The University Of Sheffield.

# Aerospace Engineering

## MSc Dissertation Cover Sheet

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Aerospace Engineering

# Aerospace Engineering MSc
# Dissertation

# Kinetic Modelling Study of Alternative Aviation Fuel

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**August 2025**

**Academic supervisor:**

**Dr. Kevin Hughes**

**A thesis submitted to the Department of Mechanical, Aerospace and Civil Engineering, University of Sheffield in partial fulfilment of the requirements for the degree of Masters in Aerospace Engineering**

# ABSTRACT

Kerosene-based fuels remain the primary energy source in aviation due to their favorable combustion properties, but the growing need for cleaner and more efficient propulsion demands a deeper understanding of their combustion behavior. Accurate modeling of laminar flame speeds and ignition delay times is crucial for designing advanced combustors and developing reliable surrogate fuel mechanisms. This project investigates the combustion characteristics of kerosene surrogates through computational modeling using ANSYS Chemkin-Pro. Several multi-component and single-component mechanisms were evaluated over a wide range of operating conditions, including temperatures, pressures, and equivalence ratios. Predictions of laminar flame speed and ignition delay times were compared against experimental datasets to assess each mechanism's accuracy.

The results demonstrate the CRECK mechanism performs better at atmospheric conditions, while the five-component mechanism offers superior predictions under sub-atmospheric conditions. Among single – component models, JetSurF 2.0 and a novel global n-decane mechanism provides acceptable performance near stoichiometry, while CRECK captures n-heptane trends effectively. However, ignition delay predictions exhibit strong pressure sensitivity, highlighting the need for further refinement. Overall, this work provides insights into mechanism selection for kerosene surrogates and establishes a framework to guide future optimization efforts, supporting the development of more reliable combustion models for sustainable aviation fuels.

# ACKNOWLEDGMENT

I would like to express my sincere gratitude to my supervisor, Dr. Kevin Hughes, for his invaluable guidance, continuous support, and encouragement throughout the course of this research. His expertise, insightful feedback, and patience have been instrumental in shaping the direction of this work and helping me overcome challenges along the way to accomplish this project.

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# NOMENCLATURE

## Symbols

| | |
|---|---|
| $S_L$ | Laminar flame speed (cm/s) |
| Φ | Equivalence ratio |
| T | Temperature (K) |
| P | Pressure (atm/ kPa /bar) |
| IDT | Ignition delay time (ms) |
| APD | Average percentage deviation (%) |
| RMSE | Root-mean-Square Error (cm/s or ms) |
| N | Number of experimental data points |

## Abbreviations

| | |
|---|---|
| LFS | Laminar Flame Speed |
| IDT | Ignition Delay Time |
| CFD | Computational Fluid Dynamics |
| UQ | Uncertainty Quantification |
| DRGEP | Directed Relation Graph with Error Propagation |
| QSSA | Quasi-Steady-State Approximation |
| SAF | Sustainable Aviation Fuel |
| LLNL | Lawrence Livermore National Laboratory Mechanism |
| CRECK | Combustion Research Group Mechanism |
| JetSurF | Jet Surrogate Fuel Mechanism |

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# 1. INTRODUCTION

## 1.1 Background of Aviation and Global Warming

Since commercial aviation has emerged in the early 20th century, air travel has transformed from an exclusive luxury into a vital pillar of the world economy. The introduction of jet propulsion in the 1950s accelerated this transformation, enabling longer ranges, higher speeds, and affordable mass travel. By 2019, the aviation sector transported over 4.5 billion passengers and 58 million tonnes of cargo, generating trillions in the global economic value [1]. However, the environmental consequences of this are significant. Aviation accounts for ~2.5% of global $\mathrm{CO_2}$ emissions, but its net climate impact is greater – approximately 3.5% of total anthropogenic radiative forcing – due to high-altitude emissions of nitrogen oxide ($\mathrm{NO}_X$), water vapour, soot, and contrail-induced cirrus clouds [3]. The climatic impact of emissions released at cruising altitudes in the upper troposphere and lower stratosphere is amplified compared to equivalent missions at ground level [4]. Global demand for air travel is expected to double by 2050 [2], which means the industry's greenhouse gas emissions will grow significantly unless major changes are made. To meet its pledge of net-zero $\mathrm{CO_2}$ emissions by 2050 [2], aviation will need mix of solutions - from better aerodynamics and improved propulsion systems to more efficient operations – with the widespread use of sustainable aviation fuels (SAFs) playing the most vital role.

SAFs, made from renewable or waste-based sources can cut total lifecycle $\mathrm{CO_2}$ emissions by as much as 80% compared to fossil kerosene [5]. They can be used directly in existing engines and fuel infrastructure without expensive modifications. However, widespread use is currently limited to high production costs, restricted availability of feedstocks, and the need for extensive performance and safety testing before they can be used commercially. Certifying new fuels requires a deep understanding of their combustion characteristics-such as how they ignite, how stable their flames are, and how they tend to produce emissions – under conditions that mimic those in aviation gas turbines. While experiments using engine test rigs or lab-scale combustors are vital, they are also expensive, slow and often limited in the range of conditions they can replicate. For instance, recreating the full spectrum of flight-relevant temperatures (around 400-500 K) and pressures (0.5-2.0 atm) demands sophisticated facilities and multiple testing campaigns, a process that can stretch over months or even years [6]. Because of these limitations, it's difficult to quickly evaluate and improve new aviation fuels. Without faster and more adaptable ways to predict how fuels will burn, development will stay slow and push back the industry’s decarbonization targets. This is why chemical kinetic modelling is so valuable – it can accurately forecast combustion behaviour under many different conditions, providing an affordable and efficient alternative to extensive lab testing.

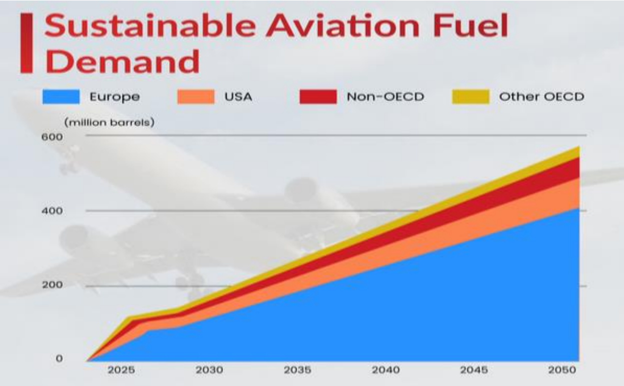


**Figure 2.1 - Projected global demand for SAF by 2050 [7]**

Figure 1.1 [7] depicts the growth in SAF demand highlights the aviation industry’s accelerating shift toward low – carbon energy sources. It shows a steady rise in SAF adoption across global regions, driven by climate commitments and technological advancements in fuel production. The projections indicate a rapid scale – up toward 2050, aligning with net – zero emission targets.

## 1.2 Significance of Kinetic Modelling

Chemical Kinetic modelling is now a key method in modern combustion research, especially for designing and certifying new aviation fuels. By simultaneously solving the coupled equation for mass, energy and species conservation together with detailed chemical reaction mechanisms, these models can predict how fuels behave across a broad range of operating conditions [8]. Two core combustion properties frequently derived from such models are laminar flame speed (LFS) and ignition delay time (IDT). LFS reflects a fuel’s reactivity and flame propagation behaviour, making it a standard reference for validating kinetic models [9]. IDT – defined as the interval between a specified ignition trigger and the start of substantial heat release – is crucial for assessing ignition quality, resistance to knock, and start – up performance in aviation engines [10]. Together, these parameters are central to maintaining combustion stability, efficiency and safety. To keep simulations manageable when dealing with complex fuels like kerosene, scientists often turn into surrogate fuel modelling. In this method, a simpler mixture of well – studied hydrocarbons – for example, n – decane, n -heptane, and certain aromatics – is used to mimic the physical and chemical properties of the real fuel [11], [12].

This strategy greatly cuts down the number of chemical species and reactions that need to be modelled, while still accurately capturing important performance characteristics. As a result, it allows for detailed studies across broad range of pressures, temperatures, and fuel – air mixtures which are relevant to aviation.

## 1.3 Objectives and Novelty of the Thesis

This research aims to assess and validate chemical kinetic models/mechanisms for kerosene surrogate fuels by using simulations and comparing results with experimental data, with the goal of determining the most accurate methods for modelling aviation fuels.

The main objectives of this research are fourfold. First, to conduct comprehensive review of published experimental data sets on kerosene and surrogate fuel mixtures, together with publicly available chemical kinetic mechanisms. Second, to develop proficiency in the use of ANSYS Chemkin – pro, validated through benchmark simulations of methane flame speeds. Third, to construct laminar flame speed and ignition delay models employing selected surrogate species and their blends. Finally, to evaluate and compare the predictive capabilities of various chemical kinetic mechanisms against experimental data. Based on these analyses, the thesis offers a critical appraisal of the mechanisms and identifies those most appropriate for future application in future investigations.

The novelty of this work lies in the comprehensive evaluation of several surrogate – based mechanisms across a range of temperatures, pressures, and equivalence ratios. By validating the results against both laminar flame speed and ignition delay time datasets, this study provides more extensive understanding of combustion behaviour than many earlier investigations.

## 1.4 Structure of the Thesis

This thesis is composed of the following chapters:

**Chapter 1: Introduction**

This chapter outlines the background and motivation of the study, highlighting the environmental challenges of the aviation and urgent need for cleaner, more sustainable fuels. It also explains the role of chemical kinetic modelling as a complementary tool for the experiments. The research aims, objectives and the novelty of this work is also discussed.

**Chapter 2: Literature review**

This chapter provides a critical survey of previous work on kerosene surrogates, experimental studies of flame speed and ignition delay, and chemical kinetic mechanisms of kerosene surrogates, by which it provides scientific context for the present work.

**Chapter 3: Methodology**

This chapter describes the details of the tools, models and the simulation strategies adopted in this study. It introduces ANSYS Chemkin – pro, outlines the selection of surrogate fuel mechanisms, and explains the boundary conditions used in laminar flame speed and ignition delay studies. The rationale for conducting comparisons of the various mechanisms within a uniform set of operating conditions.

**Chapter 4: Results**

This chapter provides the outcomes of the simulations, evaluating the performance of the different mechanisms in relation to experimental data. Points of convergence and divergence are identified, with particular attention to their significance.

**Chapter 5: Discussion**

The discussion examines the implications of these results, assessing the relative strengths and limitations of each mechanism, and considers their overall suitability for application in surrogate – based aviation fuel modelling.

**Chapter 6: Conclusions and Future Work**

This study has presented and discussed the key findings of the research, highlighting its contributions to the advancement of the field. In addition, several directions for future work have been identified, such as the inclusion of the sensitivity analyses, and extension of simulations to encompass more complex surrogate fuel blends alongside higher – fidelity experimental validation.

# 2. LITERATURE REVIEW

## 2.1 Introduction to Kerosene and Aviation Fuels

Kerosene – based jet fuels, including Jet-A and Jet-A1, serve as the primary energy sources for both commercial and military aviation. These fuels consist of highly complex hydrocarbon mixtures that encompass a wide range of molecular species, such as straight- and branched-chain alkanes, cycloalkanes, and aromatic compounds, generally within the carbon number range of C8 to C16 [13]. While the precise chemical comparison varies with the crude oil origin and the refining methodology employed, all kerosene-derived jet fuels are formulated to satisfy rigorous performance specifications, including requirements for volatility, thermal stability, freezing point, and energy density [14].

From the standpoint of combustion modelling, such complexity poses a significant obstacle. Representing every hydrocarbon species and its associated reaction pathways in full detail is computationally unfeasible. In addition, variations in the proportions of alkanes, cycloalkanes, and aromatics strongly affect ignition characteristics, flame propagation, and pollutant formation, making broad generalizations across different fuel batches highly challenging [11]. Consequently, researchers have turned to surrogate fuel strategies, whereby simplified mixtures of well-defined hydrocarbons are designed to reproduce the combustion behaviour of real kerosene while alleviating modelling demands.

## 2.2 Surrogate Fuel Approach

The surrogate fuel approach has been developed as pragmatic strategy for representing the combustion behaviour of complex hydrocarbon fuels such as kerosene. Given that practical jet fuels are composed of several hundred distinct molecular species, a complete description of all constituents and their associated reaction mechanisms is computationally impractical. To address this, surrogate fuels employ a limited set of well-characterized hydrocarbons that replicate the essential physical and chemical properties of the real fuel. This methodology enables reliable combustion modelling while substantially reducing computational demands [15],[11]. An effective surrogate fuel should closely reproduce the behaviour of the real fuel across a range of critical parameters. These encompass physical attributes (e.g., volatility, density, viscosity, and boiling range), chemical characteristics (including ignition delay time and laminar speed), as well as thermochemical response. The design of surrogate fuels is therefore aimed at achieving chemical representativeness rather than exact compositional equivalence, thereby preserving the fundamental combustion behaviour of kerosene [16].

A variety of approach have been reported in the literature for formulation for surrogate fuels. One common method involves the use of single-component surrogates, such as n-decane or n-dodecane, which are selected for their structural resemblance to the normal alkanes present in kerosene. For instance, n-decane has frequently been employed as representative compound due to its linear molecular structure, which facilities both modelling and experimental characterization [13]. Nevertheless, single component surrogates generally fail to reproduce the full spectrum of combustion characteristics, particularly in cases where aromatic species significantly influence phenomena such as ignition delay and soot formation [12].

