 0.4) than that with the selection by sensitivity analysis (~ 0.7).

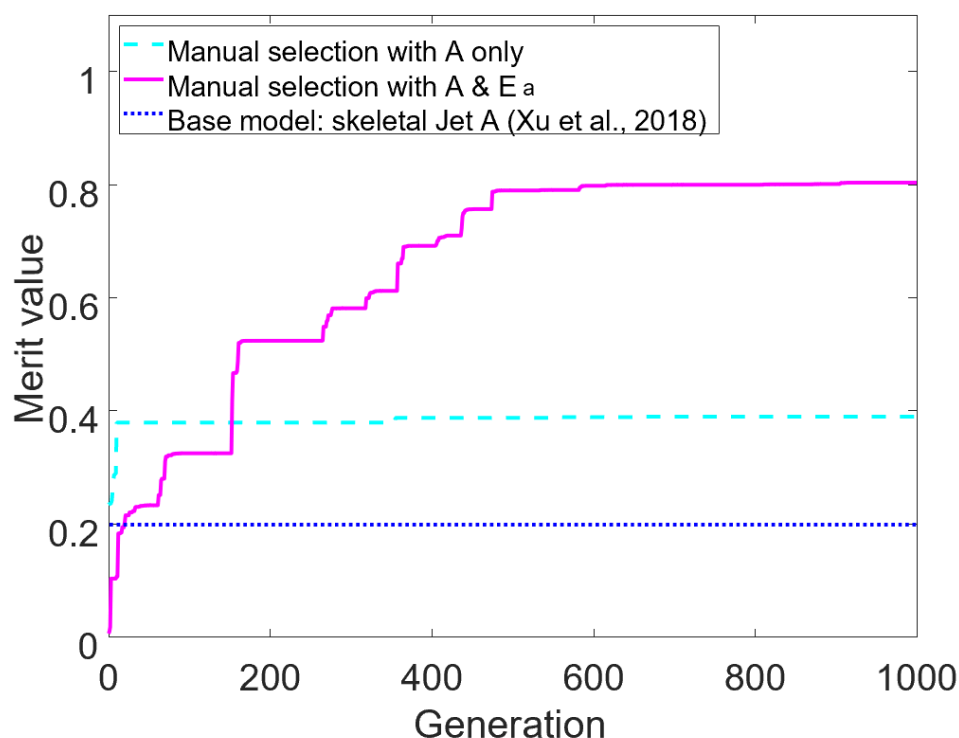


Figure 7-2 Merit values of the best child-individual over GA generations during F-24 mechanism development (with evenly-spaced points, the population size of 33, and 16 manually selected reactions)

Wang et al. [58] performed a Monte Carlo analysis showing that the impact of uncertainties in the oxidation process is much larger on the HyChem model accuracy, so the model improvement highly depends on the oxidation mechanisms. Moreover, as mentioned earlier, the optimized number for reactions to be modified is around 30, while the manual selection only has 16 reactions to modify. The code was also modified to optimize b and E_a in the reactions to overcome these issues. As b is the temperature exponent, the reaction rate is highly sensitive to b , and the GA process tends not to converge. Therefore, only pre-exponential factors and activation energy were modified during the GA optimization. I also limited the solution space within one order of magnitude for the activation energy to keep the value realistic. If the activation energy is 0 in the original model, an estimated small value was used for the initial value. The manual selection

method optimizes a total of 32 parameters (A and E_a) in 16 reactions, and the developed model shows a good optimization performance for all over the temperature range, as in Figure 7-3. The merit value of the developed mechanism is about 0.8.

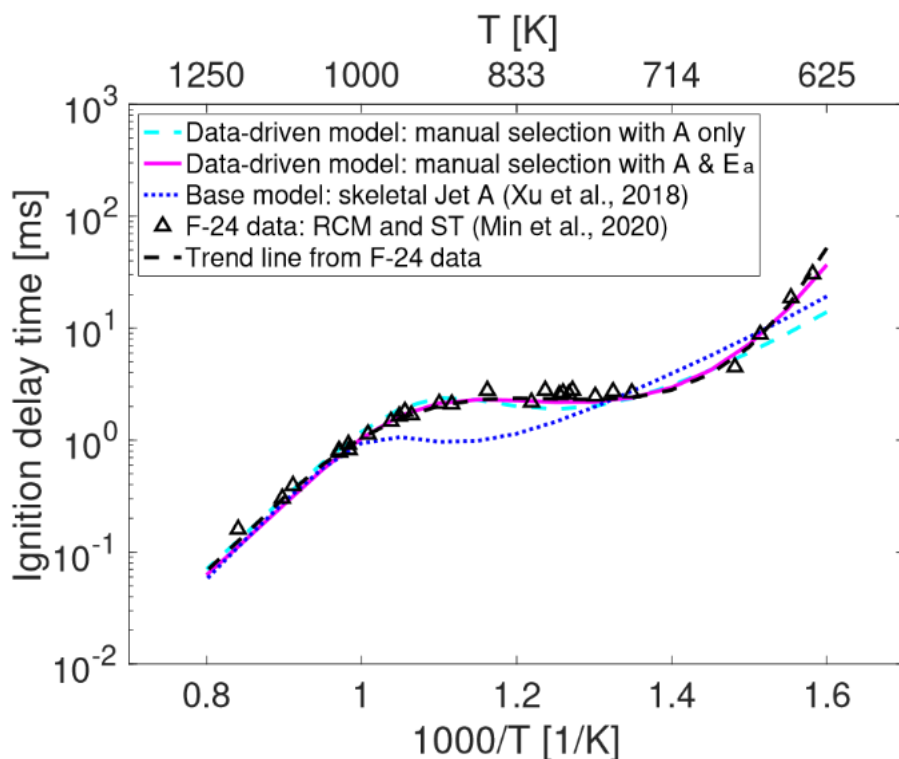


Figure 7-3 Ignition delay times from data-driven kinetic mechanisms (with evenly-spaced points, population size of 33, and 16 manually selected reactions), base mechanism, and F-24 RCM / shock tube measurements at 20 bar for stoichiometric fuel/air mixture.

Table 7-1 shows the parameters of the outcome mechanism. There was a difference between the original A2 chemistry and the optimized F-24 chemistry because of the different autoignition characteristics. The optimized values are reasonable for group additivity aspects, as the properties of lumped species lie in between normal alkane and iso alkane. The developed data-driven mechanisms (ARLMech-HC-F-24 and the alternate model) in Cantera and CHEMKIN format can be found in the published journal paper [73].

Table 7-1 The kinetic parameters of the lumped reactions in the Jet-A HyChem model (Base), the optimized model for F-24 using genetic algorithm (red)

	Reaction	Before optimization			After optimization		
		A	Beta	Ea	A	Beta	Ea
HyChem A-2 NTC enabled Mechanism	F-24=> (F-24 pyrolysis products)	1.53E+27	-2.58	8.77E+04	1.61E+27	-0.59	9.19E+04
	F-24 + H => H ₂ + F-24_R	7.66E-02	4.76	1.29E+03	4.51E-01	6.41	1.29E+03
	F-24 + CH ₃ => CH ₄ + F-24_R	3.17E-07	5.75	5.75E+03	2.95E-06	6.71	5.46E+03
	F-24 + OH => OH ₂ + F-24_R	2.96E+09	1.02	2.13E+02	2.22E+10	2.91	2.23E+02
	F-24 + O ₂ => H ₂ + F-24_R	1.78E+15	0.06	4.45E+04	7.72E+15	-1.92	4.26E+04
	F-24 + HO ₂ => H ₂ O ₂ + F-24_R	6.98E+04	2.94	1.28E+04	6.67E+05	3.25	1.22E+04
	F-24 + O => OH + F-24_R	8.94E+01	3.86	7.65E+02	1.19E+01	4.80	7.79E+02
	F-24_R => (F-24_R pyrolysis products)	6.47E+12	0	2.71E+04	1.92E+12	0	2.57E+04
	F-24_R + O ₂ => F-24_RO ₂	2.50E+10	0	0	1.13E+10	0	0
	F-24_RO ₂ => F-24_R + O ₂ (CRECK modeling n-dodecane)	5.00E+13	0	3.10E+04	2.93E+14	0	3.23E+04
	F-24_RO ₂ => F-24_QOOH	2.00E+12	0	1.70E+04	7.14E+11	0	1.79E+04
	F-24_QOOH => F-24_RO ₂	1.00E+11	0	1.25E+04	1.00E+10	0	1.30E+04
	F-24_QOOH = HO ₂ + F-24_Q	8.50E+12	0	2.56E+04	8.20E+13	0	2.69E+04
	F-24_Q => (F-24Q pyrolysis products)	3.50E+16	0	7.10E+04	3.50E+17	0	6.74E+04
	F-24_QOOH + O ₂ = F-24_O ₂ QOOH	4.00E+11	0	0	9.19E+10	0	0
	F-24_O ₂ QOOH = OH + F-24_OQ'OOH	1.50E+12	0	0	1.67E+12	0	0
	F-24_OQ'OOH => CH ₂ O + OH + (F-24_OQ* pyrolysis products)	1.00E+14	0	4.21E+04	1.00E+13	0	4.02E+04

7.2 ATJ mechanism

As mentioned earlier, there are no significant chemical composition differences among ATJ batches. I considered that the physicochemical properties and combustion behavior of POSF 12934 are the same as those of POSF11498, which is widely investigated ATJ. I used the group additivity method to estimate the thermochemical properties of low-temperature chemistry species. The estimation is based on the NIST webbook, Burcat's thermodynamic data, and iso-octane/iso-cetane mechanism from LLNL [44,45,89].

A C-1 (ATJ, POSF 11498) detailed mechanism from HyChem [56] is used as a base mechanism, and a lumped reaction model for NTC chemistry and low-temperature chemistry is added in the way of sub-mechanism. According to GCxGC analysis, the real ATJ fuel can be represented as C_{12.54±0.10}H_{27.05±0.19}. For the existing chemical kinetics computation, the mixture compositions are approximated into integer values as C₁₃H₂₈. The mechanism comprises three

parts: the HyChem C-1 lumped for high-temperature combustion, a lumped RO_2 -QOOH cycle mechanism for low-temperature combustion, and the USC mech II for a detailed foundation chemistry model.

During the optimization process, evenly distributed 15 data points from each equivalence ratio were chosen from the ignition delay trendline to minimize the weight effect of the experimental dataset. The same values from the paper [73] were used for the GA optimization parameters. The population size was 33 (32 children and 1 best parent), and the number of modified parameters was 20.

Conventionally, sensitivity analysis is utilized to select reactions to be modified. The optimization based on sensitivity analysis can predict the objective values well and be quickly converged, but the optimization results may be non-physical. I manually select the set of reactions to be optimized based on combustion theory to develop physically meaningful models. As mentioned earlier, the HyChem models have three parts: lumped pyrolysis chemistry, lumped low-temperature chemistry, and detailed small hydrocarbon oxidation. The detailed small hydrocarbon oxidation model is based on kinetic knowledge and experiments and further refined using predictive uncertainty analysis. After conventional rate coefficient evaluation and model compilation using experimental data, the model conducted a comprehensive uncertainty quantification (UQ) analysis. The mechanism is optimized against various available combustion datasets and tests. Additionally, Wang et al. [56] validated lumped high-temperature oxidation chemistry. Unless there are any discrepancies between the ignition delay from this study and modeling results, the rate coefficients of lumped high temperature will be sustained. Therefore, only the rate coefficients of low-temperature chemistry reaction represented in Table 7-2 are

modified to develop a data-driven chemical kinetic mechanism for ATJ. Pre-exponential factors were modified within one order of magnitude and activation energies within 20%.

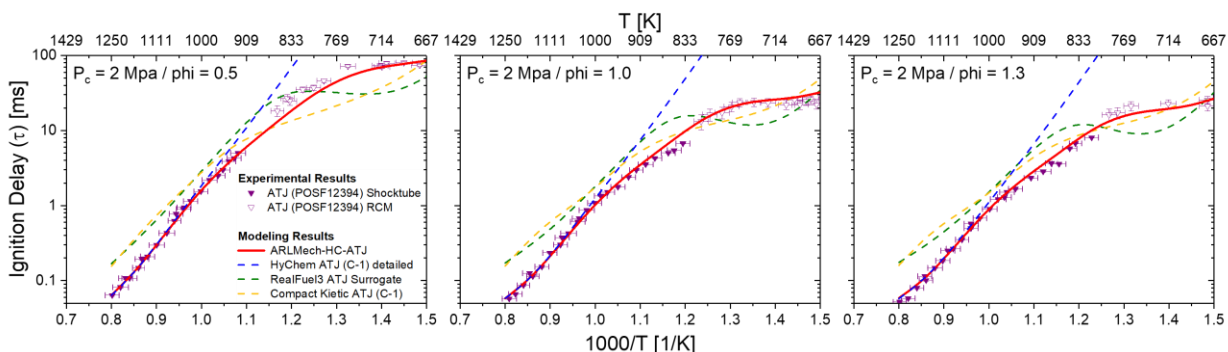


Figure 7-4 Ignition delay times at $P_c = 2$ MPa and various equivalence ratio from data-driven kinetic mechanism (red), HyChem C-1 mechanism (blue), RealFuel3 surrogate mechanism (green), Compact kinetics mechanism (yellow)

Figure 7-4 represents the ignition delay times calculated from the original HyChem, RealFuel 3 surrogate mechanism, Compact kinetic model, and the outcome data-driven ATJ mechanism with experimental values. Overall, the ignition delay from ARLMech-HC-ATJ shows more accuracy in the experimental than those from any other mechanisms, including NTC and low-temperature chemistry regime. The created kinetic mechanism can be applied to calculate between 667 K to 1250 K.

