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Machine Learned Compact Kinetic Models for Combustion

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Doctor of Philosophy

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Declaration

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Summary

Chemical kinetic models are an essential component in the development and optimisation of combustion devices through their coupling to multi-dimensional simulations such as computational fluid dynamics (CFD). Due to the significant level of detail contained within, detailed chemical kinetic models are computationally prohibitive for use in CFD. Therefore, minimally-sized kinetic models which retain good fidelity to the reality are needed, the production of which requires considerable human-time cost and expert knowledge.

In this thesis the concept of Compact Models is introduced. This concept overcomes the kinetic model detail-fidelity coupling as it describes the reaction mechanism virtually rather than retaining a physical authenticity in the reaction mechanism description. This allows for the numerical optimisation of model parameters to accurately replicate a set of combustion calculations without the constraint of maintaining a physical authenticity in the reaction mechanism description. A novel automated compute intensification algorithm called *Machine Learned Optimisation of Chemical Kinetics* (MLOCK) is constructed to produce compact models, removing the constraint of expert knowledge.

The first step in the production of a compact model (“compaction”) is the construction of a virtual reaction network. This is a network of nodes (virtual species) connected to each other by connections (virtual reactions). The strength of the connections (virtual reaction rate constants) are numerically optimised using the MLOCK algorithm. MLOCK simultaneously perturbs all three virtual Arrhenius reaction rate constant parameters of important connections and assesses the suitability of the new parameters through objective error functions, which quantify the error in the calculations of each model candidate to a set of optimisation targets. In this thesis, compact models are developed for three combustion systems in response to an Industry brief. The aim is to provide a model that is efficient and accurate to a set of calculations pertinent to the gas turbine design process.

The MLOCK methodology is first applied to the archetypal methane combustion system. Virtual reaction networks are constructed through application of conventional model reduction algorithms, followed by optimisation of sensitive virtual Arrhenius parameters using *MLOCK1.0*. It is shown that the *NUGMECH1.0* detailed model, comprised of 2,789

species, is reliably compacted to fifteen nodes, whilst retaining an overall fidelity of 79-90% to the detailed model at Industry-defined performance target calculations, outperforming the prior state-of-art models. Additionally, the 118-species *NUIG1817C3* detailed model is compacted to produce a fifteen and nineteen-node compact model with an overall fidelity of 75.0 – 83.9% and 93.6 – 95.0% respectively.

The MLOCK methodology is then applied to the task of NO_x formation. A virtual reaction network comprised of three nodes (N, NO and NO₂) is constructed using a combinatorial method, and is appended to the fifteen-node model for methane/air combustion. *MLOCK1.1* is applied to find the optimal set of virtual Arrhenius parameters for these NO_x connections. A state-of-art eighteen-node compact model is produced with a fidelity of 89.5% to NUIGMECH1.0 perfectly stirred reactor (PSR) calculations of NO_x. Although, for flame calculations, it was found that it is not possible to find one model of over 57% fidelity across the entire industry-defined performance envelope using a three-node NO_x network.

Finally, the MLOCK methodology is applied to the task of liquid fuels. A step-by-step generalised methodology that allows for the creation of a compact model for a liquid fuel was developed and demonstrated for the case of Arabian Extra Light (AXL) crude oil, at the behest of Siemens Energy. This led to the creation of a thirty-five-node compact model with fidelities of 79.6 – 89.1% to the 6,476 species detailed model at the Industry-defined set of performance conditions for high temperature combustion. The method was then extended to the task of low temperature chemistry. A virtual reaction network for low temperatures was created and the virtual bin scheme was simplified. *MLOCK1.2* was used to find the optimal set of virtual Arrhenius parameters for sensitive connections. This led to the creation of a thirty-two-node compact model with a high S_u fidelity at lean conditions and a high fidelity to detailed model 0-D calculations across the complete performance envelope.

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Chapter 1

Introduction

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1.1 Global Energy Outlook

The battle against global warming is one of the most pressing challenges facing humanity today. Global warming refers to the long-term trend of rising average global temperatures, which is primarily caused by the increase in greenhouse gases (GHGs) in the Earth's atmosphere. These gases, such as carbon dioxide (CO₂), methane (CH₄), nitrous oxide (N₂O), and water vapor (H₂O), trap thermal energy from the Sun, leading to an increase in surface temperature. Human activities, such as the burning of fossil fuels, deforestation, and agricultural practices, have significantly increased the concentration of GHGs in the atmosphere, exacerbating the natural greenhouse effect and causing global warming. The continued increase of GHG emissions poses a significant threat to the planet, resulting in more frequent and severe weather events, rising sea levels, and ecosystem disruption. As such, it is vital to take immediate and significant action to reduce GHG emissions and mitigate the impacts of global warming.