To enhance the accuracy of surrogate fuel representations, researchers have developed multi-component formulations. These surrogates generally consist of mixtures of alkanes, cycloalkanes, and aromatics, combines in a proportion designed to replicate kerosene’s key characteristics, including its hydrogen-to-carbon ratio, volatility profile, and combustion reactivity. Common examples include simple binary systems, such as n-heptane/toluene blends, which are frequently employed in experimental investigations. More advanced surrogates, such as five component kerosene formulation, extend this approach by incorporating normal alkanes, branched alkanes, and aromatics to provide improved consistency across ignition delay and flame propagation behaviors [15],[18]. This process of selecting surrogate components is typically informed by property-targeting strategies, whereby blend compositions are iteratively adjusted to reproduce specific experimental benchmarks, such as shock-tube ignition times or laminar flame speed measurements [16]. Although notable progress has been achieved, the construction of surrogate fuels still involves balancing accuracy with computational feasibility. Expanding surrogates to include a greater number of components generally enhances their ability to replicate real-fuel behavior, but this also increases computational expense and mechanistic complexity. On the other hand, simplified surrogates are more practical to implement but may neglect critical phenomena, such as influence of aromatic species on soot formation [27]. The inherent trade-off remains a fundamental challenge in the ongoing development of kerosene surrogates.

In summary, the surrogate fuel methodology serves as a foundational element in contemporary aviation fuel research. By reducing the need to model the vast chemical complexity of real kerosene, it allows researchers to capture the critical combustion characteristics with far greater efficiency. Moreover, the adaptability of surrogate design offers a robust pathway for investigating emerging sustainable aviation fuels (SAFs), which will necessitate carefully tailored formulations to reflect the unique properties of bio-derived and synthetic hydrocarbons.

## 2.3 Experimental Studies of Combustion Properties

Experimental measurements of combustion properties such as laminar flame speed (LFS) and ignition delay time (IDT) have played a central role in advancing the understanding of kerosene and surrogate fuels. These datasets serve as essential benchmarks for validating chemical kinetic mechanisms models but also offer valuable insights into fuel behavior across the diverse operating conditions characteristic of aviation gas turbines.

### 2.3.1 Laminar Flame Speed Studies

The laminar flame speed ($S_L$) refers to the propagation velocity of an unstretched, one-dimensional premixed flame advancing through a stationary combustible mixture under defined thermodynamic conditions [9]. The parameter is strongly affected by factors such as the nature of fuel, the equivalence ratio, as well as the initial temperature and pressure of the mixture. In the case of kerosene and its surrogate fuels, a variety of experimental approaches have been utilized to determine laminar flame speeds, including the Bunsen burner technique, the spherical bomb method, and counterflow flame configurations. [13] conducted some of the earliest investigations on Jet-A flames, highlighting that flame speed is highly sensitive to both the equivalence ratio and the degree of preheating. Subsequent research on surrogate fuels, particularly single-component hydrocarbons such as n-decane and n-heptane, indicated that while these simplified models can reproduce certain flame speed characteristics, they frequently mispresent the actual behavior of kerosene, largely due to the absence of aromatic chemistry [26]. To address these limitation, later studies have focused on multi-component surrogate. Ji et al. (2010), for instance, compared flame speed measurements of n-decane/toluene blends against Jet-A, showing that the inclusion aromatic species markedly improves the fidelity of surrogate predictions.

### 2.3.2 Ignition Delay Time Studies

Ignition delay time (IDT) measurements, serves as a key parameter for evaluating fuel reactivity is mostly determined by using shock tubes or rapid compression machines. Davidson et al. (2005) investigated Jet-A ignition delays across pressures ranging from 10 to 40 bar, demonstrating a pronounced sensitivity to both pressure and equivalence ratio, with reduced delays observed at elevated pressures. Comparable experimental datasets have also been reported for single-component surrogate fuels, such as n-heptane and n-decane, both of which exhibit characteristic two stage ignition phenomena under intermediate temperature conditions.

Multi-component surrogates have been demonstrated to improve consistency with experimental kerosene data. Dooley et al. (2010) validated a three-component surrogate (n-dodecane, iso-octane, toluene) against ignition delay time measurements across multiple pressures and equivalence ratios, highlighting the importance of including both alkanes and aromatics. More recently, Yao et al. (2017) and Ranzi et al. (2014) expanded the datasets to high pressure and low temperatures, producing benchmark for validating mechanisms.

## 2.4 Chemical Kinetic Mechanisms for Kerosene Surrogates

The advancement of chemical kinetic mechanisms tailored for surrogate fuels has made it possible to model kerosene combustion with predictive accuracy. In this study, a selection of mechanisms from existing literature was utilized, encompassing both single-component and multi-component surrogate representations. A concise overview of these mechanisms is presented below.

For n-decane combustion, two kinetic mechanisms were evaluated. The first was the JetSurF 2.0 mechanism, developed through collaboration between Stanford University and Lawrence Livermore National Laboratory (LLNL). This mechanism has been extensively applied to long-chain alkanes and rigorously validated against experimental measurement data of the combustion properties [Wang et al., 2011]. Complementing this, a more compact alternative was considered: the multi-step global mechanism proposed by Xiong and Bi (2015). This reduced scheme offers significant computational efficiency while preserving predictive accuracy for low-temperature laminar propagation, thereby making it a practical choice for benchmarking studies at moderate pressures and temperatures.

For the case of n-heptane, a distinct kinetic mechanism was employed to investigate laminar flame speed behavior, simulations involving pure n-heptane were conducted using CRECK mechanism developed by Ranzi et al. (2014), which is recognized for its modular structure and comprehensive validation which has been done across a wide range of alkanes and aromatic compounds.

In this study, three kinetic mechanisms for multi-component kerosene surrogates were examined. The first was the Lawrence Livermore National Laboratory (LLNL) mechanism developed by Mehl et al. (2011), which provides detailed chemical pathways for larger alkanes, iso-alkanes, and aromatics, with particular focus on low-temperature oxidation behavior. The second was the CRECK kerosene surrogate mechanism, which incorporates alkanes, cycloalkanes, and aromatics, and has been extensively utilized in surrogate fuel validation studies. The third mechanism was a five-component surrogate model proposed by Yang and Zhen (2019), originally designed for gasoline surrogates under lean conditions. This mechanism combines n-decane, iso-octane, toluene, cyclohexane, and 1-hexene in carefully selected proportions to reproduce the physical and chemical characteristics of multi-component fuels. While its initial application targeted gasoline systems, its composite offers valuable insights for modeling kerosene-like fuel mixtures.

Collectively, these mechanisms span a continuum of modelling strategies, ranging from simplified global formulations to detailed multi-component surrogates. Their integration within this thesis provides a structured framework for evaluating and comparing predictive performance in simulations of laminar flame speed and ignition delay under conditions relevant to aviation

## 2.5 Comparative Studies and Knowledge Gaps

Over the past twenty years, research on kerosene combustion modelling has advanced considerably through the development of surrogate-fuel approaches. Numerous comparative investigations have evaluated alternative reaction mechanisms against the experimental observations; however, a unified agreement on the most accurate or dependable models has yet to be established. This lack of consensus largely stems from the intricate nature of hydrocarbon chemistry and the inherent variability within experimental measurements.

Previous research has frequently employed single-component surrogates, such as n-decane and n-heptane, due to their structural resemblance to the straight-chain alkanes prevalent in kerosene. Dagaut et al. (2000), for instance, demonstrated that n-decane could reproduce certain ignition delay characteristics under atmospheric conditions. However, Ji et al. (2009) had observed that single-component surrogate models generally underestimate laminar flame speeds when compared with those of real kerosene. Such findings underscore the limitations of single-component surrogates, particularly their inability to represent the role of aromatic and branched constituents that significantly affect flame propagation behavior and pollutant emissions.

Multi-component surrogate fuels have been shown to provide superior predictive capability compared to simpler formulations. Dooley et al. (2010) validated a three-component surrogate composed of n-dodecane, iso-octane, and toluene against shock-tube ignition delay measurements, reporting significantly improved agreement with Jet-A behavior over a range of pressures and equivalence ratios. Building on this, Yang and Zhen (2019) proposed a five-component mechanism tailored for lean conditions, demonstrating that the combined inclusion of linear alkanes and aromatic species enhances the accuracy of both flame speed and ignition delay predictions. Similarly, Ranzi et al. (2014) highlighted the role of cycloalkanes by showing that CRECK mechanisms incorporating these species more effectively reproduce sooting tendencies than alkane-only models. Nevertheless, despite such progress, establishing universally valid surrogate formulations remains challenging, as the relative importance of specific chemical pathways is strongly dependent on the operating conditions under consideration.

Comparative analyses of large-scale kinetic mechanisms highlight the inherent trade-off between chemical detail and computationally tractability. The LLNL mechanism captures comprehensive low-temperature pathways and successfully reproduces two-stage ignition phenomena; however, its extensive size renders it computationally prohibitive for many applied simulations. In contrast, the global multi-step n-decane model developed by Xiong and Bi (2015) offers improved efficiency but sacrifices accuracy when applied to conditions with significant variability. The CRECK modular mechanism provides an intermediate solution, offering flexibility and a degree of balance between complexity and cost, though its predictive reliability remains strongly dependent on the surrogate mixture employed. Consequently, the question of which mechanism achieves the most effective compromise between fidelity and computational feasibility remains an active subject of discussion.

The literature also shows clear gaps. First, many comparative studies are limited to a narrow range of pressures and temperatures, even though a modern aeroengines operate under highly diverse conditions, from low-pressure altitudes to high-pressure environment of the combustor. Secondly, although ignition delay times have been extensively investigated, experimental data on laminar flame speeds of multicomponent surrogate fuels as elevated pressures remain comparatively scarce, thereby restricting the validation of chemical mechanisms under realistic combustor conditions. Finally, comprehensive and systematic evaluations of mechanisms that concurrently address both flame speed and ignition delay within consistent operating frameworks are still relatively limited.

This study seeks the bridge existing gaps by systematically evaluating a range of kinetic mechanisms-namely JetSurf, LLNL, CRECK and a five-component surrogate-through comparison with experimental measurements of laminar flame speed and ignition delay times across diverse operating conditions. In addition, the work examines the fidelity of single-component surrogates such as n-decane, n-heptane in reproducing key combustion characteristics representative of kerosene. By integrating analyses of single-component, multi-component, and blended surrogate models within a unified simulation framework, the thesis provides a more holistic assessment of mechanism performance, highlighting both their capabilities and limitations in the context of aviation-relevant applications.

## 2.6 Experimental Datasets Used for Validation

Experimental investigations provide the foundation for validating chemical kinetic mechanisms of kerosene surrogate fuels. Over the years, extensive measurements of laminar flame speeds have been conducted for both surrogate mixtures and real kerosene under conditions representative of aviation combustion. Important contributions include the datasets reported by Wu et al. (2018), Richter (2018), Vukadinovic et al. (2010,2012), Kumar and Sung (2009), Munzar (2013), and Hui et al. (2012), which collectively cover initial temperatures in the range of 400-473 K at atmospheric pressure. More recently, Liu et al. (2022) and Huang et al. (2023) have expanded this database with studies on RP-3 and related surrogates, even at reduced pressures which acts as benchmark for LFS predictions from both single- and multi-component mechanisms. Even for the ignition delay time measurements the work of Zhukov, Starikovskiy, and Sechenov (2012) provides reference data across ratios and high pressures.

# 3. METHODOLOGY

## 3.1 Introduction

The methodology employed in this study primarily relies on computational simulations incorporating detailed chemical kinetic mechanisms to examine the combustion behavior of kerosene surrogate fuels. Although experimental investigations remain indispensable for validation, they are often constrained by practical limitation, including facility restrictions, variability in kerosene composition, and the challenges associated with replicating the high-pressure, low-temperature conditions characteristic of aviation engines. In this context, computational modelling serves as a valuable complementary tool, providing a systematic means to analyze parametric influences on ignition dynamics and flame development within well-controlled environments. This study investigates two key combustion characteristics – laminar flame speed (LFS) and ignition delay time (IDT). Both parameters serve as essential benchmarks for evaluating chemical kinetic mechanisms, offering valuable insight into fuel reactivity and flame stabilization – factors that play a central role in gas turbine development. To examine their predictive accuracy for the kerosene-like combustion behavior, a selection of surrogate mechanisms was drawn from the literature, encompassing both single-component and multi-component blends.

The method employed in this work centers on the implementation of the proposed mechanisms within ANSYS Chemkin-Pro, a widely recognized platform for chemical kinetics simulations. Simulations were carried out over a broad range of pressures, temperatures, and equivalence ratios. The outcomes were systematically compared against experimental datasets reported in the literature, thereby enabling an assessment of the mechanisms, predictive accuracy as well as the identification of their strengths and limitations. The subsequent sections present an overview of the computational framework, the chemical mechanisms and fuel systems considered, the simulation configurations for flame speed and ignition delay analyses, and the adopted validation strategy.

## 3.2 Computational Tool

All the computational analyses presented in this work were carried out using ANSYS Chemkin-Pro, a well-established commercial software package for chemical kinetics that is extensively employed in both combustion research and industrial applications. The program offers a comprehensive platform for solving the fundamental conservation equation of mass, species, and energy, while simultaneously incorporating detailed chemical reaction mechanisms. Through its advanced solvers, Chemkin-Pro enables the accurate prediction of key combustion characteristics, also including laminar flame speed ($S_L$) and ignition delay time, across diverse operating conditions.