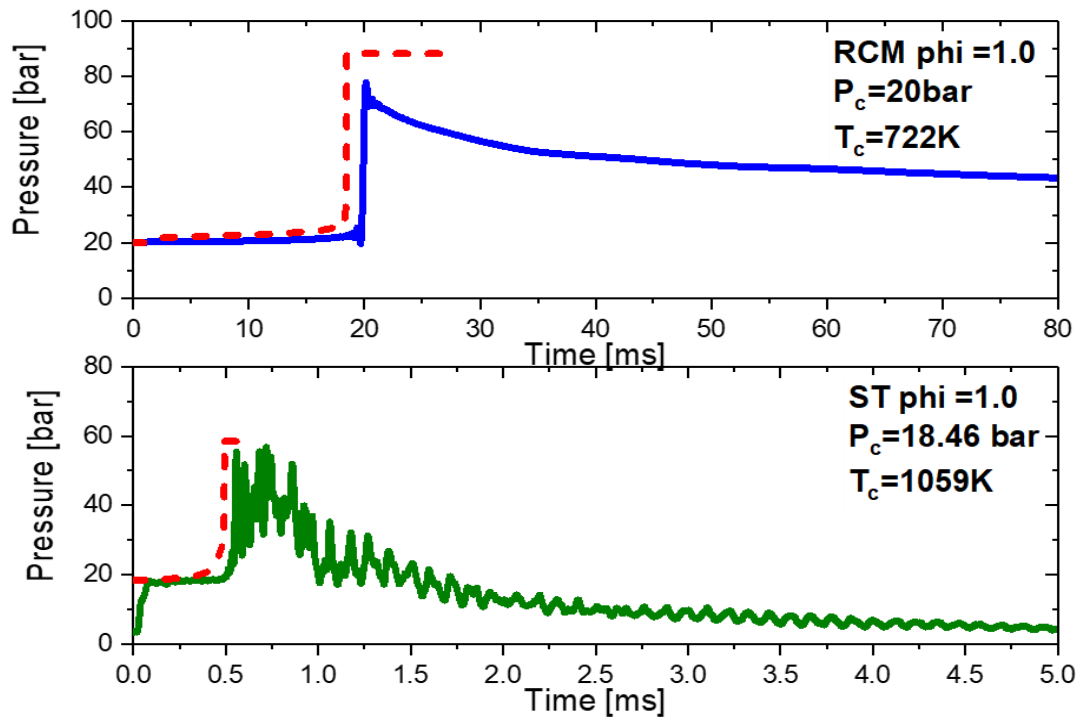


Figure 7-5 Comparison of pressure trace between experimental and simulation from ATJ data-driven kinetic mechanism

Figure 7-5. shows a comparison between examples of experimental pressure traces and the constant-volume-based modeling results under identical compressed conditions. The overall shape of the simulation profiles, the peak pressure, and the pressures at which they rise are in good agreement with the experimental results. A slight discrepancy may come from the constant-volume and adiabatic assumptions of the simulation.

Table 7-2 The kinetic parameters of the lumped reactions in the C-1 HyChem model and detailed model of isododecane (Base), the optimized model using genetic algorithm (red)

	Reaction	Before optimization			After optimization		
		A	Beta	Ea	A	Beta	Ea
HyChem C-1	ATJ=> (ATJ pyrolysis products)	2.83E+26	-2.58	8.02E+04	2.83E+26	-2.58	8.02E+04
	ATJ + H => H ₂ + ATJ_R	8.72E+05	2.4	2.58E+03	8.72E+05	2.4	2.58E+03
	ATJ + CH ₃ => CH ₄ + ATJ_R	4.64E+00	3.46	4.60E+03	4.64E+00	3.46	4.60E+03
	ATJ + OH => OH ₂ + ATJ_R	4.88E+10	0.51	6.40E+01	4.88E+10	0.51	6.40E+01
	ATJ + O ₂ => H ₂ + ATJ_R	1.49E+15	0	4.30E+04	1.49E+15	0	4.30E+04
	ATJ + HO ₂ => H ₂ O ₂ + ATJ_R	9.03E+03	2.77	1.05E+04	9.03E+03	2.77	1.05E+04
	ATJ + O => OH + ATJ_R	7.85E+04	2.5	1.11E+03	7.85E+04	2.5	1.10E+03
Estimated low T sub mechanism	ATJ_R => (ATJ_R pyrolysis products)	1.44E+11	0	3.08E+04	1.12E+12	0	3.01E+04
	ATJ_R + O ₂ => ATJ_RO ₂	1.15E+11	0	7.15E+03	9.66E+10	0	0.00E+00
	ATJ_RO ₂ => ATJ_R + O ₂	2.06E+10	0	2.16E+04	5.25E+13	0	3.01E+04
	ATJ_RO ₂ => ATJ_QOOH	2.06E+10	0	2.16E+04	9.70E+10	0	2.10E+04
	ATJ_QOOH => ATJ_RO ₂	2.71E+10	0	1.47E+04	5.81E+10	0	1.26E+04
	ATJ_QOOH = HO ₂ + ATJ_Q	8.50E+12	0	2.56E+04	1.76E+13	0	2.43E+04
	ATJ_Q => (ATJ_Q pyrolysis products)	1.00E+16	0	7.10E+04	1.34E+17	0	5.54E+04
	ATJ_QOOH + O ₂ = ATJ_O ₂ QOOH	4.52E+11	0	0.00E+00	2.20E+10	0	0.00E+00
	ATJ_O ₂ QOOH = OH + ATJ_OQ'OOH	1.98E+10	0	2.04E+04	1.04E+12	0	1.93E+04
	ATJ_OQ'OOH => CH ₂ O + OH + ATJ_OQ*	6.26E+13	0	3.90E+04	1.15E+11	0	2.71E+04
	ATJ_OQ* => (ATJ_OQ* pyrolysis products)	1.39E+19	0	4.41E+04	3.92E+18	0	5.44E+04

Table 7-2 shows the parameters of the outcome mechanism. Although the reaction parameters of the high-temperature combustion pathway did not change, the result shows a good agreement under high-temperature combustion. However, there was a difference between the original low-temperature chemistry and the modified low-temperature chemistry. The optimized values are reasonable for group additivity aspects, as the properties of lumped species lie in between isooctane and isocetane. The published journal paper can find the developed data-driven mechanisms (ARLMech-HC-ATJ and the alternate model) in Cantera and CHEMKIN format.

In this study, other groups' ATJ pyrolysis and experimental oxidation results were digitized to validate and then compared with ARLMech-HC-ATJ. The simulation matches compressed pressure and reaction time over a temperature range of the experiments.

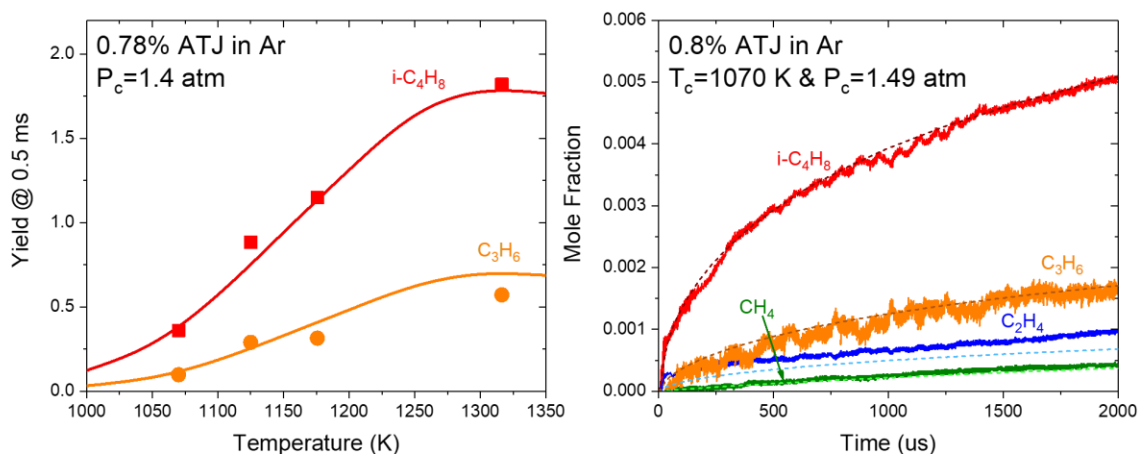


Figure 7-6 Experimental and modeling predictions of ethylene (C_2H_4) and iso-butene ($i-C_4H_8$) in the pyrolysis data from [56]

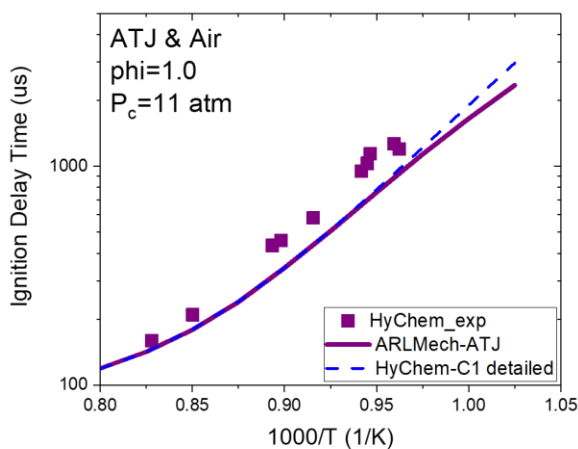


Figure 7-7 Experimental and modeling predictions of ignition delay at $P_c = 11$ atm and stoichiometric condition in the oxidation data from [56]

Pyrolysis comparisons are indicated in Figure 7-6. Important products in the modeling: $i-C_4H_8$, C_3H_6 , C_2H_4 , and CH_4 are compared within 2ms of measurement time under two different temperature conditions. The overall concentrations of molecules show a good agreement with the experimental results. Minor differences between the computed and experimental results can be attributed to the kinetic rate uncertainty of detailed small hydrocarbon chemistry as reported in

[56,57]. It also can be an effect on a small discrepancy of ignition delay times under different compressed pressure in Figure 7-7. Comparing compressed pressure and temperature, pressure exhibits less impact on either production distributions or temperature. Further studies such as density functional theory or experiment-based research at different equivalence ratios may validate the developed mechanism in this study, and the approach can be improved by optimizing toward additional experimental results.

Sensitivity analysis

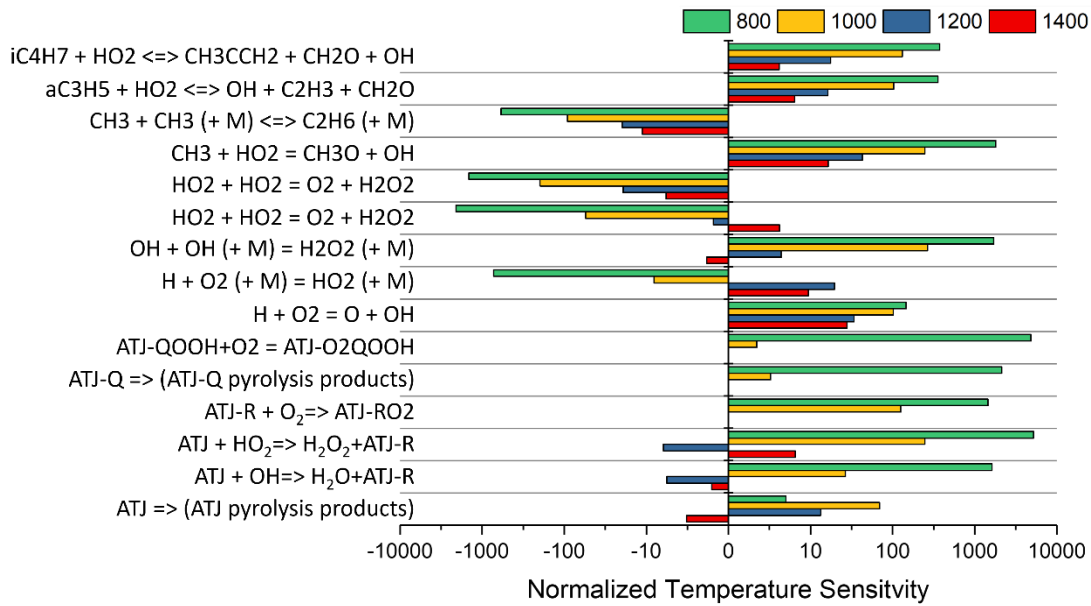


Figure 7-8 Sensitivity analysis of temperature of ATJ at fuel-air stoichiometric equivalence ratio under different compressed temperatures: 800, 1000, 1200, and 1400 K

Figure 7-8 shows temperature sensitivity analysis computed for ATJ/Air mixture at the initial temperature of 800, 1000, 1200K, and 1400K and compressed pressure of 2 MPa and stoichiometric condition. Each temperature represents low-temperature, intermediate temperature, high-temperature with pyrolysis dominant, and high-temperature, respectively. Overall, one of the

chain branching reactions of $\text{H} + \text{O}_2 = \text{OH} + \text{O}$ by oxygen and abstracted hydrogen from the fuel molecules is the most important as they provide radical pools to the combustion system. At a high temperature above 1400 K, mostly reactions of small hydrocarbon radicals are dominant. The lumped reactions of fuel molecules are not sensitive as fuel can be easily thermal decomposed. On the other hand, fuel pyrolysis is a rate-limiting step followed by radical reactions around 1200K. At a temperature around 1000K, a slower chain branching reaction between hydrogen atoms and oxygen molecules results in intermediate temperature combustion. In this range, the formation and decomposition of hydrogen peroxide mainly control the combustion rate. Hydroxyl radical produces hydrogen peroxide by either detaching hydrogen from fuel molecules or reacting with hydrogen atoms directly. Accumulated hydrogen peroxide decomposes into two hydroxyl radicals to cause ignition. In low temperatures, we can observe that ATJ follows generic low-temperature chemistry well in sensitivity analysis results.