In recent years, there has been a surge in efforts to mitigate emissions and transition towards a sustainable energy system, as the world tackles the monumental challenge of displacing fossil fuels with renewable or carbon-neutral sources. This historic shift in energy generation demands a mix of incentivising measures, including financial support for

renewable energy projects, and penalties for high-emission activities. The Paris Agreement, among other international agreements, has established goals to restrict the rise in global temperatures to below 2°C requiring net-zero, followed by net-negative (i.e., carbon capture) carbon emissions in the latter half of the century. The European Union (EU) has committed to achieving carbon neutrality by 2050, a commendable but formidable objective. The transition to renewable energy sources has seen some progress in terms of the recent growth in carbon-neutral technologies, as shown in Figure 1.1, but much more needs to be done. Achieving such a transformation necessitates a united global effort to move society's energy sources away from fossil fuels and towards renewables within the next 30 years. This shift must include financial incentives and assistance to developing countries that may encounter obstacles in transitioning away from cheaper fossil fuels.

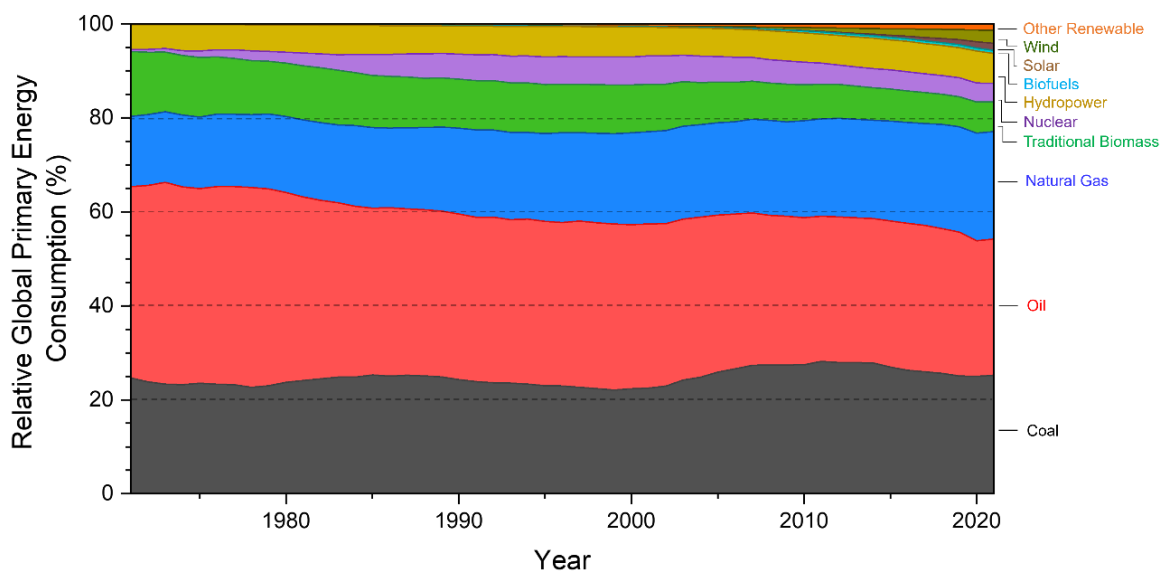


Figure 1.1. Global primary energy consumption by source from 1971-2021. Data from BP [1] and Smil [2].

Figure 1.2 shows the global CO₂ energy-related emissions in the year 2021. Energy-related CO₂ emissions account for around 89% of total greenhouse gas emissions [3]. Although considerable progress has been made in the electrification of road transportation, which is responsible for around 17% of energy-related CO₂ emissions, there are several sectors, such as heavy industry, shipping, and aviation, that are unlikely to be electrified in the near future.