In this, the simulations of laminar flame speed (LFS) were carried out using the PREMIX solver. This solver is tailored for modeling one-dimensional freely propagating flames, where the flame speed is obtained as an eigenvalue of the governing equations. PREMIX incorporates detailed transport phenomena, including multi-component diffusion, thermal conductivity and temperature-dependent transport properties, which makes it particularly suitable for assessing the accuracy of surrogate fuel mechanisms against experimental flame speed data. To predict ignition delay times (IDTs), simulations were conducted using the Closed Homogeneous Batch Reactor (SENKIN-type) available in Chemkin-Pro. This solver captures the time-dependent behavior of spatially uniform gas mixture under constant volume and energy conservation constraints. Within this framework, ignition delay is determined from the onset of a sharp temperature rise or significant heat release. The methodology effectively reproduces the operating conditions of shock tube and rapid compression machine experiments frequently documented in prior studies.

Chemkin-Pro was selected for this study due to its proven balance of accuracy, versatility, and user-oriented design. Its broad compatibility with various mechanism formats (such as 5-comp, LLNL, AND CRECK) allows for efficient integration and application of detailed reaction models. In addition, its widespread adoption in surrogate fuel research provides a reliable basis for comparison with existing experimental and simulation data. Collectively these attributes establish Chemkin-Pro as a suitable and robust platform for the systematic assessment of kerosene surrogate mechanisms under diverse conditions.

## 3.3 Mechanisms and Fuels Considered

A core focus of this thesis lies in evaluation of chemical kinetic mechanisms developed for kerosene surrogate fuels. The mechanisms, drawn from existing literature, include both single-component and multi-component surrogates, enabling a comprehensive examination of their predictive performance across varying degrees of chemical complexity.

### 3.3.1 Single-Component Surrogates

In this, fuels provide a practical approach for simplifying the modelling of kerosene combustion. In the present work, two-hydrocarbons – n-decane and n-heptane – were selected as representative species, owing to their close structural resemblance to the linear alkanes that constitute a major fraction of Jet-A fuel. For n-decane, two kinetic mechanisms were employed. The first was the JetSurf 2.0 mechanism [20], a detailed model that has been extensively validated for long-chain alkanes and has widely been applied in combustion research. The second was a reduced mechanism developed by Xiong and Bi (2015), which adopts a multi-step global reaction scheme to replicate n-decane flame propagation while substantially decreasing the number of reactions, therefor by offering improved computational efficiency.

For the case of n-heptane, a modelling strategy was applied. The CRECK mechanism [18] was utilized to predict LFS of pure n-heptane at atmospheric pressure, taking advantage of its modular framework and extensive validation record.

### 3.3.2 Multi-Component Surrogates

While single-component surrogates are useful for establishing the fundamental behavior of alkanes, multi-component surrogates offer a more presentative description of the chemical complexity present in kerosene. Accordingly, three mechanisms were chosen for detailed examination:

- The LLNL surrogate mechanism developed by Mehl et al. (2011) integrates large alkanes, iso-alkanes, and aromatic species, with particular focus placed on accurately representing low-temperature chemical pathways.
- The CRECK surrogate mechanism developed by Ranzi et al. (2014) incorporates cycloalkanes and aromatics, thereby providing a more comprehensive representation of Jet-A fuel composition.
- A five-component surrogate mechanism was proposed by Yang and Zhen (2019), incorporating n-decane, iso-octane, toluene, cyclohexane, and 1-hexene. While initially

formulated to represent the gasoline surrogates, the underlying design methodology also enables it to capture the essential combustion characteristics of kerosene with reasonable accuracy.

### 3.3.3 Rationale for Mechanism Selection

This work integrates both single-component and multi-component strategies, allowing for focused analysis of specific species such as n-decane and n-heptane, while also enabling a broader evaluation of the surrogate mixtures for kerosene, including LLNL, CRECK, and five-component models. The range of mechanisms employed facilities systematic comparisons that highlight the balance between computational efficiency, chemical detail, and predictive reliability under diverse operating conditions.

## 3.4 Simulation Setup

All computational analyses in this study were performed using ANSYS Chemkin-Pro. LFS predictions were obtained through the PREMIX solver, while ignition delay times were evaluated using the closed homogeneous batch reactor solver. The simulation framework was constructed to closely replicate the conditions documented in experimental datasets, thereby facilitating direct comparison and validation of surrogate fuel mechanisms. The investigated conditions spanned initial temperatures of 400 K and pressures ranging from sub-atmospheric levels up to 20 bar, encompassing both Laboratory-scale measurements and operating regimes relevant to aero-engine applications.

For the laminar flame speed simulations, which were conducted using three multi-component surrogate mechanisms: the five-component model proposed by Yang and Zhen (2019), the LLNL mechanism developed by Mehl et al. (2011), and the CRECK mechanism formulated by Ranzi et al. (2014). For the five-component surrogate, simulations were performed at 1 atm over initial temperatures of 400, 423, 445, and 470 K, with equivalence ratios ($\Phi$) ranging from 0.6 to 1.35. At 0.5 atm, the temperature range was adjusted to 400, 420, 450, and 480 K, with $\Phi$ spanning 0.8-1.4. Additional simulations were carried out at 450 K for sub-atmospheric pressures of 25, 50, 75 and 100 kPa using the same $\Phi$ range of 0.8-1.4. These ranges were applied to the LLNL mechanism and as well as CRECK mechanism to compare with the experimental data.

To establish baseline comparisons with multi-component surrogate predictions, single-component surrogates were also examined. For n-decane, simulation employed both the JetSurf

2.0 mechanism [Wang et al., 2011] and the reduced global scheme proposed by Xiong and Bi (2015), conducted at 1 atm and temperatures of 400-423 K over an equivalence ratio range of 0.6-1.45. Pure n-heptane was investigated using the CRECK model under the same pressure and Φ at 400 K. For all LFS simulations, the flame speed was determined from the peak value of the axial velocity profile predicted by PREMIX and subsequently plotted as a function of equivalence ratio for direct comparison with experimental measurements.

Ignition delay time simulations were carried out using a five-component surrogate mechanism, selected for its ability to most accurately represent the compositional complexity of kerosene surrogates. The batch reactor was initialized under specified temperature and pressure conditions, with IDT defined as the time at which the maximum temperature rise rate (dT/dt) occurred. Simulations were performed at pressures of 7, 15 bar, with equivalence ratios of 0.7, 1.0 and 1.3, along with additional case at 20bar for Φ = 1.0. The computed results were subsequently presented as IDT versus inverse temperature (1000/T), consistent with the conventional approach for comparison with shock tube and rapid compression machine data [Davidson et al., 2005; Dooley et al., 2010].

**Table 3.1 - Overview of Kinetic Mechanisms with Species and Reaction**

| Mechanism | Surrogate Type | Species | Reactions |
|---|---|---|---|
| CRECK (POLIMI) | Multi-component | 231 | 5591 |
| Five-component | Multi-component | 115 | 414 |
| LLNL -Reduced Mechanism I | Multi-component | 679 | 5935 |
| Pure n-heptane (CRECK) | Single-component | 106 | 1738 |
| JetSurF 2.0 (n-decane) | Single-component | 348 | 2163 |
| n-decane Global Mechanism | Single-component | 119 | 527 |

## 3.5 Simulation Procedure

All simulations were conducted in ANSYS Chemkin-Pro, employing the corresponding thermodynamic, transport, and reaction mechanism files. The operating parameters – namely the initial temperature, pressure, and equivalence ratio – were specified in accordance with available experimental datasets to facilitate direct comparison. The laminar flame speed ($S_L$) was determined using the PREMIX solver. For all component mechanisms, the computational domain was defined with an axial length of 5 cm. A stochiometric condition ($\Phi = 1$) was first established for the kerosene surrogate, after which continuation runs were carried out for both lean ($\Phi < 1$) and rich ($\Phi > 1$) mixtures. To ensure accurate resolution of the flame front, grid adaptation was applied, and convergence was validated through the assessment of conservation residuals.

For the ignition delay simulations, a closed homogeneous batch reactor model was employed. Each simulation was initialized using the specific pressure, temperature and equivalence ratio, with the termination time chosen to extend beyond the anticipated ignition point. Consistent with flame speed analysis, the procedure began with balanced stochiometric reaction for the five-component surrogate and was subsequently extended to both lean and rich mixture conditions. The ignition delay was determined as the time corresponding to the peak rate of temperature increase.

# 4. RESULTS

## 4.1 Introduction

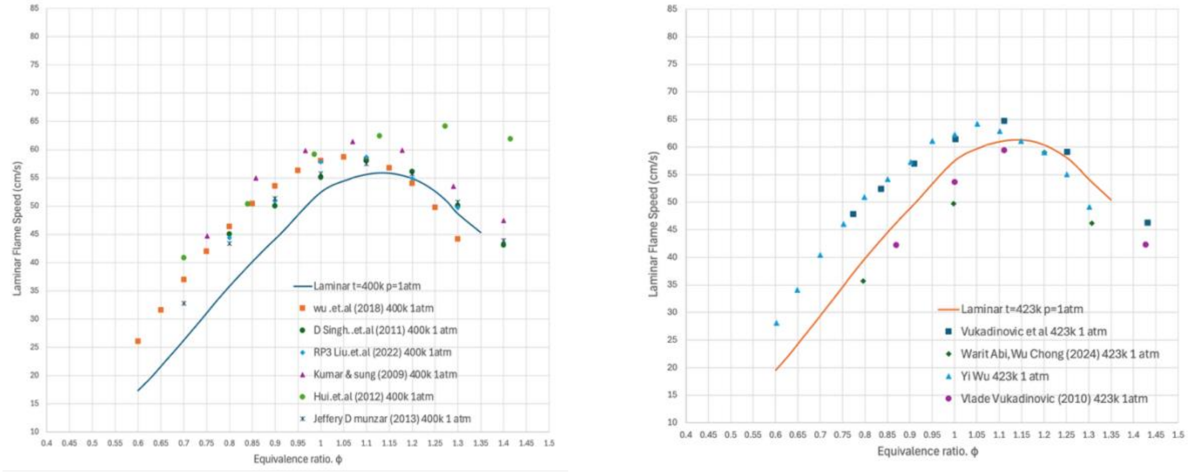
This chapter discusses the computational outcomes derived from chemical kinetic modeling of kerosene surrogate fuels using ANSYS Chemkin-Pro. The findings are presented in two primary sections: LFS and IDT. All simulations were conducted under conditions designed to reproduce available experimental data, thereby enabling direct validation of the mechanisms under investigation. The LFS section first examines predictions from multi-component surrogates, which is validated against experimental measurements across different pressures and temperatures. It the considers single-component – specifically n-decane and n-heptane – to provide baseline comparisons with simplified fuels. The IDT analysis is conducted through simulations employing the five-component surrogate mechanism. The corresponding results are evaluated at pressures 7, 15, and 20 bar, across lean, stoichiometric, and rich mixture. The aim of this chapter is not to restate the details of computational setup, which were outlined in chapter 3, but to highlight the performance of different surrogate mechanisms related to experimental benchmarks.

## 4.2 Laminar Flame Speed

Laminar flame speed ($S_L$) represents a key validation target for chemical kinetic mechanisms because it is directly influenced by the reaction pathways that control heat release and the radical formation. In, this study, simulations were performed for both multi-component surrogate mechanisms and single-component reference fuel, with the results compared against experimental data. This section first presents the outcomes from the three multi-component surrogate mechanisms – LLNL, CRECK and the five-component surrogate – followed by the single-component surrogates n-decane and n-heptane.

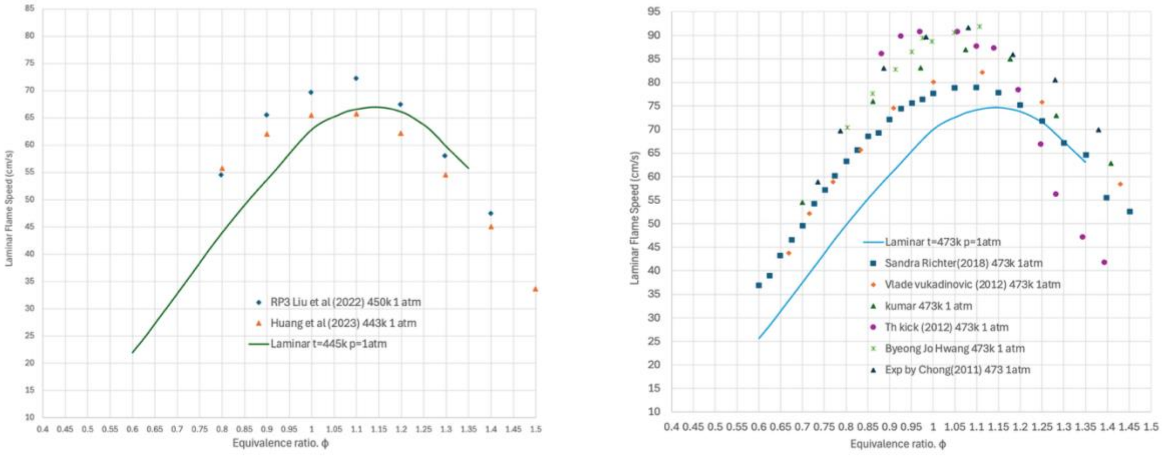
### 4.2.1 Multi-component Surrogates

Across all evaluated conditions, the five-component surrogate mechanism exhibited a systematic bias relative to experimental observations. At 1 atm and within the 400-473 K temperature range, the model consistently underestimated laminar flame speeds for all equivalence ratios, with the largest discrepancies occurring under lean conditions. Although predictions improved near stochiometric mixtures, underestimation remained evident, and in fuel-rich cases the deviation was smaller but still persistent. At 0.5 atm between 400 and 480 K, the bias shifted: while lean flames at higher temperatures were slightly underpredicted, the mechanism progressively transitioned toward overprediction in stochiometric and rich mixtures, most notably at 450 and 480 K. At lower temperatures (400-420 K), the agreement improved overall, though a tendency toward overprediction on the rich side remained. Under the sub-atmospheric pressures at 450 K (25-100 kPa), pressure effects became pronounced. At 25 kPa, predictions were closely aligned with experimental measurements, showing only minor underestimation in lean flames and mild overestimation in rich flames. At 50 kPa, the model underpredicted lean mixtures but overpredicted on the rich side, whereas at 75 and 100 kPa it underpredicted across the entire equivalence ratio range, with the magnitude error increasing with pressure. Overall, these findings demonstrate that the surrogate mechanism's predictive accuracy deteriorates as pressure increases, exhibiting a clear bias toward underprediction at elevated pressures, while at lower pressures it provides improved agreement in stochiometric and rich flames but continues to struggle in lean regimes.