7.3 Blend mechanism and alkylation reaction

Firstly, I have tried to merge two mechanisms to construct F-24 and ATJ blends mechanisms, as indicated in Figures 7-9, 7-10, and 7-11. The model was evaluated under the same condition conducted in the experiments for their predictive capabilities of autoignition characteristics. Modeling was carried out with Cantera 2.5 using a closed homogeneous reactor. Simply merged mechanism does an excellent job of representing the overall trends at the conditions studied, but the model cannot represent well for blending results. The discrepancies between the modeling and experimental results in NTC and low-temperatures regimes become more apparent.

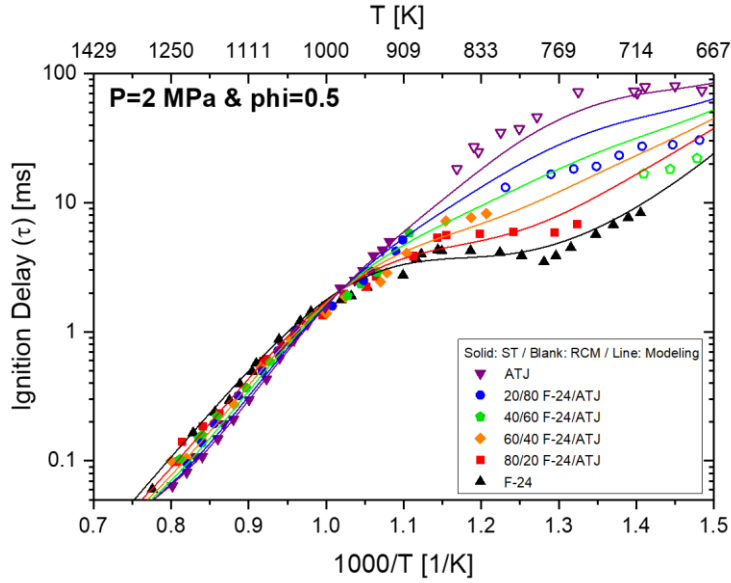


Figure 7-9 Data-driven Kinetic model results of simply merged F-24 and ATJ at $P_c = 2$ MPa and $\phi = 0.5$. Lines and dots are simulation results and experimental results, respectively. Solid points and blank points from shock tube and RCM, respectively

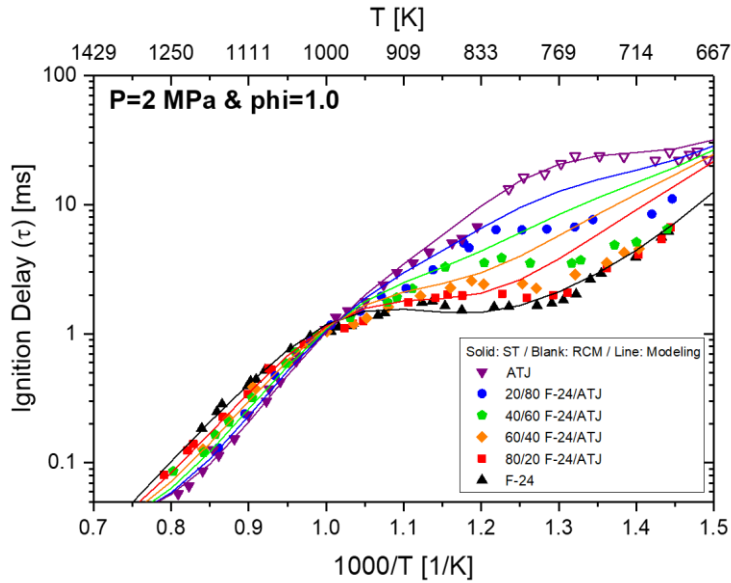


Figure 7-10 Data-driven Kinetic model results of simply merged F-24 and ATJ at $P_c = 2$ MPa and $\phi = 1.0$. Lines and dots are simulation results and experimental results, respectively. Solid points and blank points from shock tube and RCM, respectively

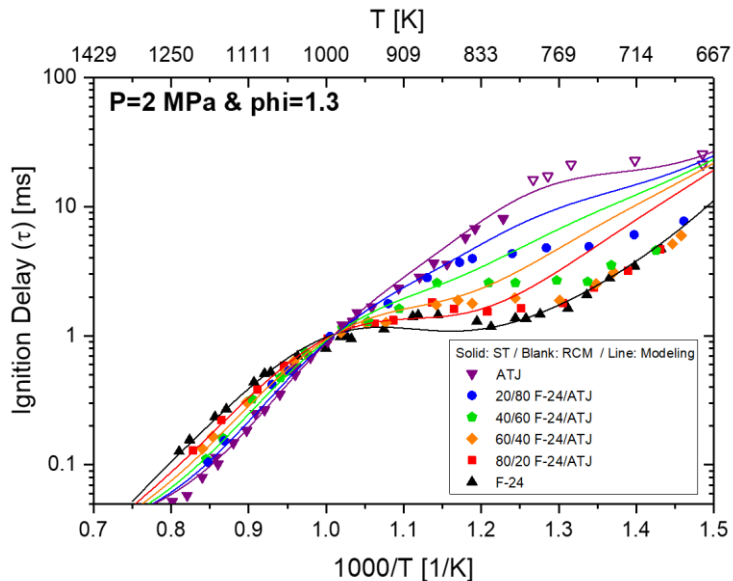
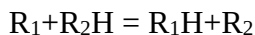


Figure 7-11 Data-driven Kinetic model results of simply merged F-24 and ATJ at $P_c = 2$ MPa and $\phi = 1.3$. Lines and dots are simulation results and experimental results, respectively. Solid points and blank points from shock tube and RCM, respectively

In low-temperature chemistry, it is controversial the importance of alkylation (also known as co-oxidation) reactions among blended or multi-fuel components. Several researchers [95–98] insisted that co-oxidation between the individual components is important, but others [66,97,99] think it is unimportant as they argue that combining two different single mechanisms can represent their mixture mechanism.

An alkylation reaction is a reaction transferring an alkyl group from one molecule to another molecule.

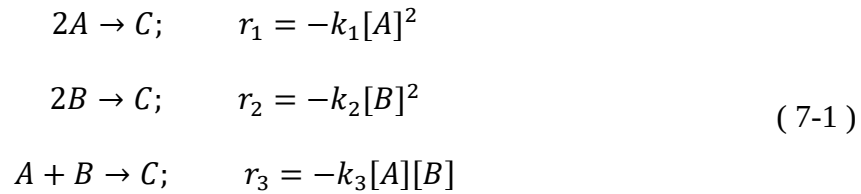


Under NTC and low-temperature regime, a common pathway of the alkyl radical is reacting with active radicals and oxygen molecules (H, OH, O, HO₂, and O₂). Most single component

mechanisms include the further reaction with regenerated active radicals. H abstracted fuel's alkyl radical can also be considered active radicals to react with less reactive fuel molecules. If we consider a co-oxidation reaction between two fuel components, an alkylation (co-oxidation) reaction can be considered as an additional pathway of chain propagating or branching steps by exchange radicals.

Kalghatgi et al.[95] mathematically proved the necessity of alkylation reactions as follows:

Assuming that two reactants, A and B, both can form C. Also, there is an alkylation reaction to each other.



If we consider the mixture of A and B, the total reaction rate would be expressed as

$$\begin{aligned}
 r &= (r_1 + r_2 + r_3) = -k_1[A]^2 - k_2[B]^2 - k_3[A][B] \\
 &= -(k_1\alpha^2 + k_2(1-\alpha)^2 + k_3\alpha(1-\alpha))[\text{mix}]^2
 \end{aligned}
 \tag{7-2}$$

where α is the portion of A in the mixture.

Assuming A and B are isotopes, the reaction rate would be written in another form.

$$r = (r_1 + r_2 + r_3) = -(k_1\alpha^2 + k_1(1-\alpha)^2 + k_3\alpha(1-\alpha))[\text{mix}]^2
 \tag{7-3}$$

Therefore,

$$\begin{aligned}
 k_1 &= k_1\alpha^2 + k_1(1-\alpha)^2 + k_3\alpha(1-\alpha) \\
 1 &= \alpha^2 + (1-\alpha)^2 + \frac{k_3}{k_1}\alpha(1-\alpha) \\
 0 &= (2 - \frac{k_3}{k_1})\alpha(1-\alpha)
 \end{aligned}
 \tag{7-5}$$

Since α cannot be zero, $\frac{k_3}{k_1}$ should be 2, which means that reaction 3, alkylation (or co-oxidation) reaction should exist.

Ra et al. [100] insisted that considering some dominant co-oxidation reaction pathways between fuel components is enough to exchange radicals with single lumped species as each model branches their representative pathways. In their mechanisms for primary reference fuels (PRF), only co-oxidation reactions that involve the radicals produced from one of the fuels through H-atom abstraction (e.g., alkyl, benzyl, and cyclohexyl radicals) and the other fuels, $R_1 + R_2H \leftrightarrow R_1H + R_2$, were included in the reduced mechanism to depict low-temperature chemistry of blended components.

The initial guessing rate constants for the alkylation reactions were employed from the PRF mechanism by Ra et al. [100]. Sufficient boundaries are given to the reaction between iso-octane and n-heptyl radical to substitute the reaction between the alkyl radical of F-24 and ATJ.

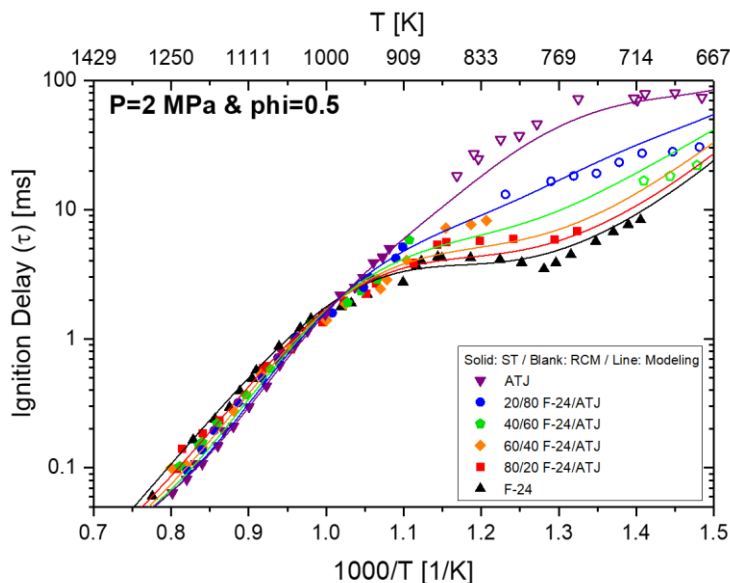


Figure 7-12 Data-driven Kinetic model results of F-24/ATJ blends with alkylation reaction at $P_c = 2$ MPa and $\phi = 0.5$. Lines and dots are simulation results and experimental results, respectively. Solid points and blank points from shock tube and RCM, respectively