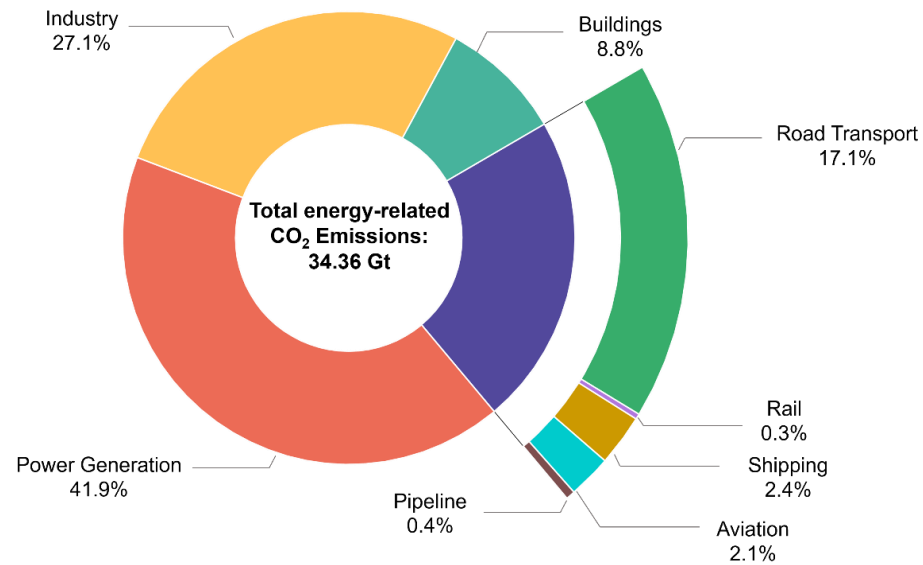


Figure 1.2 Global energy-related CO₂ emissions in 2021. Data from the International Energy Agency [4].

This is particularly challenging for the aviation sector, which accounts for 2.1% of energy-related CO₂ emissions and is projected to increase further due to the annual growth in the number of passengers. The requirements for electrification of aircraft are much more demanding than road transportation. Jet fuel, which accounts for approximately 45% of an aircraft's mass, has an energy density of around 45 MJ/kg. In contrast, lithium batteries have an energy density of only 0.7 MJ/kg. As the mass of the fuel is a critical factor that significantly impacts an aircraft's range, it is evident that a significant advancement in battery technology is required to power even short-haul commercial aircraft. In addition, battery-powered aircraft require rapid-charging infrastructure and airport facilities that can match the tight schedules of commercial airlines. Although hydrogen combustion is a potential long-term solution, significant advancements in technology are needed to ensure its safe containment and utilisation in aircraft, as such it is not expected to be a viable solution in the near-term. An attractive solution, therefore, is the use of sustainable aviation fuel (SAF), which is an advanced biofuel drop-in replacement for conventional fossil jet fuel. These fuels are physically and chemically identical to fossil jet fuel, exhibiting the same combustion behaviour and requiring no modifications to existing infrastructure.

From this short overview, it is clear to see that combustion will continue to play a leading role in the medium term as a fuel conversion technology. Therefore, it is essential to

maximise the power-emission efficiency of combustion devices to minimise the release of greenhouse gases. Gas turbines are the most widely adopted combustion device. Gas turbines operate by drawing in ambient air and compressing it to high pressures. The compressed air is then mixed with fuel, and the resulting mixture undergoes combustion, releasing its stored chemical potential energy as thermal energy. The hot gas mixture flows through the turbine, where it expands and drives the rotation of the turbine blades. This rotation of the blades converts the thermal energy of the hot gas into mechanical energy, which can be harnessed to drive a generator and produce electrical power.

Gas turbines are used in a range of applications, including power generation, aviation, and industrial processes. Gas turbines are poised to play a leading role in the future of power generation due to their flexibility in fuel type and high efficiency. As the world transitions to cleaner energy sources, the use of alternative fuels such as ammonia, hydrogen, SAF, and biomethane is expected to increase. Gas turbines have the ability to burn these fuels and produce electricity with high efficiency and low emissions. Additionally, natural gas is likely to remain a significant energy source for years to come, with gas turbines being the primary technology used to convert natural gas to electricity. As gas turbines are expected to remain a significant component of the global energy mix in the coming years, it is crucial to continue advancing gas turbine technology to enhance power generation efficiency and reduce emissions. The quality of combustion can be influenced by various factors, including fuel-to-air mixing, turbulence, and combustion chamber geometry. Poor combustion can result in increased emissions, decreased fuel efficiency, and reduced performance. Hence, it is crucial to study the effect of these variables to optimise gas turbine devices.