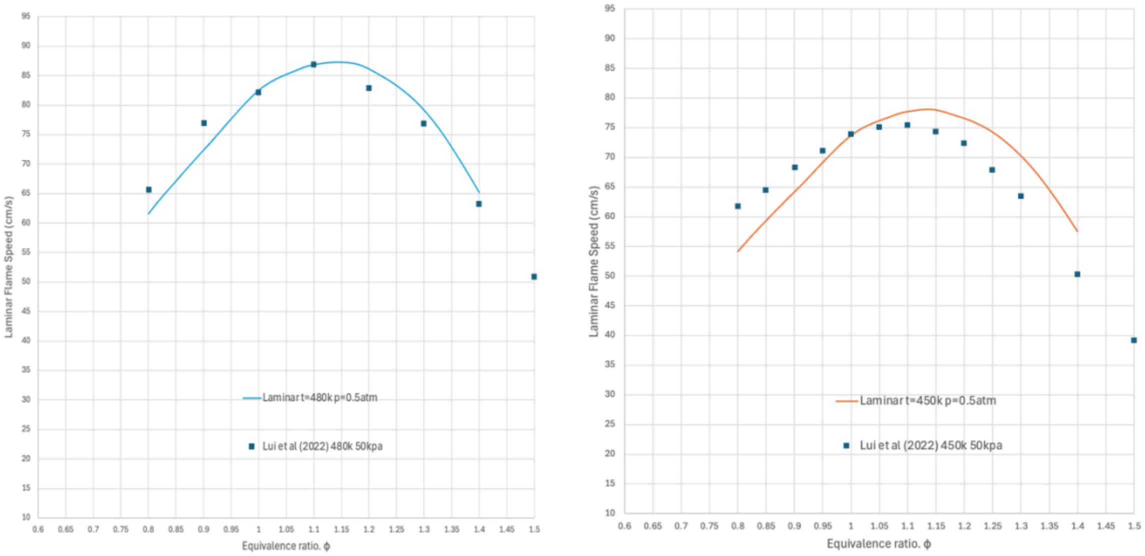
(a) (b)

**Figure 4.1 - Comparison of simulated five-component surrogate mechanism predictions with experimental data for laminar flame speeds at 1 atm – (a) 400 K and (b) 423 K**



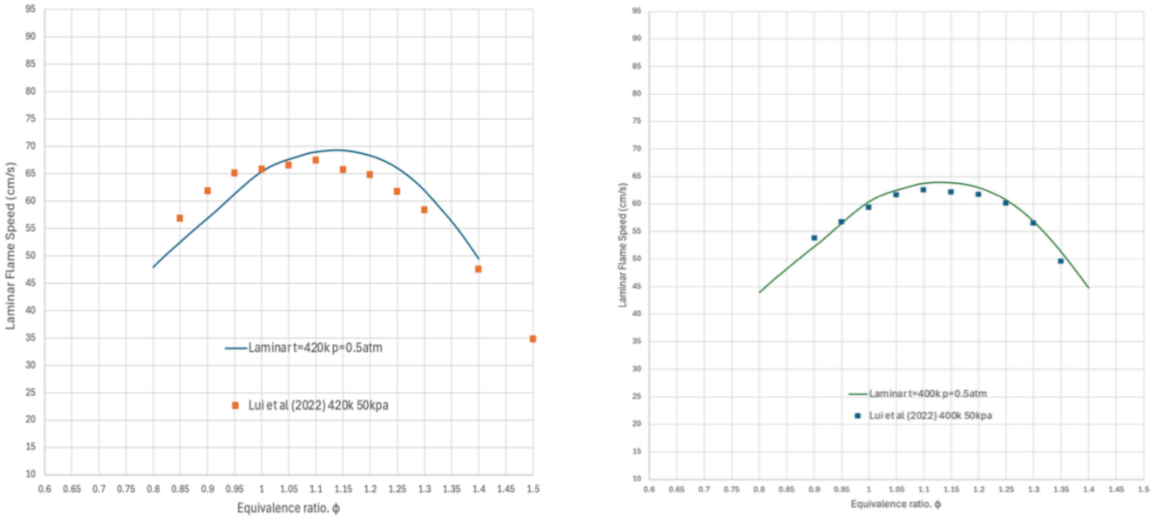
(a) (b)

Figure 4.2 - Comparison of simulated five-component surrogate mechanism predictions with experimental data for laminar flame speeds at 1 atm – (a) 445 K and (b) 473 K



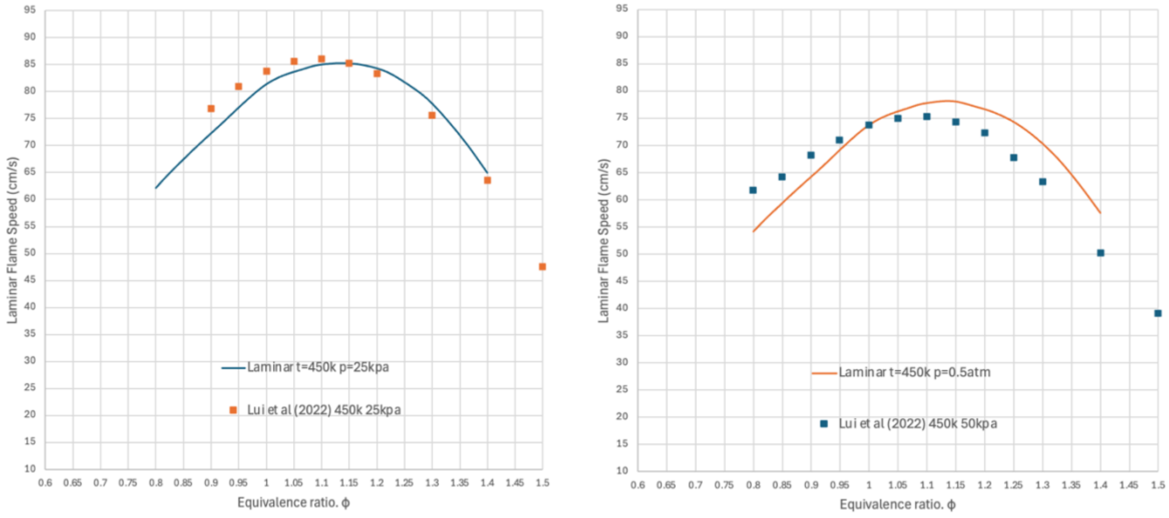
(a) (b)

Figure 4.3 - Comparison of simulated five-component surrogate mechanism predictions with experimental data for laminar flame speeds at 0.5 atm – (a) 480 K and (b) 450 K



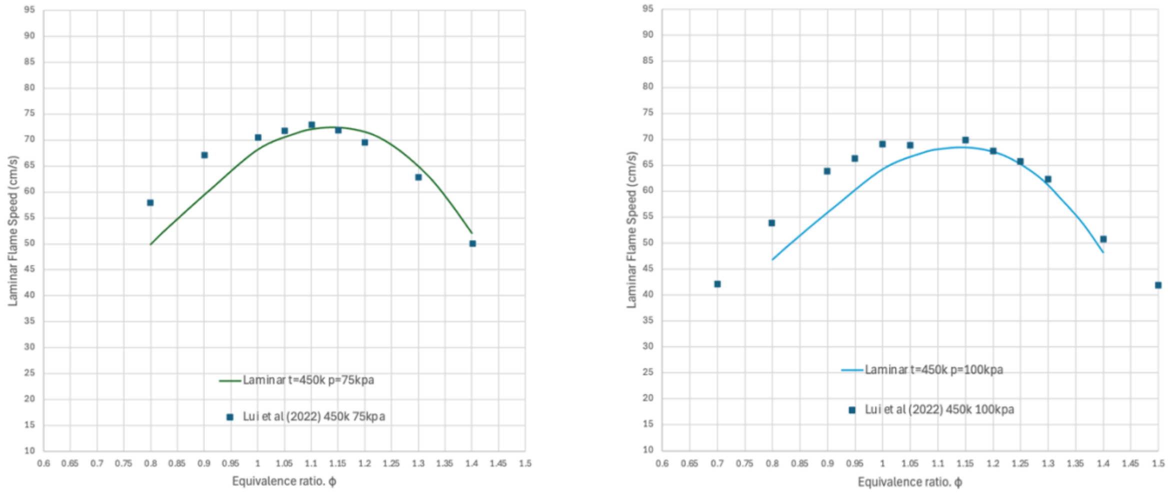
(a) (b)

**Figure 4.4- Comparison of simulated five-component surrogate mechanism predictions with experimental data for laminar flame speeds at 0.5 atm – (a) 480 K and (b) 450 K**



(a) (b)

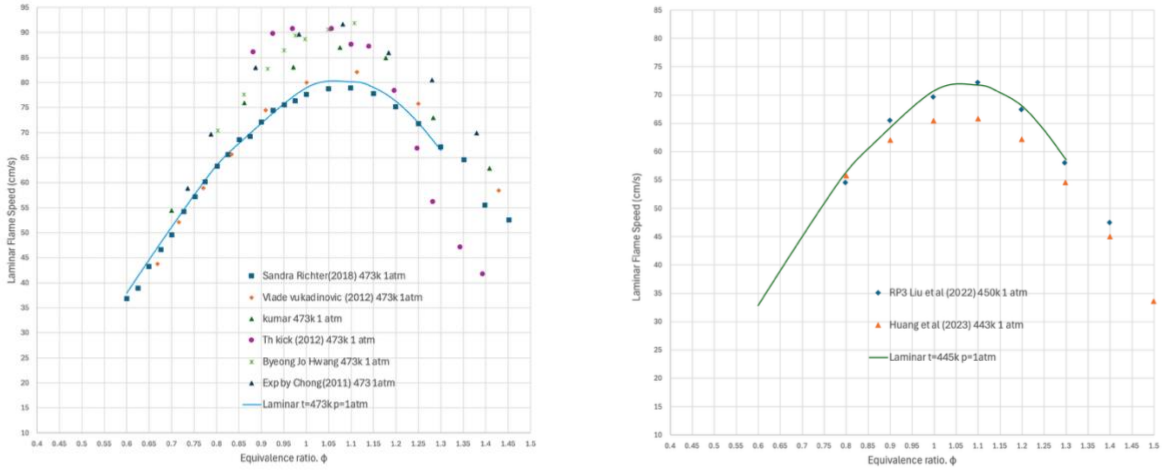
**Figure 4.5 - Comparison of simulated five-component surrogate mechanism predictions with experimental data for laminar flame speeds at 450 K under – (a) 25 kPa and (b) 50kPa**



(a) (b)

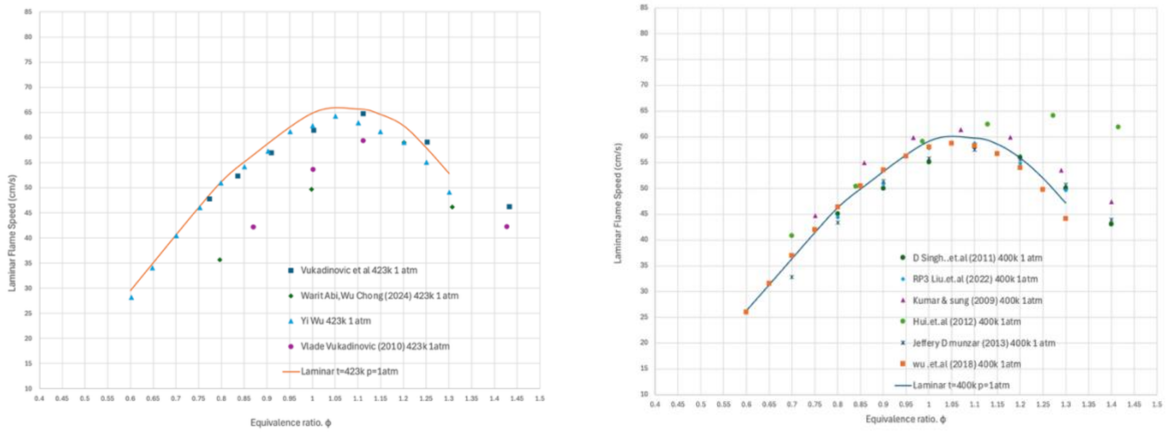
**Figure 4.6 - Comparison of simulated five-component surrogate mechanism predictions with experimental data for laminar flame speeds at 450 K under – (a) 75 kPa and (b) 100 kPa**

The CRECK mechanism demonstrated a distinct dependence on both pressure and temperature. At atmospheric pressure (1 atm) within the range of 400-473 K, the mechanism consistently underestimated flame propagation velocities across all equivalence ratios. This underestimation was most pronounced in lean mixtures, moderated near stochiometric conditions, and somewhat alleviated, though still present, under fuel-rich conditions. Conversely, at a reduced pressure of 0.5 atm and temperatures between 400-480 K, the trend reversed, with CRECK systematically overestimating flame speeds. The overprediction was most significant at elevated temperatures (450-480 K) near stochiometric conditions, whereas at lower temperatures (400-420 K), the agreement improved but a tendency toward overprediction persisted, particularly on the rich side. Further, at 450 K under sub-atmospheric pressures ranging from 25 to 100 kPa, the mechanism exhibited a progressive improvement in predictive accuracy with increasing pressure. At 25 and 50 kPa, strong overprediction was observed, most notably near stochiometric mixtures. At 75 kPa, the discrepancy was reduced though still evident, while at 100 kPa, CRECK produced its closest agreement with experimental data, slightly overpredicting yet broadly reproducing observed flame speeds across lean, stochiometric, and rich regimes. Overall, these findings underscore CRECK's characteristic behavior of underprediction at atmospheric pressure and overprediction under reduced pressures, with predictive accuracy improving progressively as pressure increases.