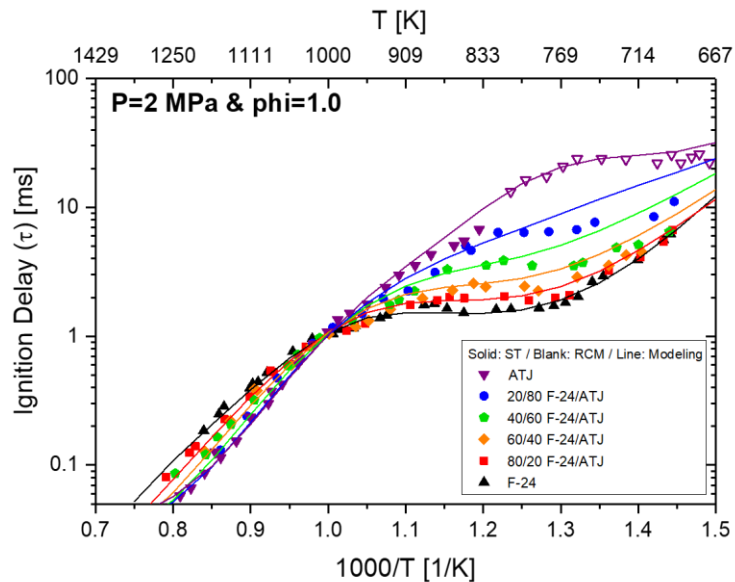


Figure 7-13 Data-driven Kinetic model results of F-24/ATJ blends with alkylation reaction at $P=2$ MPa and $\phi=1.0$. Lines and dots are simulation results and experimental results, respectively. Solid points and blank points from shock tube and RCM, respectively

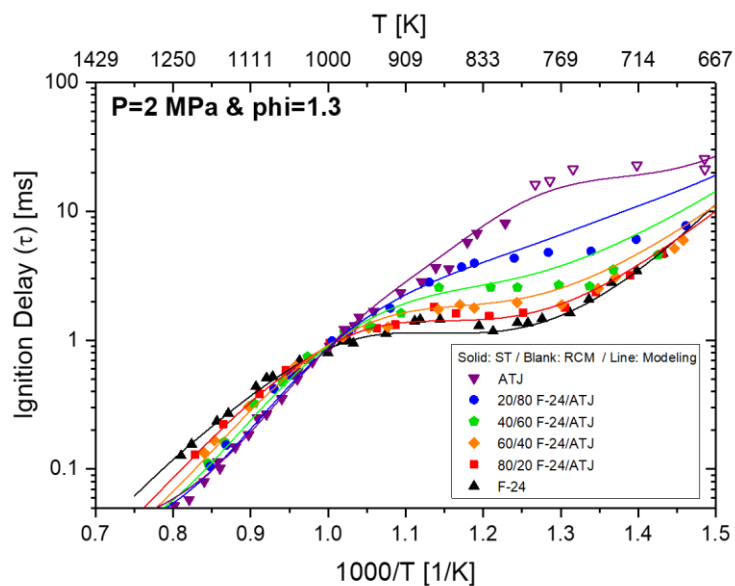


Figure 7-14 Data-driven Kinetic model results of F-24/ATJ blends with alkylation reaction at $P=2$ MPa and $\phi=1.3$. Lines and dots are simulation results and experimental results, respectively. Solid points and blank points from shock tube and RCM, respectively

Ignition delay predictions using the mechanism with alkylation reaction were validated with experimental data, as shown in Figures 7-12, 7-13, and 7-14. As can be seen, the model prediction is in excellent agreement with the results in Chapter 5.

7.4 Chapter summary

A data-driven kinetic mechanism of F-24/ATJ blend fuel, ARLMech-HC-F24ATJ, was introduced based on HyChem's detailed mechanism and lumped pseudo-low-temperature chemistry model by using ignition delay experiments in Chapter 5. This new mechanism consisted of 133 species and 869 reactions and can be divided into small hydrocarbon detailed chemistry reactions and experimentally optimized lumped reactions. The newly introduced data-driven mechanism for F-24/ATJ blends shows good performance across the temperature range of interest in ignition delay and some species' analysis from the other group.

The current study is meaningful in the sense that we can readily provide practical mechanisms for CFD simulations with a full description of the data-driven chemical kinetic mechanism development process. Moreover, as the HyChem type of chemical kinetic model development requires extensive efforts to estimate rate coefficients of pyrolysis and NTC submodels, this study can provide a simple and practical approach to optimize those rate coefficients. With the optimization method, the HyChem type of chemical kinetic models will be more adaptable to the community.

Chapter 8 Data-driven modeling of Varied CN fuels

The preceding chapters suggested F-24/ATJ blend mechanisms by applying and improving readily available mechanisms. Unlike F-24 and ATJ, it is especially notable that varied CN fuels are specially designed and nearly experimented with. The lumped chemical equations for high temperatures are formulated by following the HyChem theory and chemical composition analysis. The main purpose of this study is to obtain practical varied CN fuels mechanisms across wide temperature and equivalence ratio ranges, with a particular focus on the negative temperature coefficient and low-temperature regions. The same approach in chapter 7 is used with the experimental results in Chapter 6. These practical mechanisms are suitable for numerical simulations, and they will give an insight into CN effects on combustion characteristics by comparing between F-24/ATJ blend mechanism and Varied CN fuels mechanisms.

8.1 *Varied CN fuels' backbone mechanism*

The present chapter focuses on Varied CN fuels. GCxGC analysis results are requested and acquired from the Alternative Jet Fuel Test Database for detailed chemical information about Varied CN fuels. GCxGC allows for higher resolution data with additional dimensionality. The summary report includes the chemical composition in the weight percentages of hydrocarbon groups and carbon number range. Table 8-1 listed essential properties of the fuels to build chemical kinetic models, including the average molecular formula, molecular weight, and chemical composition. Other physical and chemical properties have already been mentioned in Chapter 6.

Table 8-1 Key properties of Varied CN fuels based on detailed hydrocarbon analysis from GCxGC results

	ARL Jet CN30 (POSF13197)	ARL Jet CN40 (POSF13199)	ARL Jet CN50 (POSF13201)	ARL Jet CN55 (POSF13202)
Average Formula	$C_{11.6}H_{23.1}$	$C_{11.7}H_{23.3}$	$C_{11.1}H_{22.5}$	$C_{11.5}H_{23.3}$
Hydrogen content wt%	14.3	14.3	14.5	14.5
Molecular weight (g/mol)	162.92	164.41	156.31	161.91
Aromatic wt%	13.08	12.83	8.25	8.35
n-paraffin wt%	9.36	11.56	17.54	24.44
Iso-paraffin wt%	65.01	47.78	39.41	34.74
Cyclo-paraffin wt%	12.55	27.83	34.81	32.47

For the modeling purpose, each fuel is assumed to be C_mH_n , where m and n are integers, to accommodate the existing chemical kinetic solvers. The model formula is decided to match both the hydrogen contents and the closest integer round-off of an average formula. I also used the group additivity method to estimate the thermochemical properties of low-temperature chemistry species in chapter 7. The estimation is based on the NIST webbook, Burcat's thermodynamic data, and iso-octane/iso-cetane mechanism from LLNL [44,45,89]. The detailed information of varied-CN fuels' lumped reactions is following:

ARL Jet CN30 – $C_{12}H_{24}$

Due to the high portion of iso-paraffin and relatively lower cetane number, the model is assumed to be combined F-24 (40%) and ATJ (60%). As the CN of 40/60 F-24/ATJ is 29.4, CN30 fuel's surrogate will be represented as 40/60 F-24/ATJ, and its molecular formula will be $C_{12}H_{24}$. To match the model's formula, F-24 ($C_{11}H_{22}$) is converted into $C_{12}H_{21}$, and ATJ ($iC_{13}H_{28}$) is converted into $iC_{12}H_{26}$. The detailed reactions for ARLJetCN30 are written as follows:

- CN30 fuels ($C_{12}H_{24}$) $\rightarrow$ 0.4 modified F-24 pyrolysis + 0.6 modified ATJ pyrolysis

$$k = 0.4 \text{ (rate constant of F-24)} + 0.6 \text{ (rate constant of ATJ)}$$

$$k = A_3 * T^{b_3} * \exp(-E_{a3}/RT) = 0.4 A_1 * T^{b_1} * \exp(-E_{a1}/RT) + 0.6 A_2 * T^{b_2} * \exp(-E_{a2}/RT)$$

- ARLJetCN30 $\Rightarrow$ 0.6192259 C_2H_4 + 0.5415607 C_3H_6 + 1.3791774 iC_4H_8 + 0.0725653 C_4H_8-1 + 0.17 C_6H_6 + 0.163333316 $C_6H_5CH_3$ + 0.833438 H + 1.166562 CH_3

-ARLJetCN30+R $\Rightarrow$ CN30R+RH

-CN30R $\Rightarrow$ 0.18 CH_4 + 0.5713103 C_2H_4 + 0.5399844 C_3H_6 + 1.4894938 iC_4H_8 + 0.0636793 C_4H_8-1 + 0.20060002 C_6H_6 + 0.192733313 $C_6H_5CH_3$ + 0.708 H + 0.292 CH_3

-RO₂ and QOOH low-temperature chemistry of CN30R

ARL Jet CN40 – $C_{12}H_{23}$

According to literature studies, there is no analogous fuel having a similar chemical composition to CN40 as far as my knowledge. Among similar cetane number fuels, A3 (JP-5, POSF10289) and C5 (POSF12345) include a large amount of cycloparaffin and aromatics, respectively. Moreover, it is hard to match both chemical compositions and cetane number of CN40 by mixing two other different fuels. Unlike CN30, CN40 cannot build by combining other fuels as the different compositions of aromatic and normal-paraffinic contents. In this study, the model is assumed to be as A3 (JP-5, POSF10289), and their coefficients are employed. However, detailed pyrolysis experiments should be performed and validated to build the chemical kinetic mechanism of ARL Jet CN 40.

- ARLJetCN40 $\Rightarrow$ 1.7232779 C_2H_4 + 0.8099406 C_3H_6 + 0.0861639 iC_4H_8 + 0.2584917 C_4H_8-1 + 0.255 C_6H_6 + 0.245 $C_6H_5CH_3$ + 0.5 H + 1.5 CH_3

-ARLJetCN40+R =>CN40R+RH

-CN40R=> 0.45 CH₄ + 1.5751781 C₂H₄ + 0.7403337 C₃H₆ + 0.0787589 iC₄H₈ + 0.2362767 C₄H₈-1 + 0.3315 C₆H₆ + 0.3185 C₆H₅CH₃ + 0.3 H + 0.7 CH₃

-RO₂ and QOOH low-temperature chemistry of CN40R

ARL Jet CN50 – C₁₁H₂₂

Due to similarity in chemical composition and similar cetane number, the model is considered as A2 (Jet A, POSF10325). JP-8 is also modeled as C₁₁H₂₂, and the model does not have much to revise. The detailed reactions for ARLJetCN50 are written as follows:

-ARLJetCN50 => 1.7426762 C₂H₄ + 0.8190578 C₃H₆ + 0.0871338 iC₄H₈ + 0.2614014 C₄H₈-1 + 0.17 C₆H₆ + 0.1633333 C₆H₅CH₃ + 0.5 H + 1.5 CH₃

- ARLJetCN50+R =>CN50R+RH

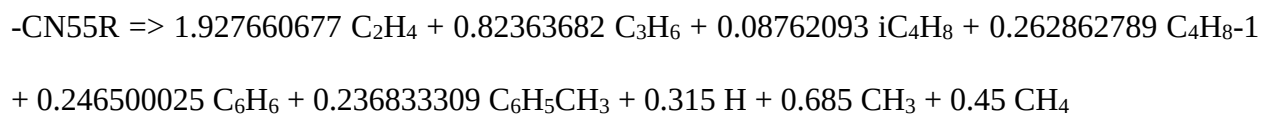
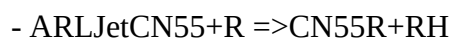
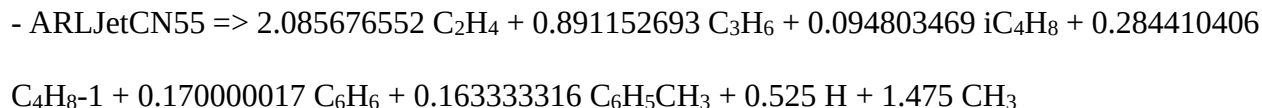
- CN50R => 0.45 CH₄ + 1.5945764 C₂H₄ + 0.7494509 C₃H₆ + 0.0797288 iC₄H₈ + 0.2391865 C₄H₈-1 + 0.2465 C₆H₆ + 0.2368333 C₆H₅CH₃ + 0.3 H + 0.7 CH₃

-RO₂ and QOOH low-temperature chemistry of CN50R

ARL Jet CN55 – C₁₂H₂₄

The chemical composition between CN55 and CN50 is similar to each other, but the difference is the portion of iso-paraffin and normal-paraffin. CN55 contains a large portion of higher n-alkanes (C14-16) which can be easily thermally decomposed into smaller hydrocarbon pyrolysis species, as discussed in Chapter 6. Moreover, ARL internal report showed that methane production

is the most significant difference between CN55 and CN50, and ethylene production is increased by about 10%. Therefore, CN55 is considered as modified CN50 to increase the fuel reactivity by changing the rate of H-abstraction and beta-scission rate. The detailed reactions for ARLJetCN55 are written as follows:



The lumped reaction model is combined with a detailed foundational fuel chemistry model to describe the autoignition characteristics of Varied CN fuels over a wide range of operating conditions. Varied CN fuels' models also utilized USC Mech II as small hydrocarbon chemistry.