1.2 Numerical Combustion

Numerical combustion refers to the use of mathematical models and simulations to study and understand the combustion process. The study of combustion is critical for many industrial and household applications ranging from power generation to fire forensics. With the ever-increasing demand for more efficient energy and transport systems, numerical combustion provides a powerful tool in the development and optimisation of combustion devices.

Gas turbine engineers utilise reactive turbulent flow computer simulations, such as computational fluid dynamics (CFD) simulations, as essential tools in the combustor design process. These simulations accurately capture the dynamic thermophysical and thermodynamic properties of the fuel-air mixture as it undergoes combustion within the reactor. Given the high-pressure and high-temperature operating conditions of gas turbines, such computer simulations offer a faster and more cost-effective alternative to physical experiments.

To ensure reliability of simulation results, an accurate description of the pertinent chemistry occurring inside the combustor is required. This is provided in the form of a chemical kinetic model. A chemical kinetic model is a mathematical representation of the chemical reaction mechanism of a specific fuel. These models contain information on the thermodynamic properties of each chemical species that participate in the reaction mechanism, as well as inputs to compute the rate at which each reaction proceeds as a function of the local thermodynamic environment of the mixture. By employing reactive turbulent flow computer simulations coupled with accurate chemical kinetic models, gas turbine engineers can gain valuable insights into the combustion process occurring within a gas turbine of a certain geometry under a set of operating (pressure, temperature, fuel mixture composition) conditions. The ability to analyse the effect of operating conditions and reactor geometry on pollutant formation, as well as temperature and pressure gradients within the combustor, allows for targeted design modifications or operational optimisation, resulting in gas turbine engines of improved power-emission efficiencies.

Despite humanity's long reliance on combustion as a source of energy, the complexity of the phenomena means that a detailed understanding of reaction mechanisms only exists for a small number of fuels. Constructing an accurate description of a fuel's combustion behaviour requires many years of theory development stemming from careful physical and computational experiments. The complexity of combustion is due to the simultaneous occurrence of multiple physical and chemical processes. Therefore, a comprehensive understanding and modelling of combustion requires expertise in chemistry, physics, thermodynamics, engineering, fluid dynamics, computer science, and mathematics, making it the ultimate interdisciplinary field [5].

1.3 Thesis Objectives

To facilitate the efficient integration of kinetic models into high-repetition CFD simulations, the level of detail in the kinetic model must be minimised. Therefore, due to the considerable levels of detail contained within, kinetic models that describe the reaction mechanism at a fundamental level are not viable for this purpose. Consequently, kinetic models that are typically used by Industry provide a simplified description of the reaction mechanism. These models tend to only be valid for calculating specific macroscopic properties at very narrow operating conditions and require expert knowledge to construct. Hence, to enable high-fidelity simulations of combustion in realistic gas turbine geometries, kinetic models are required that accurately capture key combustion phenomena at the large range of operating conditions of interest, while also being computationally tractable in high-resolution CFD simulations, such as large eddy simulations (LES). To achieve this, kinetic models that provide a virtual description of the reaction mechanism, rather than a simplified version that attempts to retain some form of physical authenticity, are developed.

The objective of this thesis is to devise an automated methodology that facilitates the development of minimally-sized CFD-ready kinetic models, exploiting modern high-performance computing facilities. These models must maintain a high level of fidelity to a comprehensive set of calculations that our industry partner, Siemens Energy, has identified as essential for their gas turbine design endeavours. To abide by the FAIR [6] principles of data science, the models must be interoperable, meaning they can be readily used with current software infrastructure. This means that the kinetic models must retain the ChemKin [7] format. Additionally, the methodologies produced should be suitably general such that they can be used for a range of different fuels.

1.3.1 Thesis Structure

In this thesis, the concept of Compact Models is proposed as a promising approach to address this challenge. Compact Models are virtual constructs that aim to reproduce the relevant detailed combustion behaviour, allowing the model to maintain a high level of accuracy in a specific set of calculations. Reframing the problem in a data science perspective removes the constraint of physical authenticity, allowing for the creation of high-fidelity models that are compact in size and easily implementable in industry-standard software. A novel

compute-intensification algorithm, termed *Machine Learned Optimisation of Chemical Kinetics (MLOCK)*, is developed to optimise model parameters to a set of calculations to ensure high model fidelity to Industry-defined performance calculations.