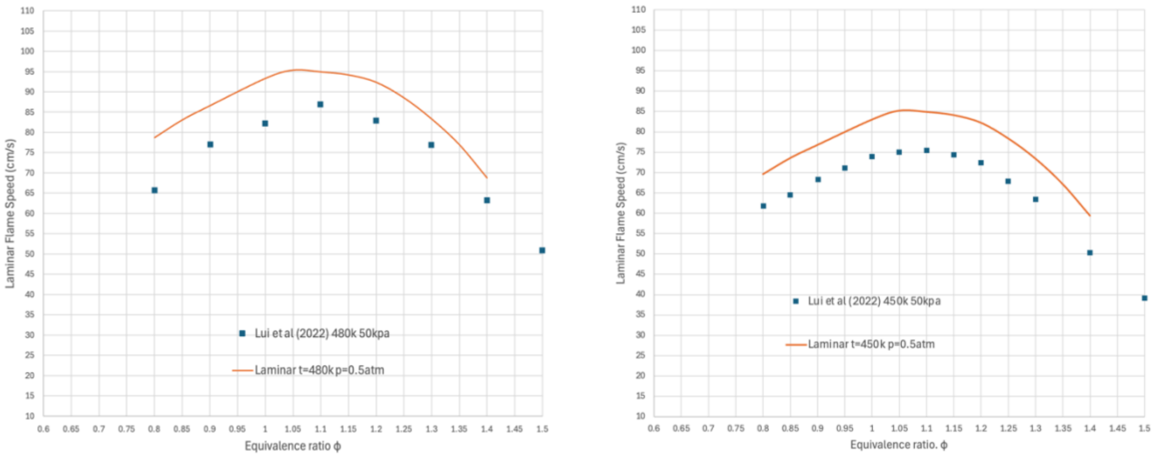
(a) (b)

**Figure 4.7 - Comparison of simulated CRECK mechanism predictions with experimental data for laminar flame speeds at 1 atm – (a) 473 K and (b) 445 K**



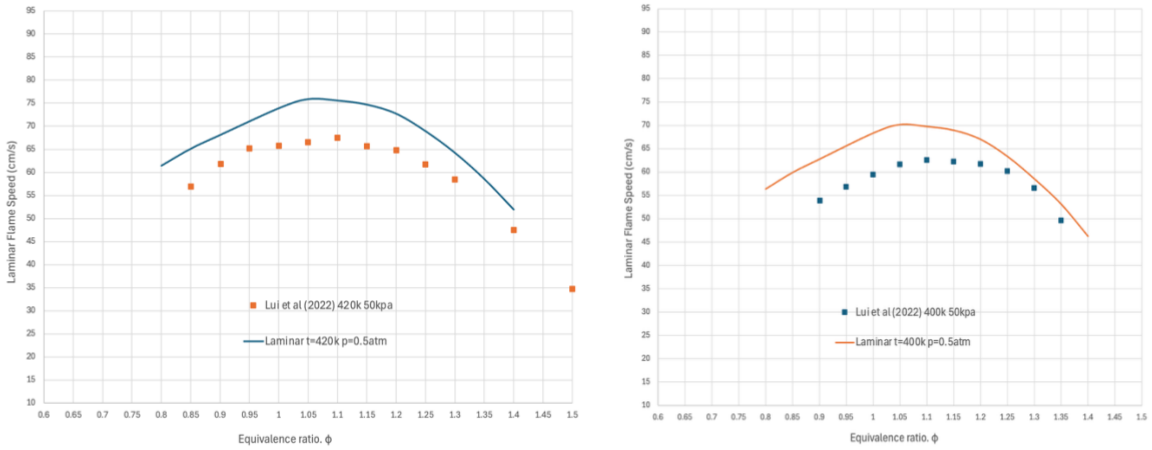
(a) (b)

**Figure 4.8 - Comparison of simulated CRECK mechanism predictions with experimental data for laminar flame speeds at 1 atm – (a) 423 K and (b) 400 K**



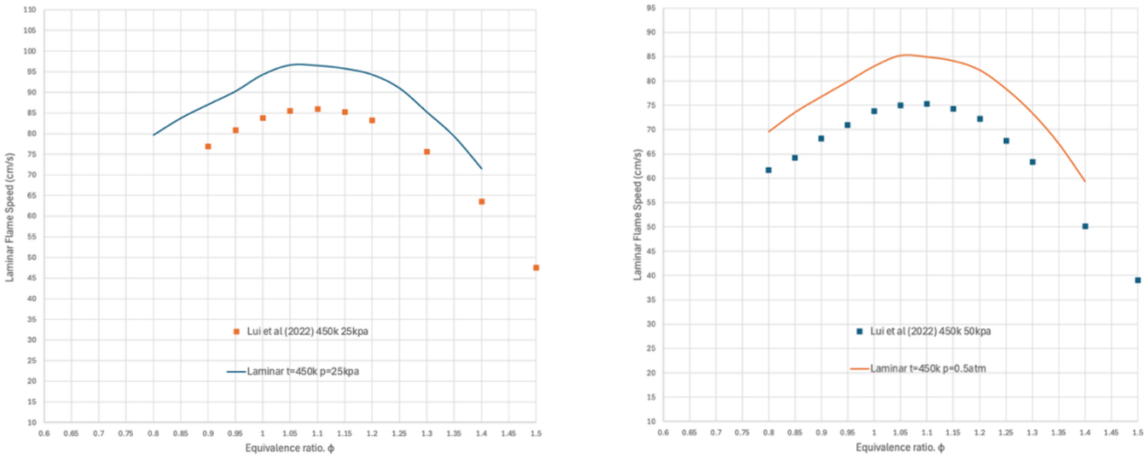
(a) (b)

**Figure 4.9 - Comparison of simulated CRECK mechanism predictions with experimental data for laminar flame speeds at 0.5 atm – (a) 480 K and (b) 450 K**



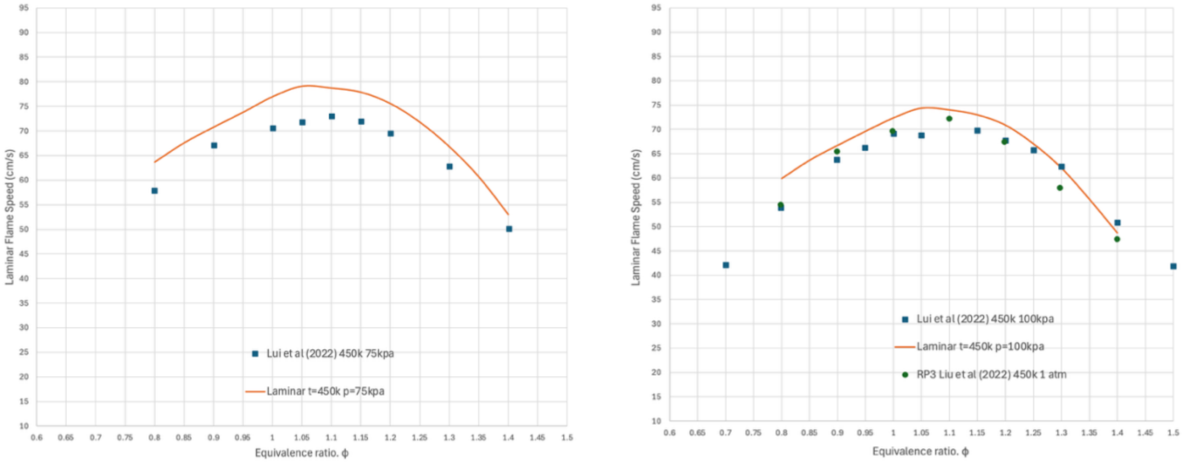
(a) (b)

**Figure 4.10 - Comparison of simulated CRECK mechanism predictions with experimental data for laminar flame speeds at 0.5 atm – (a) 420 K and (b) 400 K**



(a) (b)

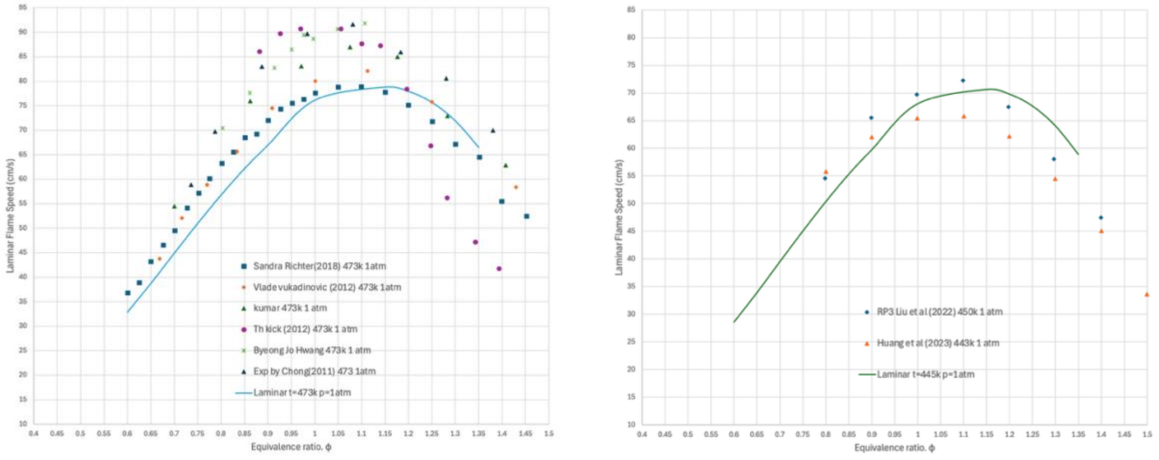
**Figure 4.11 - Comparison of simulated CRECK mechanism predictions with experimental data for laminar flame speeds at 450 K under – (a) 25 kPa and (b) 50 kPa**



(a) (b)

**Figure 4.12 - Comparison of simulated CRECK mechanism predictions with experimental data for laminar flame speeds at 450 K under – (a) 75 kPa and (b) 100 kPa**

The LLNL mechanism demonstrated systematic deviations from experimental measurements, though the trends differed from those observed in the five-component and CRECK models. At atmospheric pressure and within the temperature range of 400-473 K, the mechanism consistently underpredicted laminar flame speeds relative to experimental data. The largest discrepancies occurred under lean conditions, whereas predictions near stochiometric equivalence improved, though they remained below measure values. In rich mixtures, the underprediction persisted but with a reduced magnitude. At reduced pressure (0.5 atm) over 400-800 K, the mode's bias shifted, showing a general tendency to overpredict flame speeds across equivalence ratios. The effect was most pronounced at 450 and 480 K near stochiometric conditions. At lower temperatures (400-420 K), the overprediction persisted but was less serve, particularly under fuel-rich conditions. A clear pressure dependence was also evident at 450 K under sub-atmospheric conditions. At 25 and 50 kPa, the mechanism significantly overpredicted flame speeds, most notably around stochiometric mixtures. The overprediction remained at 75 kPa, though with reduced deviations. At 100 kPa, the model achieved its best performance, slightly overpredicting in lean and stochiometric regimes while closely matching experimental flame speeds under rich conditions. Overall, the LLNL mechanism exhibits a systematic shift in predictive behavior: underprediction dominates at atmospheric pressure, while sub-atmospheric conditions Induce overprediction, with model accuracy improving at higher sub-atmospheric pressures and being most reliable at 100 kPa near stochiometric.