8.2 Optimization results

During the optimization process, evenly distributed 15 data points from each equivalence ratio were chosen from the ignition delay trendline to minimize the weight effect of the experimental dataset. Mechanism optimization is improved in this section getting results faster and more accurate. The first step is optimizing non-lumped reactions with bounds focusing on pre-exponential factors and temperature exponent values. Once the values converge, the second step

optimizes rate coefficients of all reactions starting from step 1 with tighter bounds except for temperature exponents of low-temperature chemistry. In this study, beta values of low-temperature oxidation were not dealt.

The mechanism's Ignition delay predictions were validated with experimental data, as shown in Figures 8-1, 8-2, and 8-3. As can be seen, the model prediction is in excellent agreement with the results in Chapter 6. For broader applications, further density functional theory or experiment-based research, including laminar flame speed or species history at different operating conditions, may concrete the developed mechanism in this study.

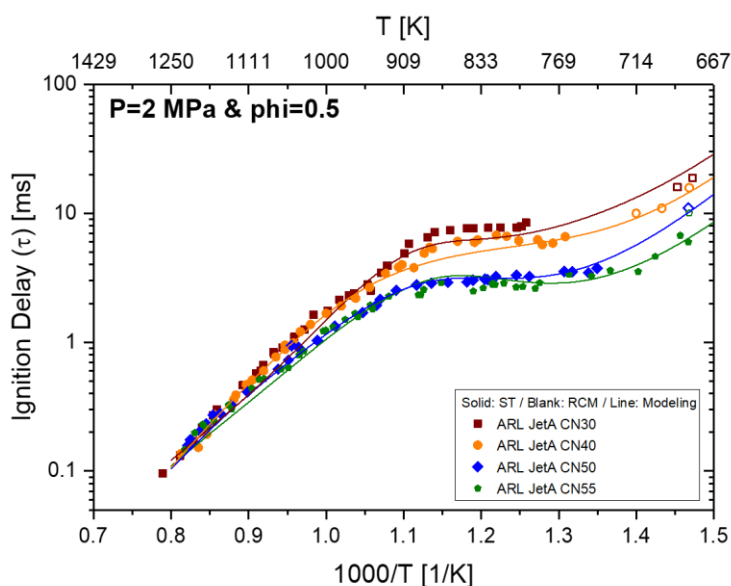


Figure 8-1 Data-driven Kinetic model results of Varied CN fuel at $P_c = 2$ MPa and $\phi = 0.5$. Lines and dots are simulation results and experimental results, respectively. Solid points and blank points from shock tube and RCM, respectively

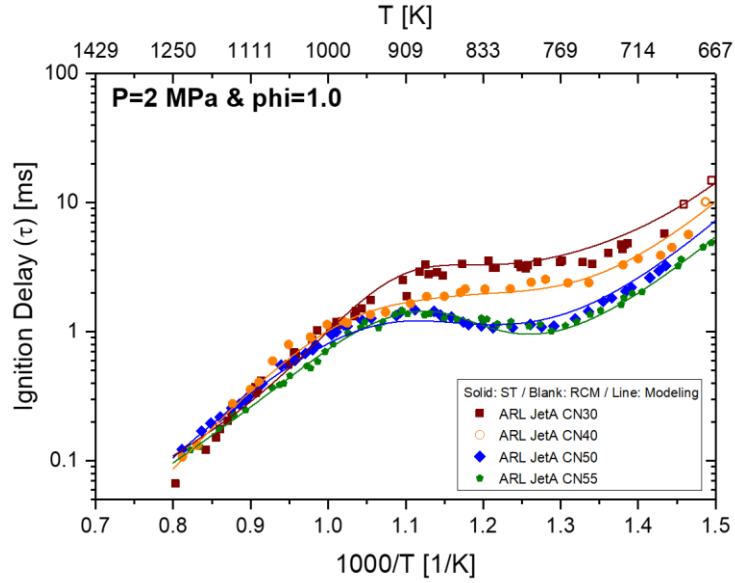


Figure 8-2 Data-driven Kinetic model results of Varied CN fuel at $P_c = 2$ MPa and $\phi = 0.5$. Lines and dots are simulation results and experimental results, respectively. Solid points and blank points from shock tube and RCM, respectively

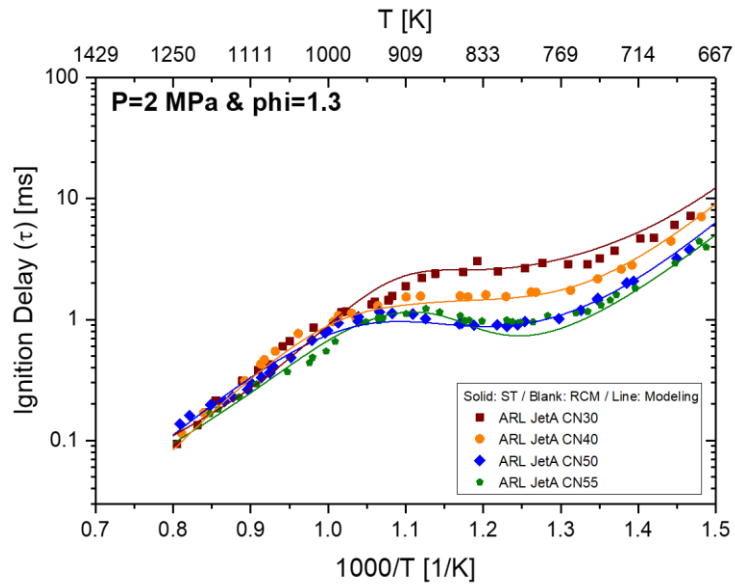


Figure 8-3 Data-driven Kinetic model results of Varied CN fuel at $P_c = 2$ MPa and $\phi = 0.5$. Lines and dots are simulation results and experimental results, respectively. Solid points and blank points from shock tube and RCM, respectively

8.3 Chapter summary

A data-driven kinetic mechanism of varied CN fuels, ARLMech-HC-VariedCN, was introduced based on HyChem detailed mechanism and lumped pseudo-low-temperature chemistry model using ignition delay experiments in Chapter 6. Unlike Chapter 7, this chapter shows how newly introduced fuels can be modeled based on the optimization of HyChem models. New sustainable aviation fuels could be simply formulated to model combustion behaviors optimization techniques.

Since the lack of experimental results of Varied CN fuels, the model can provide available mechanisms for CFD simulations to suggest cetane number effects on ignition characteristics in practical combustion facilities. Each mechanism is consisted of 125 species and 851 reactions and can be divided into small hydrocarbon detailed chemistry reactions and experimentally optimized lumped reactions. The introduced data-driven mechanism for Varied CN fuels shows good performance across the temperature range of interest in ignition delay covered in Chapter 6. The modeling results will suggest an insight into the experimental design of Varied CN fuels' experiments to the community.

Chapter 9 0-D Application

A zero-dimensional simulation with Cantera and Chemkin software was employed to provide an insight into various fuels' applications under different combustion facilities: homogeneous charge compression ignition (HCCI), internal combustion engine, and gas turbine. Whereas a zero-dimensional simulation is weak in depicting the physical properties of fuels and the spatial distribution inside the combustor, it can provide a qualitative understanding and overall prediction of temperature, pressure, and emissions quite well as a guidance of fuel application. Moreover, the computation is cheaper than 3-D CFD methods and real experiments. Two examples compare conventional jet fuel (Jet A, POSF10325) and ATJ using the HyChem A2 and data-driven ATJ mechanisms (ARLMech-HC-ATJ).

9.1 Internal combustion engine – Homogeneous Charge Compression Ignition (HCCI)

The main advantages of the Homogeneous Charge Compression Ignition, or HCCI, are the potential for lowering emissions and improving fuel efficiency. The single-zone IC HCCI engine model is employed to simulate the HCCI process. The simulation solves the thermodynamic equations to account for the piston movement. The model simulates the time between the intake valve close (IVC) and the exhaust valve open (EVO) in the engine cycle, and the fuel-air mixture is fully homogeneous and charged at starting the simulation time. The detailed thermodynamic theories, mathematical formulations, and the validation of simulation can be found in the Chemkin manual [101].

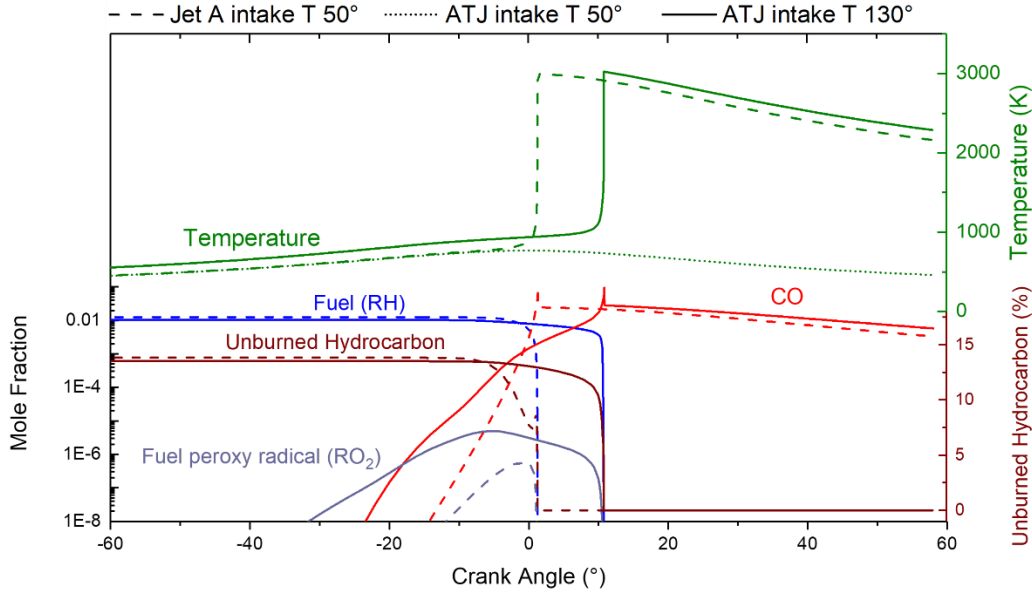


Figure 9-1 In-cylinder pressure and species histories according to the crank angle under 0-dimensional HCCI modeling with Jet A (dashed line) and ATJ (solid line). Temperature (Green), the mole fraction of fuel (blue), carbon monoxide (red), fuel peroxy radical (light purple), and unburned hydrocarbon (brown) are represented.

Figure 9-1 shows the in-cylinder temperature and species histories according to crank angle. In the case of ATJ, no discernable ignition happened within the engine cycle under the identical intake condition (intake temperature as 50°C). According to simulation results, ATJ starts to ignite from a high compression ratio of 25:1, which is higher than a typical gasoline combustion engine. Not only are there chances of knocking, but all engine components are also subjected to high stresses and safety issues with a high compression ratio. Instead of increasing the compression ratio, this simulation assumes additional equipment to heat the intake fuel-air mixture up to 130°C, which is acceptable under the HCCI engine [102].

Because of the low derived cetane number, the ignition timing of ATJ is retarded at about 10 CA even under a higher intake temperature. Dickerson et al. [103] reported that lower bulk

modulus results in retarded start of injection at approximately 2 degrees in all operating conditions, and ATJ requires enough pre-mixing time to burn under blended JP-5 and ATJ experiments. Comparing the emissions of carbon monoxide and unburned hydrocarbon, there is no significant big difference between conventional Jet A and ATJ in this simulation results. Kurzawska et al. [104] experimentally showed the emission characteristics of blended ATJ with Jet A. They also reported that carbon monoxide is slightly increased for ATJ blends. On the other hand, the main advantage of using an ATJ blend is that the total number and mass of particulate matter can be reduced at the entire condition. Precursors, including some unsaturated hydrocarbons and PAHs (polycyclic aromatic hydrocarbons) from combustion causes to produce soot or particulate carbon matter through the process: nucleation, surface growth, and agglomeration. As aforementioned, the main pyrolysis products of ATJ are stable tertiary radicals, unlike straight chain normal alkane. Thermodynamically, aromatic hydrocarbons are less likely reformulated from tertiary radicals. In summary, ATJ in engine combustion is hard to implement under compression ignition engines, but it can reduce harmful emissions.