Chapter 1: Thesis Context

This Chapter provides an overview of the current global energy situation, highlighting the urgent need for improvements in gas turbine technology. Additionally, the Chapter outlines the industry context for this study, emphasising the importance of developing efficient and effective gas turbine technology to meet the growing demand for energy in a sustainable manner.

Chapter 2: Combustion and Numerical Combustion

This Chapter provides an overview of combustion theory, including the equations necessary for modelling a chemically reacting flow. The methods and equations used to calculate thermodynamic properties, chemical kinetics, and chemical equilibrium are presented. The combustion regimes utilised in this thesis are described in detail, and the corresponding governing equations are presented. Additionally, this Chapter briefly discusses the numerical solvers employed in this study.

Chapter 3: Chemical Kinetic Models for Combustion

This Chapter provides an overview of the various types of kinetic models used by the combustion community. Kinetic model reduction is introduced, and the major techniques discussed. The motivation for this study is then presented and the concept of Compact Models is introduced. The Chapter finishes with a review of various optimisation algorithms that have been used to optimise kinetic models in literature.

Chapter 4: MLOCK – An Automated Compaction Methodology

The Machine Learned Optimisation of Chemical Kinetics (MLOCK) algorithm is introduced. The definition of a Compact Model is provided, along with a description of the components that comprise it. A detailed step-by-step accounting of the first version of the algorithm, *MLOCK1.0*, is then presented.

Chapter 5: Compact Models for Methane/Air Combustion

The efficacy of the MLOCK approach is showcased through its application to the archetypal methane combustion system. By employing the *MLOCK1.0* algorithm to two distinct detailed kinetic models, Compact Models are generated comprised of fifteen to nineteen nodes (virtual species). These models are benchmarked to existing reduced-order models to demonstrate the potential of MLOCK. The behaviour of the MLOCK algorithm is analysed, highlighting the impact of various optimisation parameters.

Chapter 6: Compact Models for NO_x Formation in Methane/Air Combustion

The MLOCK methodology is applied to produce a series of Compact Models for oxides of nitrogen (NO_x) formation during methane/air combustion. A combinatorial approach is taken to construct a virtual reaction network for NO_x which comprises three nodes, N, NO and NO₂. This virtual reaction network is appended to a fifteen-node model presented in Chapter 5. The kinetics component of the virtual NO_x network is then found through optimisation using *MLOCK1.1*. The performance of the Compact Models is benchmarked and compared to the state-of-art.

Chapter 7: Compact Models for NO_x Formation in Methane/Air Combustion

Compositional and surrogate modelling is discussed and a review of the state-of-art methods for the production of reduced-order kinetic models for liquid fuels is presented. A novel methodology for the production of Compact Models for liquid fuels is presented. This method is demonstrated on Arabian Super Light (AXL) crude oil, producing a thirty-five-node Compact Model for high temperatures from a detailed model comprising over six thousand species. Additionally, a number of approaches to produce a Compact Model accurate to low temperature combustion are presented. This results in the production of a thirty-two node compact model for AXL combustion at low and high temperatures.

Chapter 8: Conclusions and Perspectives

This Chapter provides conclusions from this thesis, summarising the results of each application of the MLOCK method. The application of MLOCK to other tasks aside from compaction is presented. Suggested avenues of further work are presented to further improve the method and to benchmark the MLOCK algorithm to other algorithms in literature for the task of kinetic model optimisation.

Chapter 2

Combustion Chemistry and Numerical Modelling

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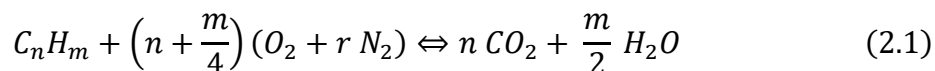
2.1 Introduction to Combustion

Combustion is an exothermic chemical process that occurs when a fuel reacts with an oxidiser, typically air. This is a complex phenomenon owing to the multitude of physical

and chemical processes simultaneously occurring across large time, temperature, pressure, and length scales.

The burning of a candle is a seemingly simple process, yet it provides a tangible example of the complex phenomena that occur during combustion. The three primary phenomena that contribute to the burning of a candle are chemical reactions, mass transfer, and heat transfer. As fuel molecules are oxidised by the surrounding air, intermediate products are formed, releasing energy as heat. This occurs most intensely at the outer edge of the flame, called the flame front. This heat is then transferred to the surrounding area by a combination of convection and radiation. In addition to these heat transfer mechanisms, fuel moves up the wick by capillary action, which involves mass transfer of the wax. Additionally, a series of phase changes occur as the solid wax is transformed into a liquid and then into a gas, which diffuses towards the flame front to undergo combustion.