(a)

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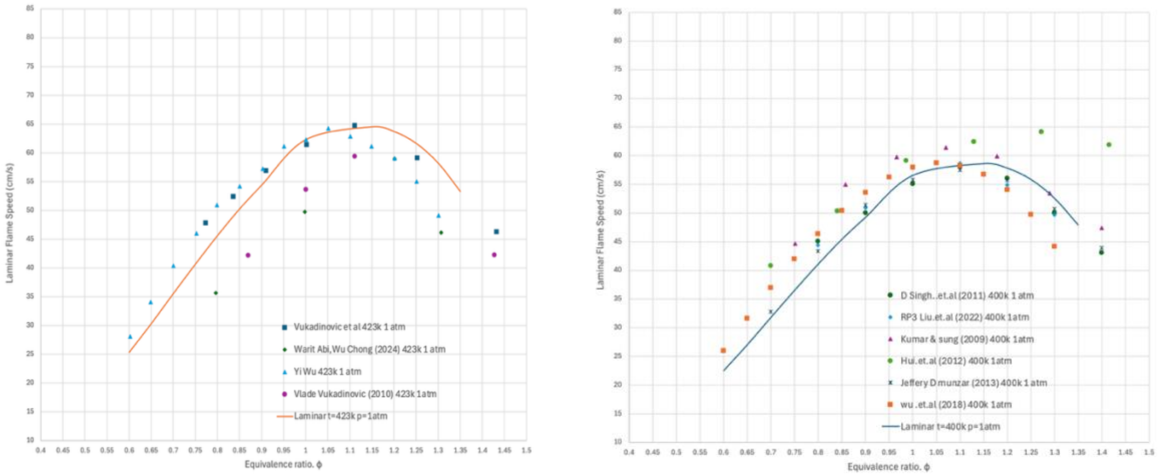
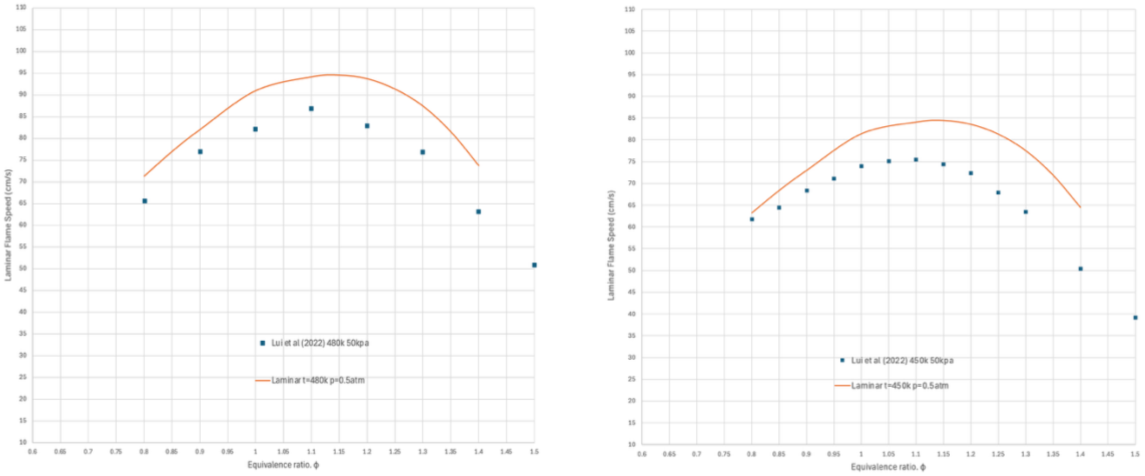
**Figure 4.13 - Comparison of simulated LLNL mechanism predictions with experimental data for laminar flame speeds at 1 atm – (a) 473 K and (b) 445 K**



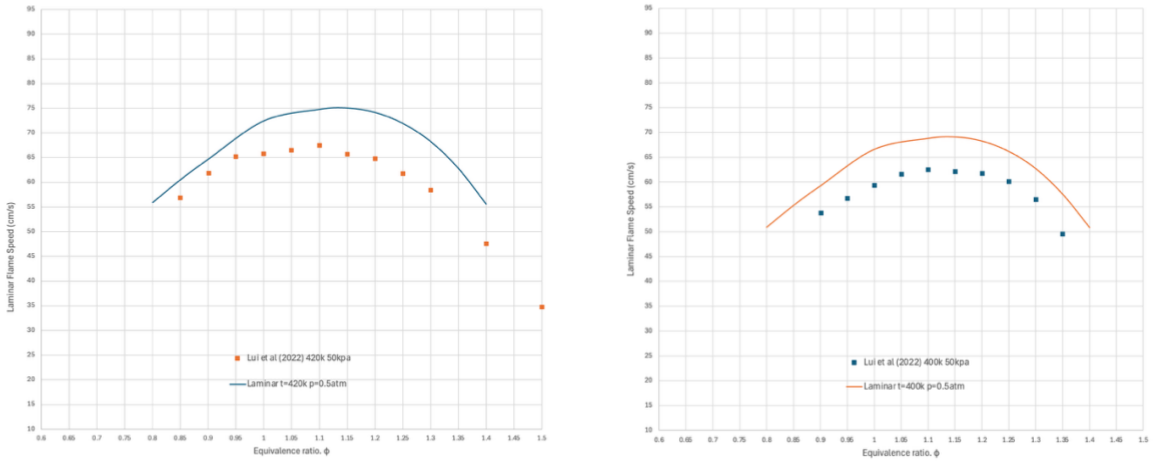
(a) (b)

**Figure 4.14 - Comparison of simulated LLNL mechanism predictions with experimental data for laminar flame speeds at 1 atm – (a) 423 K and (b) 400 K**



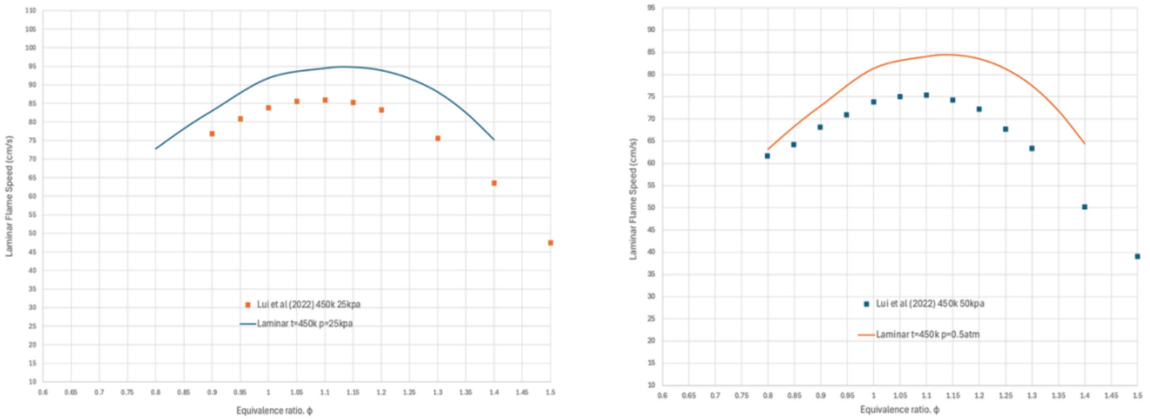
(a) (b)

**Figure 4.15 - Comparison of simulated LLNL mechanism predictions with experimental data for laminar flame speeds at 0.5 atm – (a) 480 K and (b) 450 K**



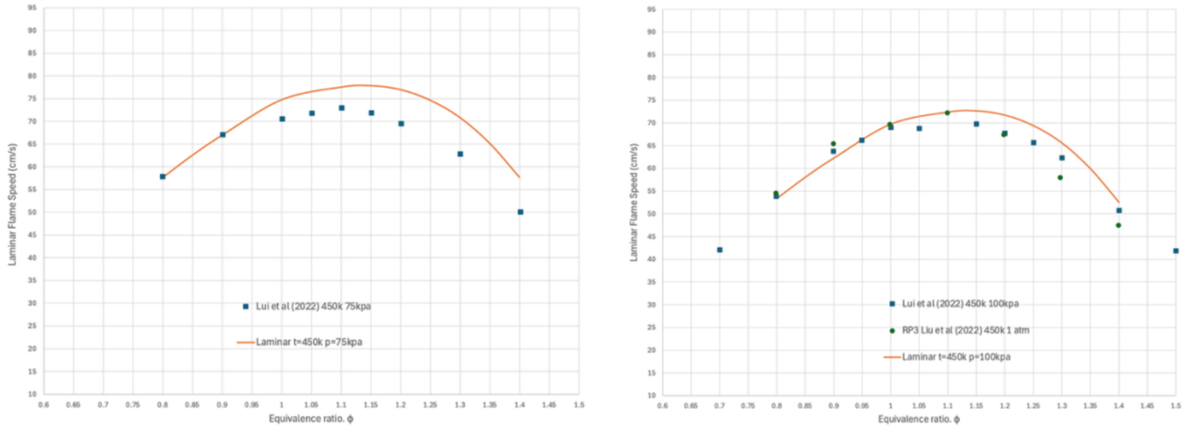
(a) (b)

**Figure 4.16 - Comparison of simulated LLNL mechanism predictions with experimental data for laminar flame speeds at 0.5 atm – (a) 420 K and (b) 400 K**



(a) (b)

**Figure 4.17 - Comparison of simulated LLNL mechanism predictions with experimental data for laminar flame speeds at 450 K under – (a) 25 kPa and (b) 50 kPa**

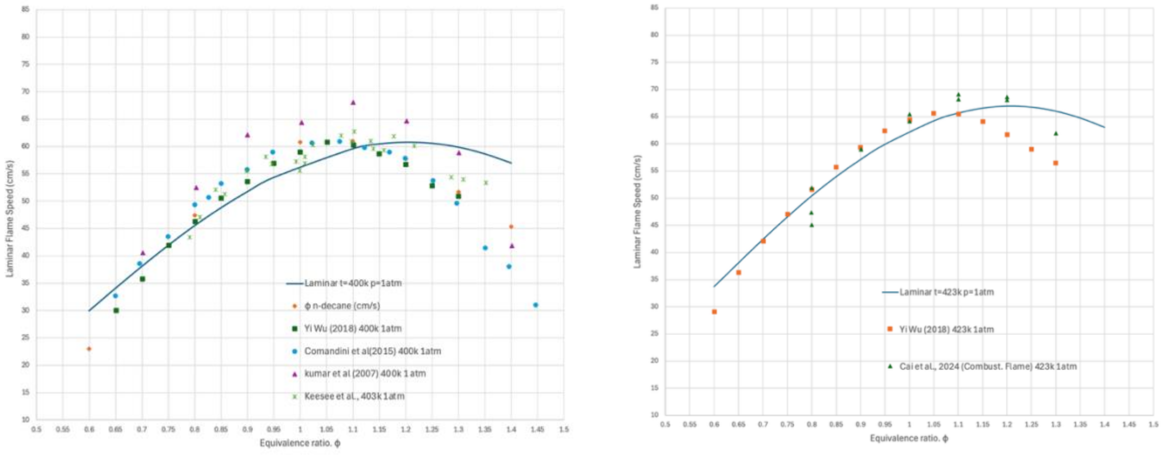


(a) (b)

**Figure 4.18 - Comparison of simulated LLNL mechanism predictions with experimental data for laminar flame speeds at 450 K under – (a) 75 kPa and (b) 100 kPa**

### 4.2.2 Single-component Surrogates

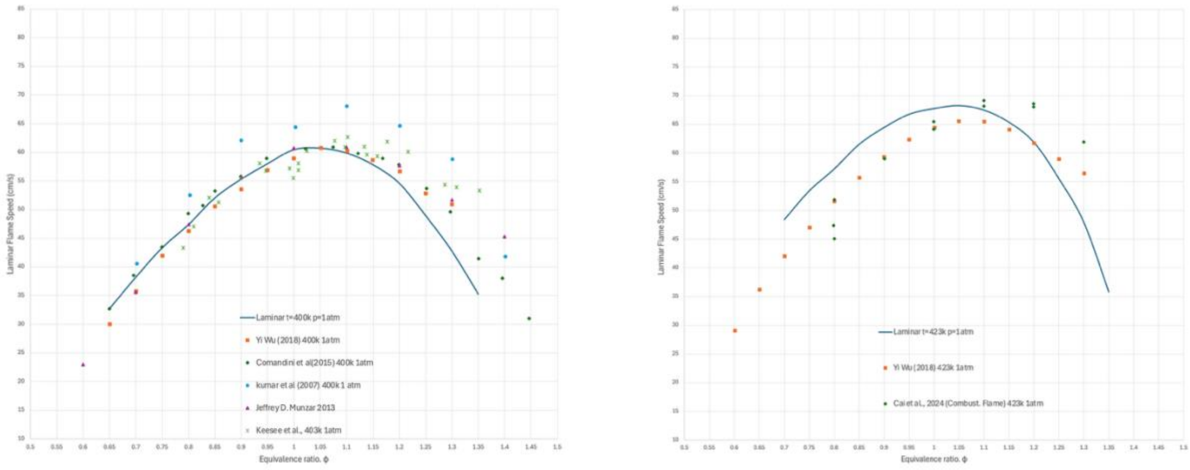
For the newly developed global mechanism of n-decane, model predictions at 400 K and 423 K under 1 atm exhibited good qualitative agreement with experimental observations, successfully reproducing both overall trend and the location of the peak laminar burning velocities. Nonetheless, systematic discrepancies were identified. In lean mixtures ($\Phi < 1$), the mechanism consistently underestimated flame propagation speeds relative to experimental data, whereas in rich mixtures ($\Phi > 1$), it tended to overestimate, sustaining higher flame speeds even as experimental values declined more sharply. These deviations indicate that, although the mechanism captures the fundamental flame behavior, further refinement is required – particularly to improve representation of low-temperature chain-branching processes in lean regimes and termination pathways under fuel-rich conditions.