9.2 Gas turbine

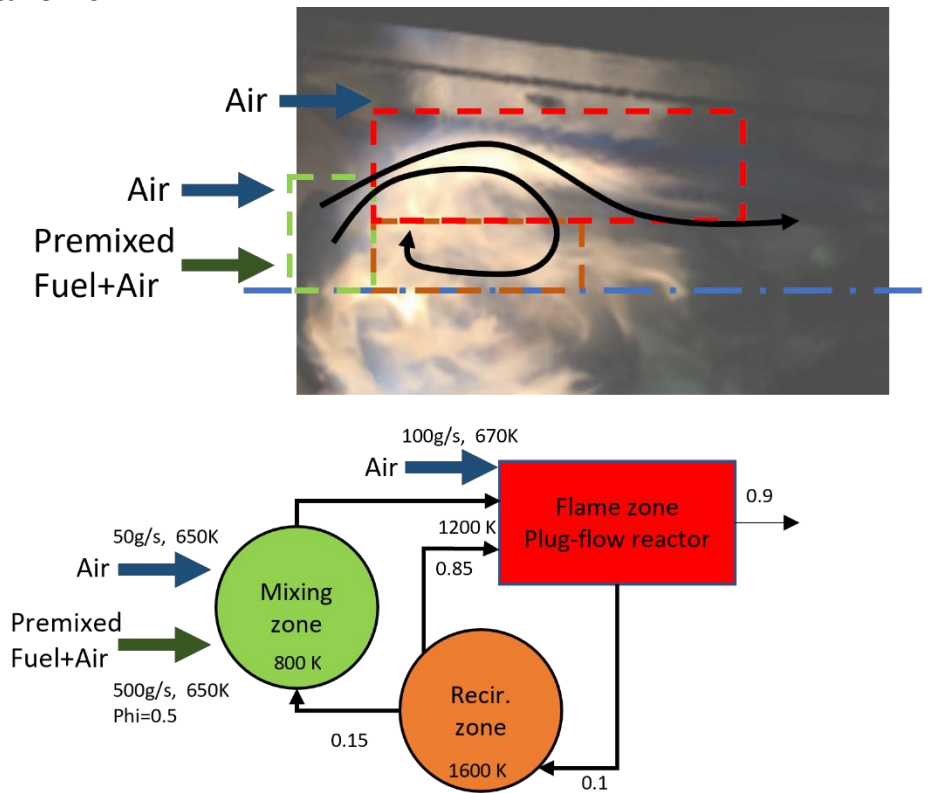


Figure 9-2 Schematic of 0-D gas turbine modeling (below) using real gas turbine image (upper) from [105]

The internal dynamics of liquid-fueled gas turbine combustors are complex due to combustion, spray physics, and turbulence. Computational tools help understand these processes. The hybrid PSR(Perfectly Stirred Reactor) and PRF(Plug Flow Reactor) reactor network are constituted to simulate mixing and flow characteristics under the gas turbine combustion process. The simulation focuses on the combustion process, as shown in Figure 9-2. In this reactor network, a gas turbine network is divided into three parts based on experimental results from Mayhew et al. [105]: a mixing zone (PSR), a flame/ignition zone (PFR), and a recirculation zone (PSR). A flame zone uses the air from the mixing zone and a recirculation zone for back mixing of hot combusted gas. The detailed thermodynamic theories, mathematical formulations, and the validation of simulation can be found in the Chemkin manual [101].

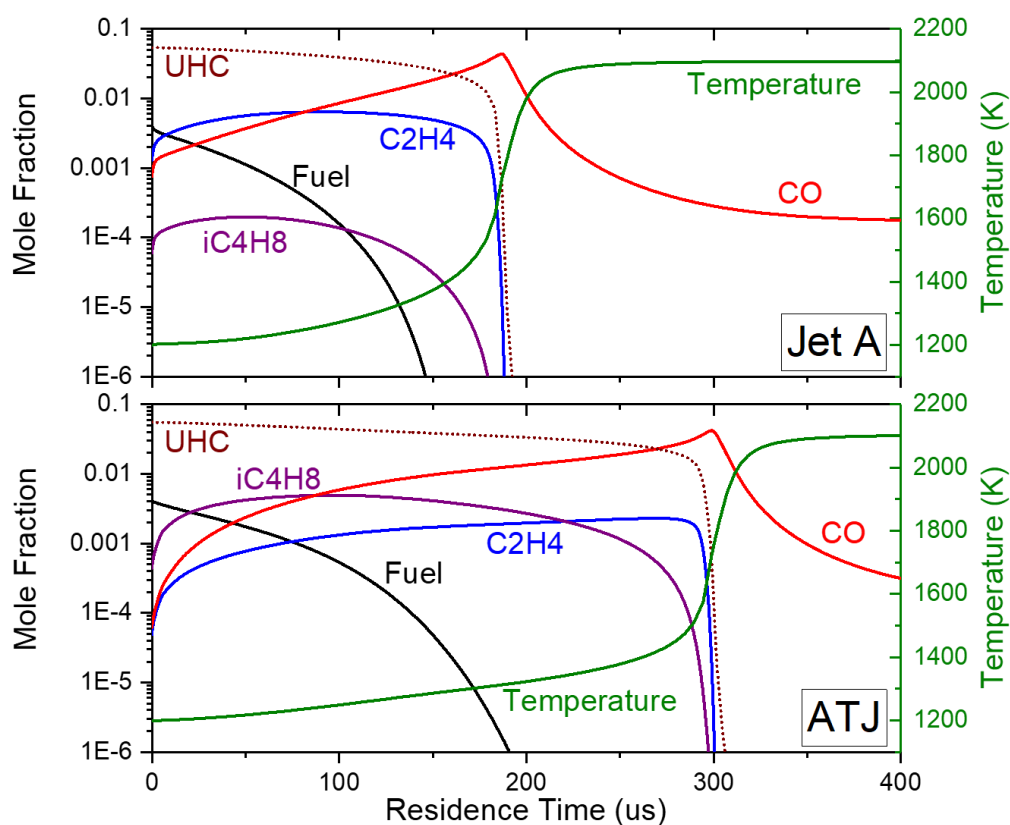


Figure 9-3 Temperature and species histories according to residence time under 0-dimensional gas turbine modeling with Jet A (Upper) and ATJ (below). Temperature (Green), the mole fraction of fuel (black), carbon monoxide (red), C₂H₄ (blue), iC₄H₈ (purple), and unburned hydrocarbon (brown) are represented.

According to the temperature profile and species histories in a flame zone indicated in Figure 9-3, ATJ also has a longer ignition delay under the gas turbine combustion. The C₂H₄ and i-C₄H₈ formation in all fuels are sensitive to high-temperature combustion, and the oxidation of stabilized i-C₄H₈ is slower than the oxidation of C₂H₄. The fuel consumption rate is similar because of the high temperature (~1200 K), but higher contents of i-C₄H₈ pyrolysis from ATJ result in retarded ignition. Mayhew et al. [105] reported that the flame of ATJ anchors more closely to the smaller angle of the spray zone. It can be explained by the longer ATJ's lower chemical reactivity.

Chapter 10 Conclusions and Future work

10.1 Summary and contributions of this dissertation

This dissertation is focused on investigating autoignition characteristics and developing data-driven based chemical kinetic models of various operationally relevant fuels. Chapter 1 described the motivation and background of alternative fuels and the importance of fuel research for human beings as fuels could dramatically differ in combustion and emissions characteristics due to differences in fuel properties and chemical composition. Conclusions drawn in this research are summarized below.

Chapter 2 provided the methodology of this study to investigate the autoignition properties of various fuels. Physiochemical properties of traditional fuels, alternative jet fuels, and sustainable aviation fuels (SAFs) are acquired from the Alternative Jet Fuel Test Database (AJFTD). This database was developed and is maintained at the University of Illinois Urbana-Champaign (altjetfuels.illinois.edu). The detailed chemical composition of fuels was examined by performing a gas chromatography/mass spectrometry analysis. Using physicochemical properties of fuels, two primary experimental devices -RCM and shock tube- were used to study the ignition behavior over a wide range of compressed temperatures. Because of the characteristics of the experimental apparatus, the RCM and the shock tube were used for investigating autoignition and chemical reactivity in low-temperature regimes and at high temperatures, respectively. By tailoring gas conditions and modifying the driver section end wall, the testing time of shock tube was increased to have better integration between the ignition delay data from the shock tube and RCM. In addition, experimental uncertainty was mathematically assessed to analyze the accuracy of ignition delay time and ignition temperature acquired from both experimental setups. Factors such as signal

sampling, reliability of the equipment used, and computational algorithms were considered for the uncertainty analysis.

Chapter 3 explained the background of combustion chemistry and chemical kinetics according to the compressed temperature. The chemical pathway of hydrocarbon oxidation is highly sensitive to experimental conditions, especially the ignition temperature. In the high-temperature combustion process, around and above 1000K, fuel species first undergo the pyrolysis process of alkyl radical decomposition or beta-scission, producing radicals. The produced radicals then oxidize with oxygen molecules and oxidative radicals. Intermediate and low-temperature combustion, below 1000 K, is more complicated and relevant to practical engine applications such as a lean-blow out and cold start. It can be summarized as the isomerization reaction between a peroxy radical (RO_2) and a hydroperoxy radical ($QOOH$). Based on combustion chemistry, chemical kinetic models are used to solve the chemistry component of governing equations during the numerical simulations of reactive flows. Combustion characteristics are typically modeled for practical applications using either the surrogate approach or the HyChem approach. Between these two approaches, this study utilized and demonstrated the formulation of the HyChem approach. Between surrogate and HyChem approach, this study utilized and demonstrated the formulation of the HyChem approach to model combustion characteristics. The mechanism comprises the HyChem lumped mechanism for high-temperature combustion, a lumped RO_2 - $QOOH$ cycle mechanism for low-temperature combustion, and the USC mech II for a detailed foundation chemistry model.

Chapter 4 concisely illustrates the overview of the optimization method used in this study. Stochastic and deterministic optimization are introduced and their advantages and disadvantages are assessed by implementing three different optimization methods applied to a chemical kinetic

problem. With the suggested techniques, the data-driven mechanisms can be generated with an efficient computational cost and a general sufficiently accurate ignition behavior prediction. The genetic algorithm was primarily utilized to optimize the reaction rate coefficients in this study to develop data-driven based chemical kinetic mechanisms of various fuels.

In Chapters 5 and 6, the ignition delay measurements of F-24/ATJ blended fuels and specially formulated CN fuels were performed at a compressed pressure of 2 MPa and equivalence ratio range (0.5, 1.0, and 1.3) in a temperature range from 650 K to 1250 K. The result showed that the chemical composition of the fuel significantly influences ignition characteristics. The main components of jet fuels can be divided into three groups: normal-alkane, cyclo-alkane, and iso-alkane. In the high-temperature regime, the branched structure of iso-alkanes results in the decomposition of fuel into tertiary radicals easily, but its stable states hinder oxidization. In the intermediate and low-temperature regimes, H-abstraction and radical isomerization in branched structures slow the ignition delay due to its high number of primary C-H bonds. A non-linear relationship between blending ratio and ignition characteristics has been observed concerning blending ratio. The reactivity of blends likely tends to follow the component of the blended fuel with higher reactivity. When the more reactive fuel undergoes the chain branching step in the mixture system, it will sufficiently provide OH radicals and heat to the system. The blending experiments revealed the importance of chemical structure on ignition chemistry under low temperature and the guideline for the fuel blending of two different neat fuels for optimal utilization in advanced combustion. Furthermore, the results from varied CN fuels indicated that DCN could not be a sole property used to predict ignition delay except in the intermediate temperature or NTC region, where DCN shows the best correlation to ignition delay. The variation

and/or similarities in ignition behavior observed amongst fuels arises from the inherent chemical structure of fuel components.

Based on the measured ignition delay dataset in Chapters 5 and 6, data-driven chemical kinetic mechanisms for the fuels: ARLMech-HC-F24ATJ and ARLMech-HC-VariedCN, were developed for numerical simulation of the ignition process in Chapters 7 and 8. The ultimate purpose of this study was to obtain a practical chemical kinetic mechanism across wide temperature and equivalence ratio ranges, with a particular focus on the negative temperature coefficient and low-temperature regions. The mechanisms were designed using the HyChem approach with a lumped low-temperature chemistry model, followed by metaheuristic optimization of reaction coefficients. To represent the non-linearity blending effects under intermediate and low-temperature chemistry, an alkylation (also known as co-oxidation) reaction was added to the blend mechanism. The mechanism development methodology for newly suggested fuels was suggested by developing varied CN fuels mechanisms. The newly introduced data-driven mechanisms based on these techniques show better performance and represent the ignition behavior more accurately than existing mechanisms.

Developed mechanisms were applied to practical combustion problems: homogeneous charge compression ignition internal combustion engine and gas turbine, to examine the fuel effects on ignition in chapter 9. Whereas a zero-dimensional simulation is weak in depicting the physical properties of fuels and the spatial distribution inside the combustor, it can provide a qualitative understanding and overall prediction of temperature, pressure, and emissions quite well as guidance for fuel application. Both examples indirectly reflected the experimental results from other published results, and also, the chemical kinetic modeling results from the mechanisms could provide theoretical reasoning bypassing costly experiments.

The experimental data and introduced chemical kinetic mechanisms in this dissertation will provide guidance and information regarding the autoignition characteristics of various fuels: conventional hydrocarbon fuels and alternate fuels. Moreover, this study's data-driven chemical kinetic mechanisms also guide the development of next-generation drop-in fuels and are specifically relevant to practical combustion applications with computational fluid dynamic simulations. In addition, as part of the Multi-fuel Capable Hybrid Electric Propulsion (MCHEP) program, hosted by the US Army Research Laboratory, this research helped investigate the autoignition reactivity of diverse fuels and develop ignition models

10.2 Future work

10.2.1 Reference Mechanisms of Pure components and blending

Assessing jet fuel's relevant pure hydrocarbon components is crucial to understanding the autoignition characteristics of real multi-component fuels, as discussed in Chapters 5 and 6. It will provide the fundamental knowledge of fuels' combustion and the influence of specific chemical species on the ignition of fuels. Hydrocarbon species in conventional and alternative fuels can be broadly classified into four major groups: normal alkanes, isoalkanes, cycloalkanes, and aromatics. The classification, the carbon number, and isotope structure will also affect the chemical combustion process in terms of isomerization and thermal decomposition.