The global reaction for the combustion of any hydrocarbon molecule in air can be written as:



where r is the ratio of N_2 to O_2 in the air ($r = 3.762$).

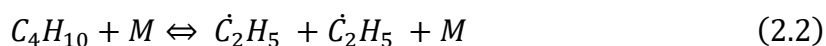
Despite this straightforward global description, on the molecular level the chemical process of combustion is complex with hundreds of elementary reactions occurring between tens of chemical species for even the simplest of hydrocarbons, with the number of species rising to the thousands in the case of liquid fuels (e.g., diesel and kerosene). The set of all elementary reactions that are responsible for the chemical transformation of a molecule is called its *reaction mechanism*. An accurate description of which is required to accurately describe the evolution of the chemical system. Elementary reactions can be categorised into three distinct classes based on the number of reactant molecules involved in the reaction.

- 1) Unimolecular reactions: This form of reaction involves the decomposition of a molecule into two or more products, e.g., $AB \Leftrightarrow A + B$. These reactions are typically first-order, meaning the rate at which they proceed is a linear function of the reactant concentration.

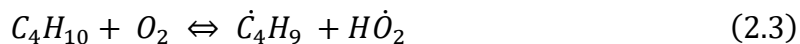
- 2) Bimolecular reactions: This form of reaction involves the collision of two reactant molecules to form one or more products through the breaking and forming of chemical bonds, e.g., $A + B \rightleftharpoons C + D$. Bimolecular reactions are typically second-order, meaning that the reaction rate is proportional to the product of the reactant concentrations.
- 3) Termolecular reactions: This form of reaction involves the collision of three reactant molecules to form products. Termolecular reactions are typically third-order, meaning that the reaction rate is proportional to the product of the reactant concentrations (i.e., cubic relation). Three-body reactions are a type of termolecular reaction that require an additional inert species, termed a collision partner, to be present for the reaction to proceed, e.g., $A + B + M \rightleftharpoons AB + M$ where 'M', is required to dissipate some reaction energy to stabilise the product 'AB'. When this reaction proceeds in the reverse direction, 'M' provides additional energy to break the bonds between 'A' and 'B'.

Combustion proceeds as a series of chain reactions beginning with an initiation reaction in which the fuel is decomposed to produce *radicals*. This instigates a series of subsequent reactions where these radicals act as reactants, i.e., a chain reaction. Radicals are highly reactive species that possess one or more unpaired electrons, which can be transferred to stable molecules to initiate further radical formation and sustain the reaction chain. The reactions in this chain reaction can be categorised based on the number of additional radicals produced.

- 1) Chain initiating: These reactions involve the formation of radicals from the stable fuel molecule. This can occur by homolytic cleavage of covalent bonds in the fuel molecule, for example butane decomposition to two ethyl radicals,



However, these type of processes have high activation energies, and so only proceed at significant rates at high temperatures. At lower temperatures, chain initiation is dominated by hydrogen atom abstraction reactions, for example butane oxidation by oxygen, to produce a butyl radical and a hydroperoxyl radical,



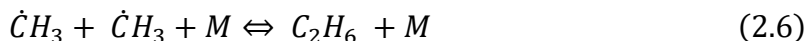
- 2) Chain propagating: These are reactions in which the number of radicals as reactants and products are equal, e.g., a radical reacts with a molecule to produce a molecule and a radical. Another form of chain propagation reaction is isomerisation, which involves the rearrangement of atoms to form a different isomer, which has the same molecular formula but a different structural arrangement. Hence, as the number of radicals is maintained, the reactivity of the system is maintained. For example, in the case of butane combustion, butane reacting with methyl radical to produce a butyl radical and methane,



- 3) Chain branching: These are reactions in which the number of radicals produced is greater than the number of reactant radicals. These reactions lead to an increase in the reactivity of the system. For example, ethane reacting with an oxygen radical to produce an ethyl radical and a hydroxyl radical,



- 4) Chain terminating: These are reactions in which the number of radicals produced is less than the number of reactant radicals. Typically, this involves the recombination of two radicals to form a stable molecule, leading to a decrease in the reactivity of the system. For example, the recombination of two methyl radicals to form ethane,



The rate of a combustion system is controlled by the competition between chain branching and chain propagating reactions. This competition, and the specific reactions that occur, are dependent on various factors including the initial mixture composition, temperature, and pressure.