(a) (b)

**Figure 4.19 - Comparison of simulated novel global n-decane mechanism predictions with experimental data for laminar flame speeds at 1 atm – (a) 400 K and (b) 423 K**

For the JetSurf 2.0 mechanism applied to n-decane at 400 and 423 K under 1 atm, the model exhibited generally good agreement with experimental data in the vicinity of stochiometric conditions, where peak laminar burning velocities were accurately reproduced. In the lean regime ($\Phi < 1$), the mechanism tended to underpredict flame propagation speeds, although the predicted variation with equivalence ratio remained consistent with experimental trends. In the rich regime ($\Phi > 1$), the model initially captured the observed decay but progressively deviated beyond $\Phi \sim 1.15$, where simulated velocities decreased more rapidly than those measured. Taken as a whole, JetSurF 2.0 was able to qualitatively reproduce the flame characteristics but slowed a systematic tendency to slightly underestimate laminar flame speeds in both lean and rich mixtures, with highest predictive accuracy observed near stoichiometry



(a) (b)

**Figure 4.20 - Comparison of simulated JetSurF 2.0 for n-decane mechanism predictions with experimental data for laminar flame speeds at 1 atm – (a) 400 K and (b) 423 K**

For pure n-heptane at 400 K and 1 atm, simulations conducted using the CRECK mechanism demonstrated good qualitative agreement with experimental observations; however, the model consistently underestimated the laminar burning velocities reported in the literature. Under lean conditions ($\Phi < 1$), the predictions fell below the measurements of Kumar et al. (2004) and Chong (2011, Cambridge/Hochgreb group), with the largest deviations occurring in the range $\Phi \sim 0.7$-$0.9$. At stoichiometry ($\Phi \sim 1.0$), the model successfully reproduced the location of the velocity maximum but slightly underestimated its magnitude. Predicting ~ 63 cm/s in comparison with the 67-70 cm/s measured experimentally. On the rich side ($\Phi > 1$), the trends of underprediction persisted and became more pronounced t higher equivalence ratios, as the model predicted a steeper decline in flame speed than that observed experimentally. Overall, while the CRECK mechanism captured the qualitative shape of the laminar flame speed profile for n-heptane, it systematically underpredicted across lean, stochiometric, and rich regimes

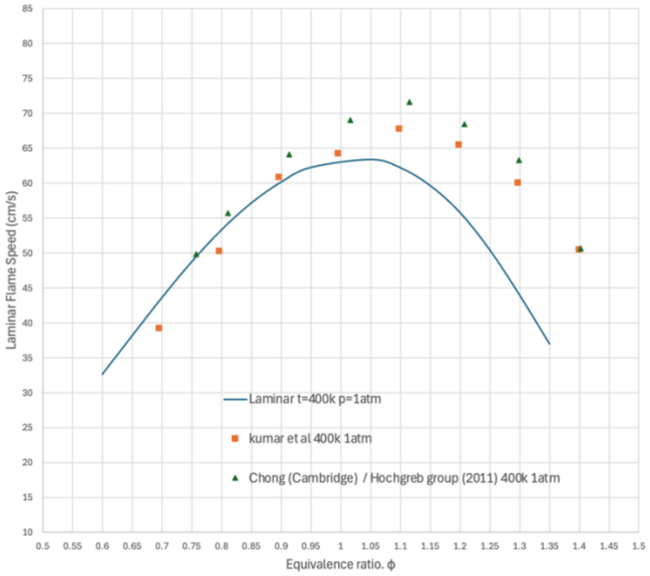
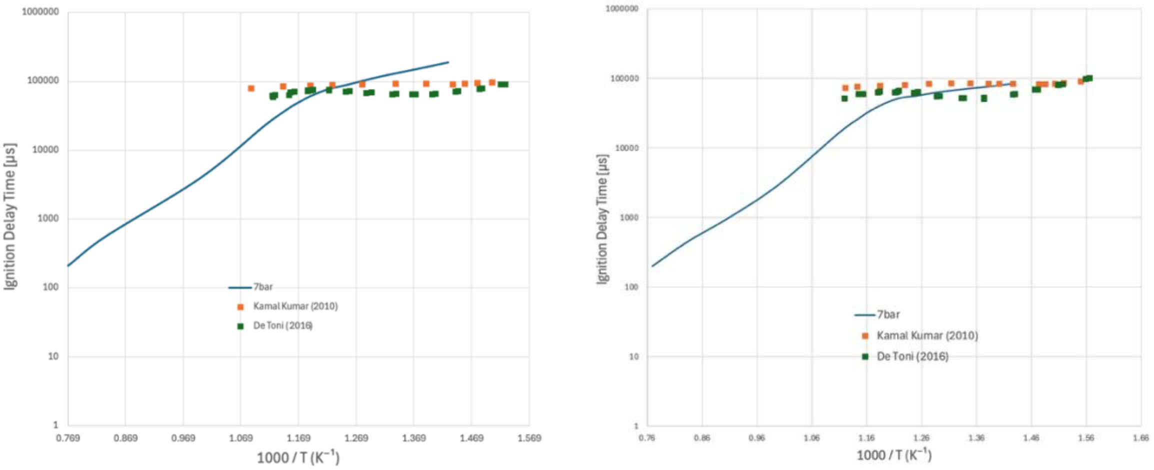


**Figure 4.21 - Comparison of simulated CRECK mechanism for n-heptane mechanism predictions with experimental data for laminar flame speeds at 400 K, 1 atm**

## 4.3 Ignition Delay Time

Ignition delay times (IDT) were simulated using the five-component surrogate mechanism across pressures 7, 15, and 20 bar for equivalence ratios of $\Phi = 0.7$, 1.0 and 1.3. The simulation results were systematically compared against available experimental measurements by presenting ignition delay as the logarithm of IDT versus the reciprocal of temperature (1000/T). This approach enables a clear distinction between low- and high- temperature reactivity regimes and facilities direct assessment of model fidelity.

At 7 bars, the mechanism successfully captures the Arrhenius-like decrease of ignition delay with increasing temperature, but the mixture-dependent bias is observed. For the lean case ($\Phi = 0.7$), the model over-predicts ignition delays at the cold end, indicating an under-reactive tendency, though the deviation decreases as temperature increases. For the stochiometric case ($\Phi = 1.0$), the model shows a slight agreement with the experimental data, with deviations as well – slightly longer delays at low temperatures and marginally shorter delays at high temperature. For rich case ($\Phi = 1.3$), the model exhibits a crossover behavior: it predicts shorter ignition delays (too reactive) at the hot end, underpredicts with mid-temperature region, and slightly overpredicting at lower temperature, which shows the mechanisms strongest reliability near stochiometric conditions.



(a) (b)

**Figure 4.22 - Comparison of simulated ignition delay times using the five-component surrogate mechanism with experimental data at 7 bar (a) Φ = 0.7 (b) Φ =1.0**

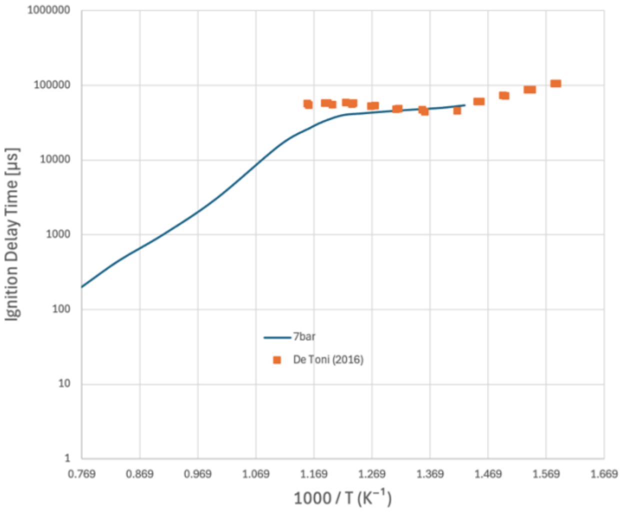
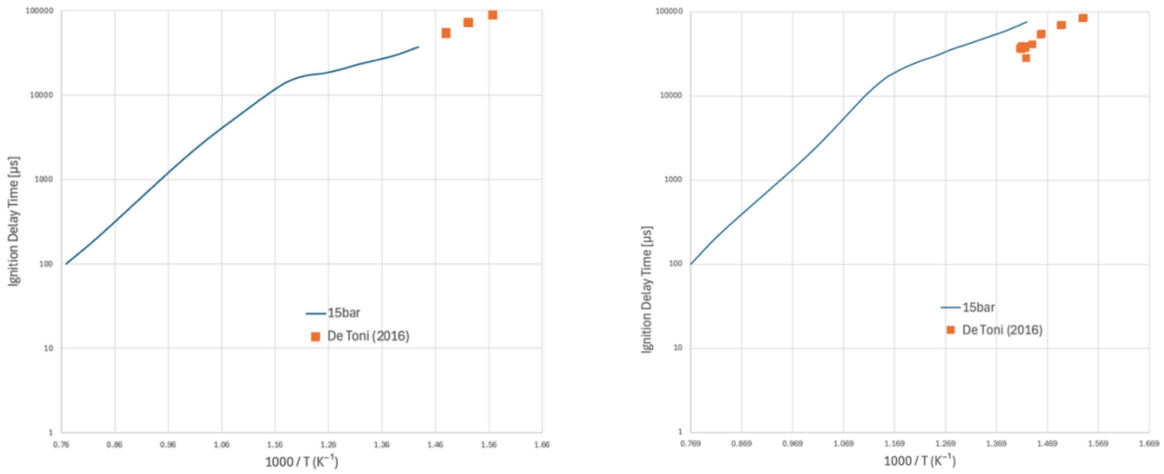


**Figure 4.23 - Comparison of simulated ignition delay times using the five-component surrogate mechanism with experimental data at 7 bar for Φ = 1.3**

At 15 bars, at the stochiometric (Φ = 1.0), the mechanism predicts ignition delays that are systematically shorter than experimental measurements, indicating too-reactive response across full temperature range. Conversely, for the lean case (Φ = 0.7), the model remains under-reactive, consistently over-predicting ignition delays by roughly a factor of 1.2-2* relative to experimental data. This highlights a sensitivity of the mechanism to pressure effects in lean combustion regimes.



(a) (b)

**Figure 4.24 - Comparison of simulated ignition delay times using the five-component surrogate mechanism with experimental data at 15 bar for (a) Φ = 1.0 (b) Φ = 0.7**

At 20 bars, the mechanism again captures the overall temperature dependence but displays a temperature-dependent crossover bias. At the hot end, it predicts longer ignition delays than measured, suggesting under-reactivity. In the intermediate temperature window (~1.05-1.15 $K^{-1}$), the trends reverse, with the mechanism under-predicting ignition delays, behaving too reactively relative to experimental data. At cold end, the model again over-predicts, showing slow→fast→slow behavior as temperature decreases. This indicates that while the mechanism correctly follows the overall slope, but it exaggerates the steepness of temperature dependence under high pressure conditions.

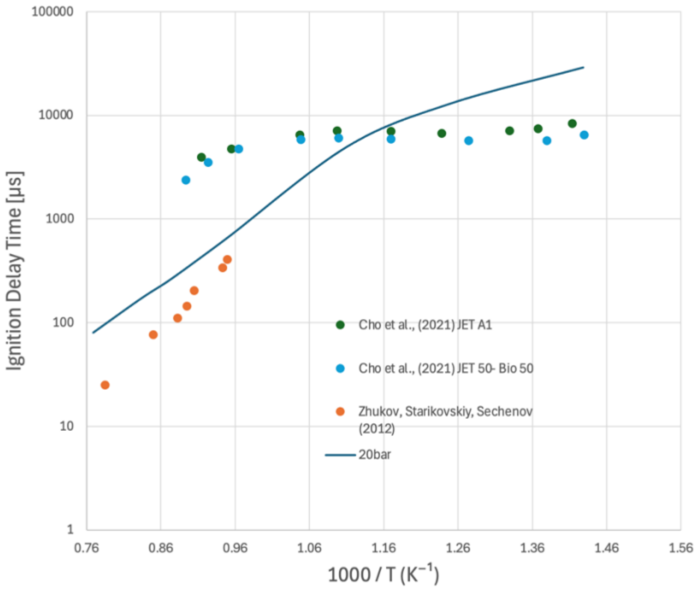


**Figure 4.25 - Comparison of simulated ignition delay times using the five-component surrogate mechanism with experimental data at 20 bar for Φ = 1.0**

In summary, the five-component mechanism captures the global Arrhenius trends of IDT but demonstrates mixture- and pressure-dependent biases. It performs adequately at the stochiometric condition, while deviations grow at higher pressures and lean mixture. This gives qualitative description of the models.

# 5. DISCUSSION

## 5.1 Multi-component Surrogates (Laminar Flame Speed) Evaluation

Multi-component surrogate mechanisms provide a more faithful representation of kerosene combustion than single-component models, as they incorporate the combined chemical contributions of alkanes, aromatics, and other hydrocarbon species. In this work, three detailed surrogates were systematically evaluated: the five-component surrogate of Yang and Zhen (2019), the CRECK mechanism of Ranzi et al. (2014), and the LLNL mechanism of Mehl eta al. (2011). Their predictive capabilities were assessed by comparing LFS simulations against experimental datasets across a range of pressures and temperatures. Quantitative evaluation employed average percent deviation (APD) and root-mean-square error (RMSE).

At atmospheric pressure (1 atm, 400-473K), the CRECK mechanism exhibited the highest fidelity, with pooled errors of APD ~ 5.24% and RMSE ~ 4.73 cm/s (N = 169). By comparison, the LLNL and five-component surrogates demonstrated larger deviations (APD ~ 9.03% and 15.10%, RMSE ~ 6.50 and 9.82 cm/s, N = 173, respectively. This ranking was consistent with qualitative observations: both LLNL and 5-component models tended to underpredict flame speeds under atmospheric conditions, particularly on the lean side ($\Phi < 0.9$), whereas CRECK more accurately reproduced the curvature and magnitude of the experimental trends. Consequently, CRECK is confirmed as the most reliable surrogate for the atmospheric kerosene combustions simulations.