In addition to the pure components' study, examining mixtures of each neat component could provide additional insight for understanding multi-component fuels as studied in chapters 5 and 7. Although the reactivity of blend components was not easily predictive, there is no perfect model

to simulate blending effects on autoignition characteristics. In this study, one of the alkylation reactions (co-oxidation) represents the blending effects in low-temperature chemistry. However, systemically evaluating the blending effect of different species should be performed to provide a detailed understanding of blending effects on ignition behavior.

All the data from the study will aid in expanding kinetic models for jet fuel-relevant components. Moreover, it will provide additional insight into creating next-generation alternative fuels in the future.

10.2.2 SAFs mechanism development

Sustainable aviation fuels (SAFs) have recently been proposed to unlock the potential for zero-carbon emissions for commercial aviation. Extension of pure components and blending studies in the previous section can provide further insight into developing chemical kinetic models of SAFs. From my perspective, HyChem is an easy and efficient approach to develop chemical kinetic mechanisms of newly introduced fuels by detouring the exhaustive endeavor of building surrogates. The current HyChem formulating framework is fuel-dependent and requires experimental information, including the detailed chemical composition of fuels and the time history of pyrolysis products.

Beyond the current HyChem framework, a generalized HyChem approach should be developed in the future. In fact, the current HyChem framework can be fuel-dependent. Specifically, the HyChem model relies on advanced species diagnostic techniques for one specific fuel, which provides the time evolution and yield data for its pyrolysis products.

It would be beneficial if one experiment could achieve the mechanism development. This study showed that the chemical compositions of fuels mainly result in ignition behavior. With detailed fuels' chemical information, a minimalist function group (MFG) approach [106] and a database from the previous section can be utilized to develop chemical kinetic modeling of completely new fuels. Instead of building surrogate compositions of fuels, the properties are anticipated by matching functional groups. Both high-temperature and low-temperature chemistry can be simplified by analyzing the functional groups of fuels rather than the fidelities analysis of chemical structures. Based on the analysis of functional groups, the HyChem approach can be generalized as semi-fuel dependent for various types of fuels with principle lumped reactions. With the database including single components, traditional jet fuels, and alternative fuels, data-driven and machine learning-based chemical kinetic development can be achieved. Using the training fuel database and the built knowledge of single components and blending effects, the approach would become an efficient and feasible solution to assess alternative fuels and SAFs.

10.2.3 Improvement of Low-temperature chemistry and optical diagnostics

Low-temperature combustion conditions are significant as they are sensitive to ignition and combustion processes and are considered the edges of stable operation. Unlike high and intermediate-temperature combustion chemistry, low-temperature chemical kinetics is a complicated process involving a series of alkylperoxy radical and hydroperoxyalkyl radical reactions. Typically, ignition of fuel components can be divided into two stages at low temperatures: chain branching process involving alkylperoxy radicals and thermal decomposition of radicals, including OH radical chain branching.

Measurements of critical species in well-designed experiments will be able to provide the constraints for developing chemical kinetic models. At this point, my suggestion would be CH₂O and CO as target species or markers of negative temperature coefficient and low-temperature chemistry behavior of the fuels for developing chemical kinetic models.

Diagnostics will include pressure trace, OH* emission, and laser absorption of CO and CH₂O to prove the reacting gas mixture during ignition. The method for laser absorption spectroscopy-based diagnostics for the measurement of CO is well-known. According to other literature, the P(20) transition of the CO fundamental rovibrational band, centered at 4.854 μm , can be used to probe CO. On the other hand, the measurement of CH₂O has interference with other species, including methane, water, and other hydrocarbons. R1(5) absorption line in the OH A-X (0,0) and C=O (carbonyl) containing compounds have interference around 307 nm. According to a two-color differential absorption technique described by Stanford research, the peak of the absorption feature of formaldehyde corresponds to 1787.05 cm^{-1} as the online wavelength and 1787.85 cm^{-1} as the offline wavelength. Using two different methods to prove formaldehyde can be a solution to measure carbonyl-containing radicals.

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Appendix. A Computed uncertainty values of experimental results

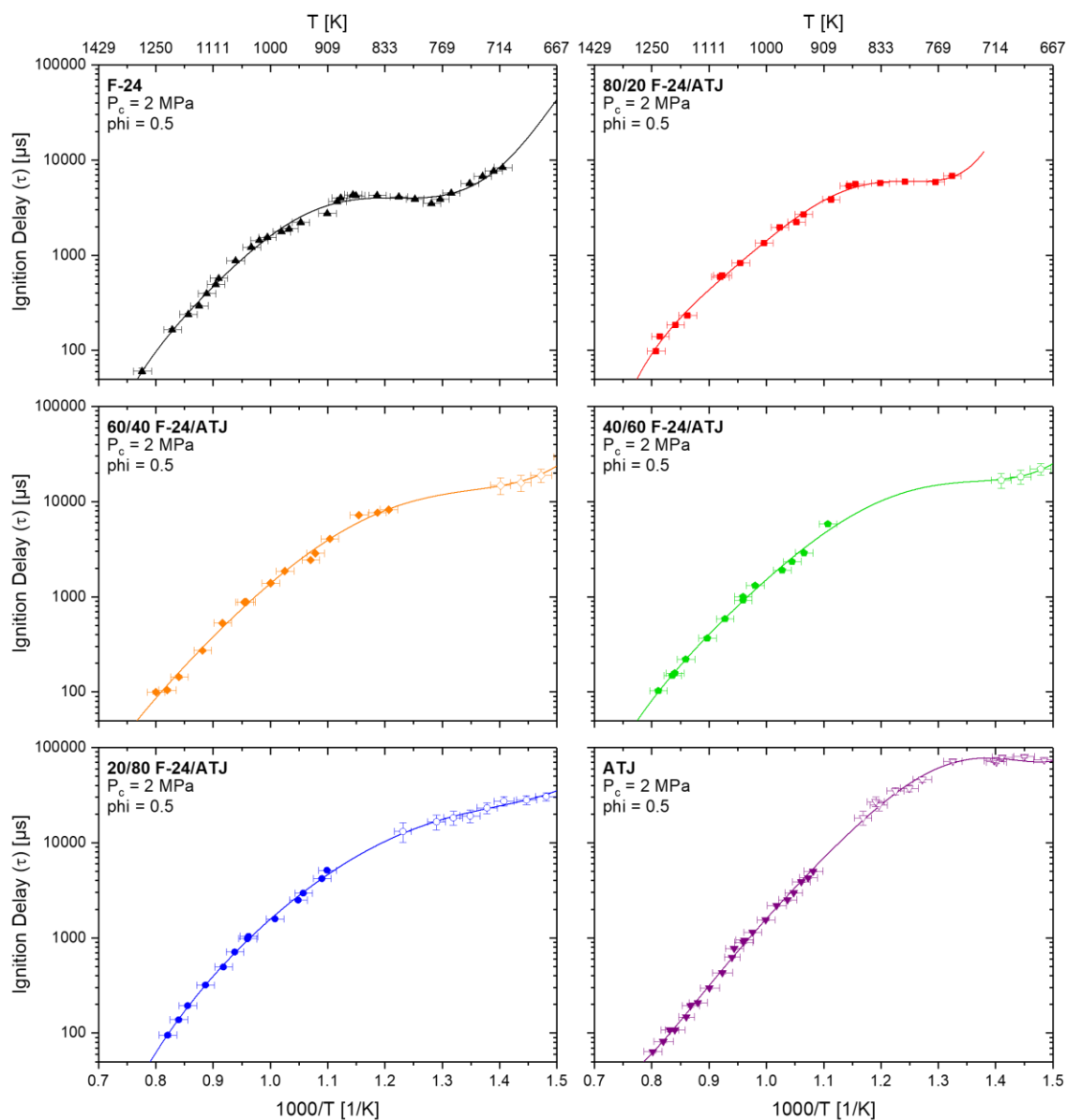


Figure A-1 Overall chemical ignition delays and computed uncertainty of results for F-24/ATJ blends with at $P_c = 2$ MPa and $\phi = 0.5$

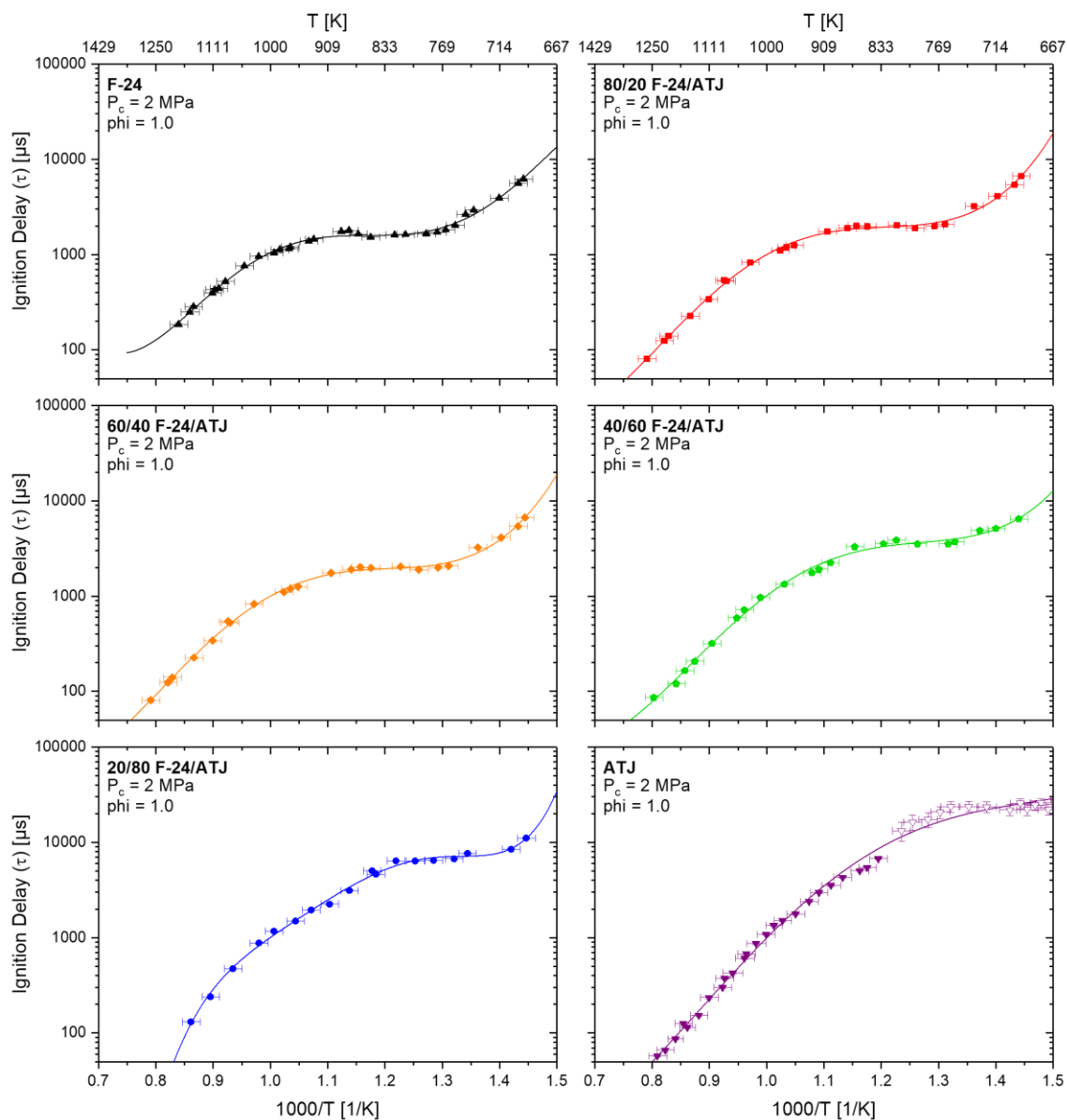


Figure A-2 Overall chemical ignition delays and computed uncertainty of results for F-24/ATJ blends with at $P_c = 2$ MPa and $\phi = 1.0$