At reduced pressure (0.5 atm, 400-480 K), however, the relative performance shifted. Here, the 5-component surrogate delivered the most accurate predictions, achieving APD ~ 4.67% and RMSE ~ 3.42 cm/s (N = 51), while CRECK and LLNL produced significantly higher deviations (APD ~ 12.57% and 12.27%, RMSE ~ 8.49 and 8.46 cm/s, respectively). The 5-component surrogate not only captured the stochiometric peak but also reproduced lean and rich behavior across all temperatures tested. By contrast, both CRECK and LLNL systematically overpredicted flame speeds, especially near $\Phi \sim 1.0$-1.2, with deviations increasing at higher temperatures. These findings identify the 5-component mechanism as the most appropriate surrogate for laboratory-scale, low-pressure combustion studies.

Further analysis of pressure effects at 450 K across 25-100 kPa reinforced this conclusion. The 5-component mechanism consistently produced the lowest pooled errors (APD ~ 1.86%, RMSE ~ 1.66 cm/s, N = 50). At 25 and 50 kPa, it achieved near -perfect agreement with experimental values (APD ~ 0.07%, RMSE ~ 0.07 cm/s at 50 kPa), whereas CRECK and LLNL significantly overpredicted LFS (APD ~ 11-14%). At higher pressures (75-100 kPa), CRECK and LLNL improved substantially (APD ~ 3.5-4.3%, RMSE ~ 2.6-3.1 cm/s), approaching but not surpassing the accuracy of the 5-component surrogate. Importantly, the 5-component model also reproduced the correct pressure dependence of flame speed curvature, underscoring its robustness in sub-atmospheric regimes.

Taken together, these results establish a pressure-dependent hierarchy of mechanism performance. At atmospheric pressure, CRECK is the most accurate surrogate due to its superior ability to reproduce both the flame speed peak and overall profile. At sub-atmospheric (0.5 atm, 25-100 kPa), the 5-component mechanism clearly dominates, yielding the smallest deviations across equivalence ratios. The LLNL mechanism consistently exhibits intermediate accuracy - aligning more closely with CRECK at 1 atm and with 5-component surrogate at reduced pressure – yet never emerging as the optimal under any tested conditions.

In conclusion, while all multi-component surrogates outperform single-component representations of kerosene, their relative accuracy is strongly dependent on pressure. CRECK is the most reliable surrogate for practical gas turbine conditions near atmospheric pressure, whereas the 5-component is preferable for low-pressure laboratory flames and studies of ignition and propagation under sub-atmospheric conditions. LLNL remains useful as an intermediate mechanism but does not achieve best-in-class performance in either regime. These findings highlight the necessity of benchmarking surrogate mechanisms across diverse operating conditions to ensure reliable and transferable kinetic models for aviation fuel applications.

## 5.2 Single-component Surrogates (Laminar Flame Speed) Evaluation

Single-component surrogate fuels remain indispensable in chemical kinetic investigations, as they enable mechanistic validation under controlled conditions while preserving relevance to kerosene-like combustion systems. In the present study, n-decane and n-heptane were systematically evaluated at 1 atm against multiple experimental datasets. Model fidelity was qualified was quantified through the average percent deviation (APD) and root-mean-square error (RMSE), with simulated laminar flame speeds interpolated to experimental equivalence-ratio (Φ) points for direct comparison.

For n-decane, two widely used mechanisms were examined: the Novel Global mechanism and JetSurF 2.0. At 400 K, JetSurF 2.0 demonstrated superior agreement with experiments (APD ~ 7.91%, RMSE ~ 5.39 cm/s) compared to Novel Global (APD ~ 9.11%, RMSE ~ 6.19 cm/s). The largest discrepancies occurred relative to the Comandini et al. (2015) dataset, while closer alignment was observed with Wu (2018). At 423 K, however, the ranking reversed. The Novel Global mechanism outperformed JetSurF 2.0 (APD ~ 5.25%, RMSE ~ 3.57 cm/s vs APD ~ 6.13%, RMSE ~ 5.01 cm/s), particularly in reproducing both the peak magnitude and curvature of LFS profile, consistent with the recent Cai et al. (2024) measurements. When results were aggregated across both temperatures, differences between mechanisms were minimal: JetSurF 2.0 yielded a slightly lower overall APD (~7.12%), while Novel Global achieved a marginally lower RMSE (~5.13 cm/s). These findings suggest that the choice of mechanism should be guided by the operating regime and research objectives - JetSurF 2.0 is preferable at lower temperatures or when relative error minimization is prioritized, whereas Novel Global is better suited for higher temperatures or when accurate reproduction of flame speed magnitudes is critical. Importantly, residual errors were comparable to inter-experimental scatter, emphasizing the necessity of using multiple datasets for surrogate validation.

For n-heptane, the CRECK mechanism was assessed at 400 K and 1 atm. Across all datasets, it produced an APD of ~ 10.68% and RMSE of ~ 8.84 cm/s (N = 14). Performance improved somewhat against the Kumar et al. dataset (APD ~ 9.70%, RMSE ~7.51 cm/s) but worsened against the Cambridge dataset of Chong and Hochgreb (2011) (APD ~ 11.66%, RMSE ~9.99 cm/s). Consistent with the laminar flame speed profiles, the CRECK model captured the general lean-to-stochiometric rise but systematically underpredicted peak values and exhibited and overly rapid decline under rich conditions. This produced discrepancies on the order of 8-10 cm/s across the evaluated Φ range. While larger than the errors seen for n-decane, these deviations still fall within experimental scatter envelope.

In summary, single-component evaluations confirm that existing mechanisms reproduce the qualitative trends of n-decane and n-heptane flames but retain systematic quantitative biases. For n-decane, JetSurF 2.0 and Novel Global exhibit complementary strengths, with accuracy dependent on temperature regime. For n-heptane, CRECK mechanism consistently underpredicts flame speeds across equivalence ratios. Collectively, these findings highlight both the utility and the limitations of single-component surrogates in representing kerosene combustion and reinforce the need for multi-component surrogate formulations to achieve robust predictive capability in practical simulations.

## 5.3 Ignition Delay Time Evaluation

The predictive performance of the five-component mechanism for ignition delay times was evaluated against the experimental datasets at 7, 15 and 20 bar, using the equivalence ratios Φ = 0.7 (lean), Φ = 1.0 (stochiometric), and Φ = 1.3 (rich) where applicable. Model predictions were interpolated to experimental temperature points, and deviations were quantified using average percent deviation and root-mean-square error in milliseconds.

At 7 bars, the mechanism reproduces the overall Arrhenius-type decrease of IDT with increasing temperature but shows strong mixture-dependent biases.

- For Φ = 0.7, the model over-predicts IDTs significantly (APD ~ 57.15%, RMSE ~ 48.59 ms), indicating it is too slow to ignite at lean conditions.
- For Φ = 1.0, agreement improves considerably (APD ~ 32.37%, RMSE ~ 24.45 ms), with only minor deviations.
- For Φ = 1.3, the mechanism slightly underpredicts delays (APD ~ 25.35%, RMSE ~ 16.72 ms), showing it becomes too reactive on rich side.

Pooled across all three conditions, the average deviation APD ~ 39.14%, RMSE ~ 33.48 ms, confirming that lean mixtures are the most challenging to capture accurately at this pressure.

At 15 bar, quantitative evaluation is limited due to restricted temperature overlap. For Φ = 0.7, the model over-predicts ignition delay times by roughly a factor of two (APD ~ 104.69%, RMSE ~ 37.26 ms) in the available range 700-770 K range. For Φ = 1.0, no meaningful comparison can be made because simulation data begin above 700 K, beyond the experimental range. Additional overlapping data would enable a more complete evaluation here.

At 20 bar for Φ = 1.0, the model captures the qualitative trend but systematically over-predicts delays (APD ~ 110.66%, RMSE ~ 9.18 ms), implying under-reactivity at high pressures. The largest deviations occur in low-temperature regime (700-900 K), where experimental delays are shorter, while agreement improves at high temperatures (≥1100 K). Overall, it shows adequate performance at stoichiometry (7 bar) and over-predicts delays at lean conditions and low temperature and under-reactivity at high pressure (20 bar), less suitable at high altitudes.

# 6. CONCLUSIONS AND FUTURE WORK

## 6.1 Conclusions

This thesis evaluated detailed chemical-kinetic mechanisms for kerosene surrogate fuels using ANSYS Chemkin-Pro, validating predictions against experimental measurements of laminar flame speed and ignition delay time. For multi-component surrogates, the CRECK mechanism [1] most closely reproduced LFS at 1atm (lowest pooled ADP/RMSE), whereas the five-component surrogate [2] performed best under sub-atmospheric pressures (0.5 atm and 25-100 kPa at 450 K). The LLNL mechanism [3] exhibited intermediate behavior: showing improved agreement at 100 kPa but not outperforming CRECK or five-component mechanism in any specific regime.

For single-component surrogates, n-decane exhibited temperature-dependent behavior: JetSurF 2.0 [4] performed better at 400 K, while novel global mechanism [5] showed superior agreement at 423 K. For n-heptane, the CRECK mechanism [1] consistently under-predicted laminar flame speeds at 400 K and 1 atm.

For ignition delay times, assessed using the five-component mechanism [2] at 7-20 bar, the model captured the general Arrhenius decrease of IDT with temperature but exhibited mixture- and pressure-dependent biases: at 7 bar, the mechanism over-predicted IDT for lean mixtures ($\Phi = 0.7$), slightly matched stochiometric conditions closely, and under-predicted IDT for rich mixtures ($\Phi = 1.3$). At 15 bar, $\Phi = 0.7$, the models overpredicts IDT near 700 K by approximately a factor of two, while $\Phi = 1.0$, comparison is currently limited due to insufficient temperature overlap between simulations and experimental data. Whereas, at 20 bar and $\Phi = 1.0$, the model significantly over-predicted IDT at lower temperatures, improving little at higher temperatures.

Overall, the results demonstrate that mechanism selection should depend strongly on the target pressure regime. While the five-component mechanism offers the most performance under sub0atmospheric and moderate pressures, its predictive accuracy deteriorates at higher pressures, where further refinement is necessary.

## 6.2 Integrated Recommendations and Future Directions

Based on the findings, several practical guidelines and future work priorities are proposed to improve surrogate fuel modeling and mechanism reliability. Mechanism selection should be based on the operating regime. The CRECK mechanism [1] is most suitable near 1 atm for lab-scale or ground-level applications, while the five-component mechanism [2] is preferred under sub-atmospheric pressures, such as altitude-relevant studies. The LLNL mechanism [3] is useful when emphasizing low-temperature chemistry, though its predictive performance remains moderate elsewhere. To enhance overall mechanism reliability, future work should focus on mechanism refinement and validation.

Sensitivity analysis using Chemkin-Pro should be conducted to identify the most influential reactions for both laminar flame speed and ignition delay time predictions, prioritizing chain-branching pathways (H + $O_2$ ⇔ O + OH), low temperature R$O_2$ ⇔ QOOH isomerization's, and $H_2O_2$ decomposition, with contributions visualized via Pareto charts [10,11].

Uncertainty quantifications (UQ) using Monte Carlo or Bayesian methods can propagate uncertainties in Arrhenius parameters (A, n, Ea) and generate robust prediction intervals, with cross-validation at unseen T, P and Φ conditions [12,13]. Furthermore, pressure-dependent kinetics should be reassessed, particularly Troe fall-off curves and third-body efficiencies, replacing defaults with surrogate-specific parameters to improve accuracy at 15-20 bar [1,3].

Improving surrogate fidelity is also critical; future kerosene surrogates should match the H/C ratio, distillation curve, density, and aromatic fraction of real Jet-A or SAF batches [8,9,15].

Additionally, extended IDT validation should address data gaps at all pressures and temperatures. For computational efficiency, mechanism reduction techniques such as DRGEP or QSSA can be applied to create skeletal mechanisms optimized for CFD simulations while maintaining predictive accuracy [17,18]. Finally, thermodynamic and transport properties should be carefully validated by re-examining NASA polynomials for radicals and intermediates and ensuring consistency across mechanisms, especially under lean flame conditions where diffusion effects dominate [4,14]. By combining sensitivity analysis, uncertainty quantification and out-of-sample validation, future mechanisms can be systematically refined, ensuring that any added or tuned reactions are physically justified and remain robust across wide range of realistic operating conditions [12,19,20].

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# Project Management

# Self-Review

This project has been an invaluable learning experience that significantly enhanced my understanding of combustion kinetics, chemical mechanisms, and simulation methodologies. At the outset, I faced several challenges, particularly working with multiple surrogate mechanisms and integrating experimental data with computational results. Through consistent effort and guidance from my supervisor, I developed a structed workflow for validating the mechanisms against lamina flame speed and ignition delay time datasets, which improved both my technical skills and problem-solving ability.

One of the key challenges was managing the discrepancies between experimental and simulated results, especially across varying pressures and equivalence ratios. Overcoming this required a deeper understanding of chemical kinetics, as the process of comparing multiple mechanisms, such as CRECK, LLNL, JetSurF 2.0, and the five-component surrogate, improved my ability to critically evaluate model performance under different operating regimes. Additionally, this project helped me strengthen my computational skills, particularly with CHEMKIN-Pro and data analysis techniques. I also learned the importance of systematically validating models against diverse datasets to ensure reliability and robustness in practical applications.

Looking back, while the project posed several challenges, it significantly my research capabilities and technical competence. If I were to continue this work, I would explore advanced sensitivity studies and surrogate optimization to further refine the predictive accuracy. Overall, this project has been both demanding and rewarding, providing me with skills and insights that will be valuable in future academic and professional endevors.