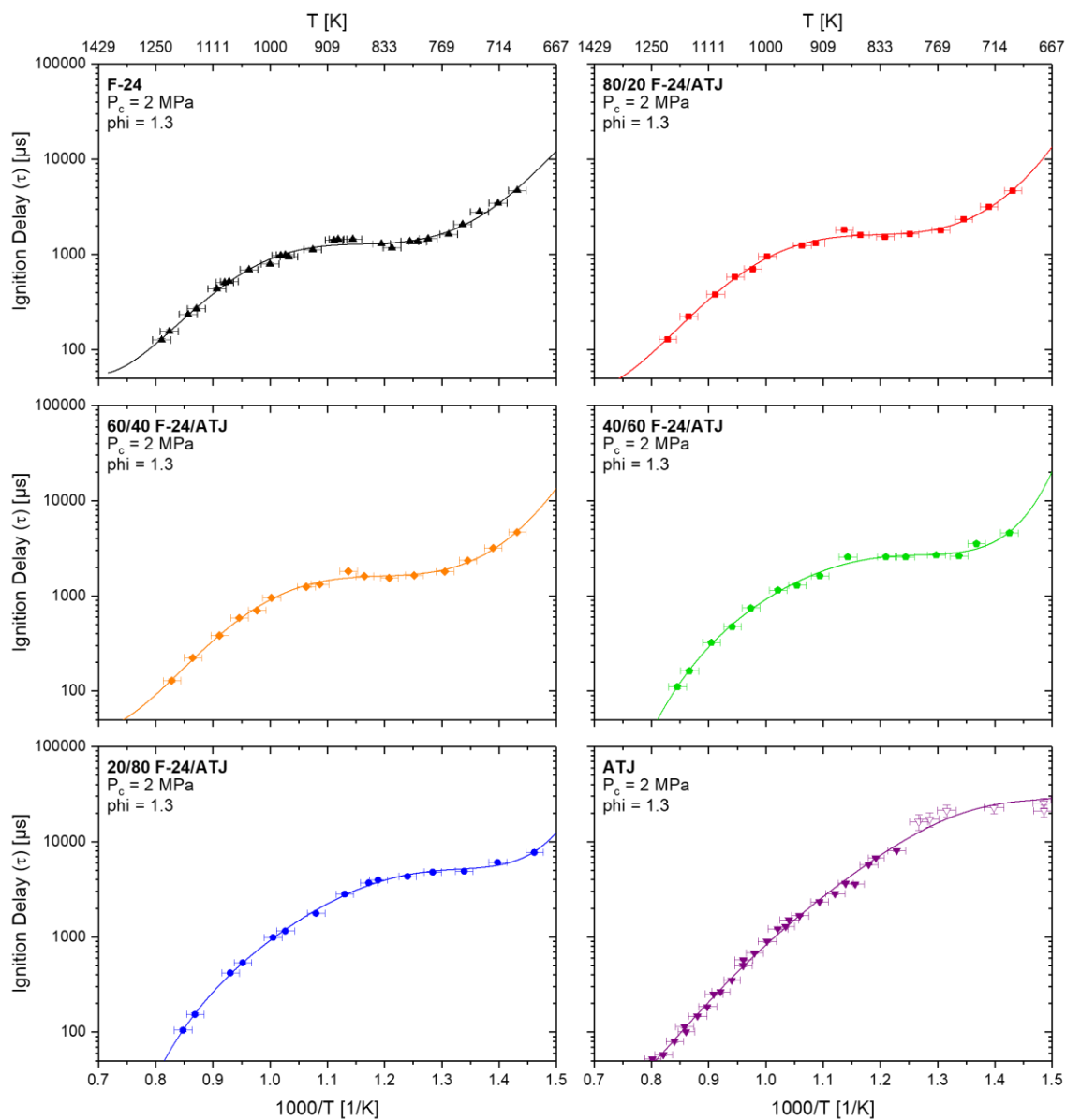


Figure A-3 Overall chemical ignition delays and computed uncertainty of results for F-24/ATJ blends with at $P_c = 2 \text{ MPa}$ and $\phi = 1.3$

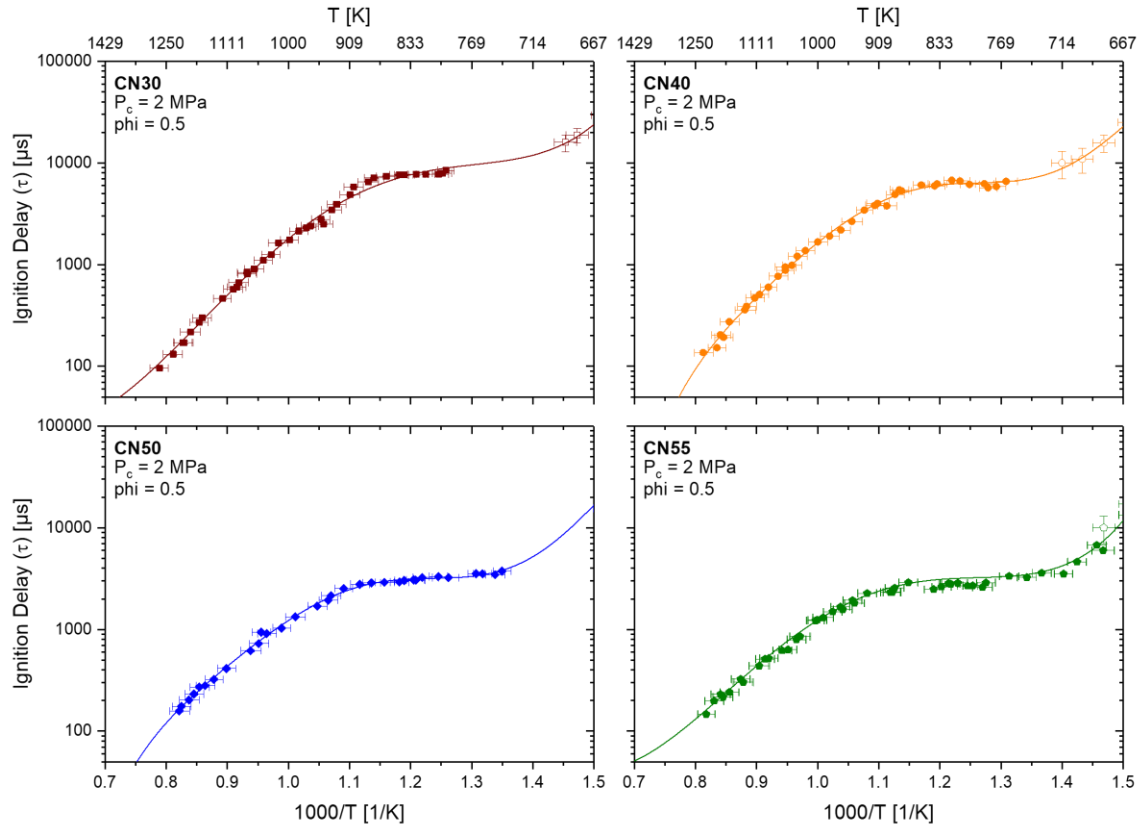


Figure A-4 Overall chemical ignition delays and computed uncertainty of results for CN varied fuels with at $P_c = 2$ MPa and $\phi = 0.5$

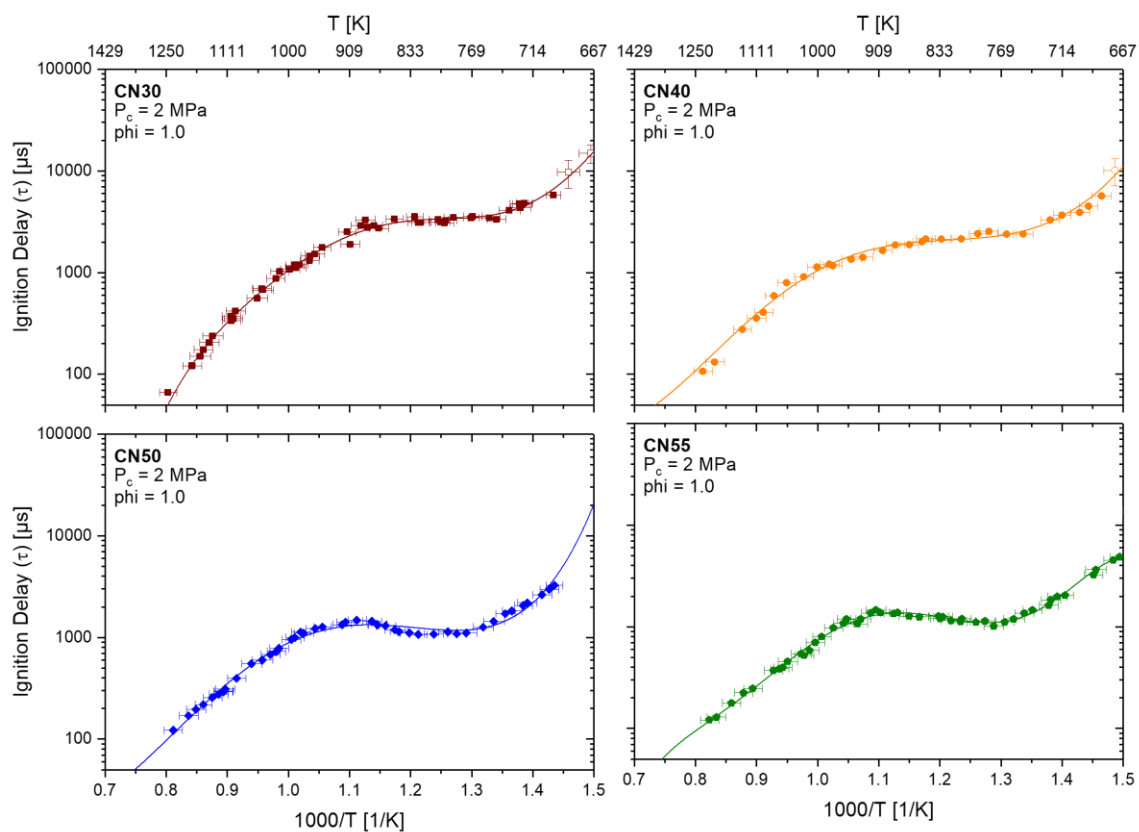


Figure A-5 Overall chemical ignition delays and computed uncertainty of results CN varied fuels with at $P_c = 2 \text{ MPa}$ and $\phi = 1.0$

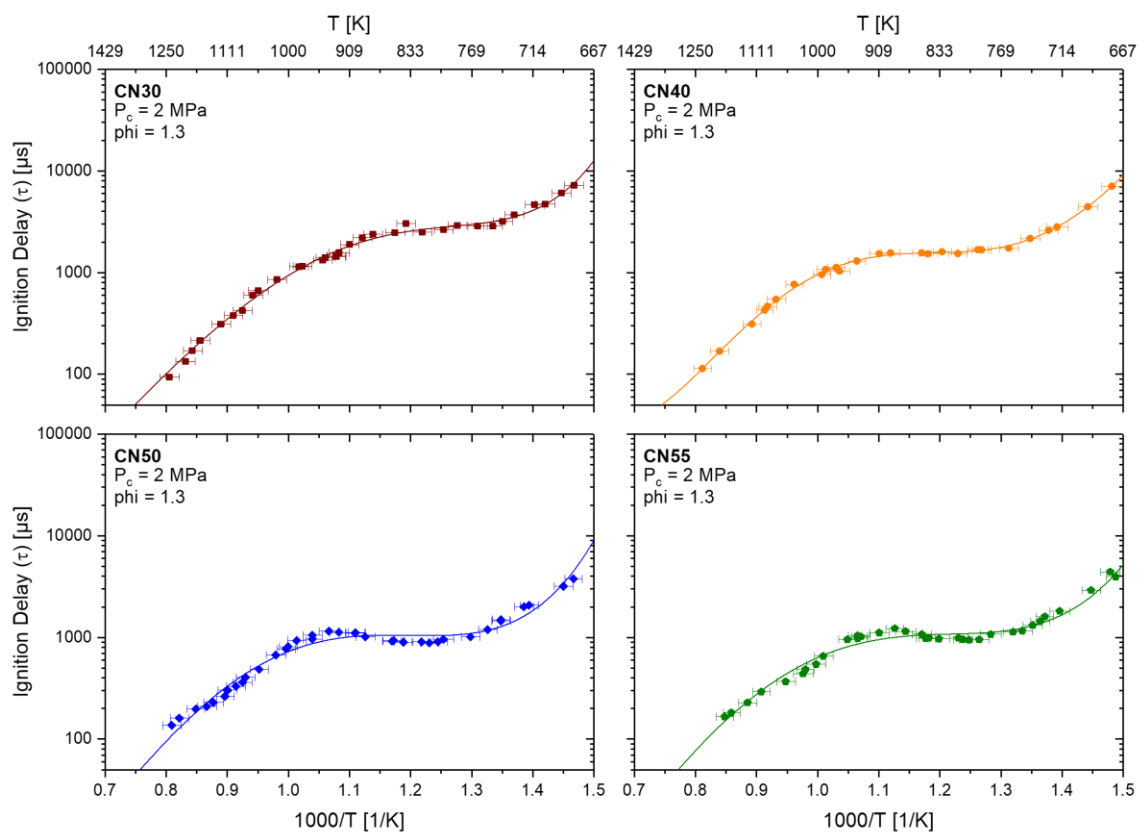


Figure A-6 Overall chemical ignition delays and computed uncertainty of results for CN varied fuels with at $P_c = 2$ MPa and $\phi = 1.3$