Consider a gaseous mixture introduced into a volume with a uniformly controlled temperature. If the temperature inside the volume is sufficient, the fuel molecule undergoes

a chain initiation reaction, to form radicals and releases energy in the form of heat. These radicals will further react with the fuel molecule through chain branching or chain propagation reactions, leading to the exponential growth in the number of radicals in the mixture and an increase in the temperature of the mixture. As a result, the rate of reaction increases, leading to further energy release. This thermal feedback results in a sharp increase in the pressure and temperature inside the volume and is referred to as *explosion*.

From this example, it is clear that accurately predicting the outcome of a combustion event requires a deep understanding of the underlying reaction mechanism of the fuel molecule. Additionally, it is necessary to consider the transfer of both heat and mass throughout the mixture to accurately simulate a combustion event. Today, computer simulations that numerically describe combustion are a critical component of fuel research and engine design. These simulations must numerically describe the simultaneous occurrence of chemical reactions, heat transfer, and mass transfer, which all play important roles in determining the overall behaviour of the system.

In this Chapter, the framework for the numerical description of gas-phase combustion is detailed.

2.2 Mixture Properties

The properties of a gas mixture are defined by the properties of the discrete chemical species that comprise it. The mass of a chemical species, k , in a mixture of N_s discrete chemical species, can be written as,

$$m_k = n_k W_k \quad (2.7)$$

where n_k and W_k are the number of moles and the molecular weight of species k respectively.

The quantity of a species in a mixture is conventionally expressed as the mole fraction, X_k , which is a dimensionless quantity representing the number of moles of species k relative to the total number of moles in the mixture,

$$X_k = \frac{n_k}{\sum_{k=1}^{N_s} n_k} \quad (2.8)$$

The quantity of a species can also be expressed as the mass fraction, Y_k , which represents the mass of species k relative to the mass of the mixture,

$$Y_k = \frac{m_k}{\sum_{k=1}^{N_s} m_k} \quad (2.9)$$

The mean molecular weight of the mixture, W , is computed from the product of mole fraction and molecular weight of each species,

$$W = \sum_{k=1}^{N_s} X_k W_k \quad (2.10)$$

The mole fraction and mass fraction are linked through the relation,

$$Y_k = \frac{X_k W_k}{W} \quad (2.11)$$

The molar concentration of a species is also an important property that is routinely used. This quantity is the number of moles of a species per unit volume and can be expressed as,

$$[X_k] = \frac{\rho Y_k}{W_k} \quad (2.12)$$

where ρ is the mean mass density of the mixture.

2.2.1 Equation of State

The equation of state conventionally used in numerical combustion is that of an ideal, multi-fluid gas. The pressure p at temperature T is given by,

$$p = RT \sum_{k=1}^{N_s} [X_k] \quad (2.13)$$

where R is the ideal gas constant. The ideal gas law is predicated on the following assumptions:

- a) The gas consists of a large number of small particles.
- b) These particles are in constant, random motion.

- c) The volume of the individual particles is negligible compared to the total volume of the gas leading to negligible intermolecular forces between the particles.
- d) The average kinetic energy of the particles is directly proportional to the absolute temperature of the gas.
- e) All collisions between particles are perfectly elastic.

2.2.2 Mixture Thermodynamics

Modelling a combustion system requires accurate thermodynamic descriptions of the participating chemical species. Chemical reactions occur due to collisions between species. If the energy of a collision is sufficient, bonds between atoms in the reactant species are broken and chemical energy is released. This energy, in the form of heat, transfers to the local environment, increasing the velocity of the particles, leading to more energetic and frequent collisions, instigating further chemical reactions. Hence, the accurate accounting of chemical species and energy release is essential to the accurate modelling of a combustion process.

The amount of energy released from a reaction, ΔQ , is equal to difference in enthalpy, H_k^0 , between the reactants and products,

$$\Delta Q_i = \sum_{k=1}^{N_s} v'_{k,i} H_k^0 - \sum_{k=1}^{N_s} v''_{k,i} H_k^0 \quad (2.14)$$

where superscript ^{0} denotes the standard-state (typically 1 atmosphere and 298 Kelvin), and $v'_{k,i}$ and $v''_{k,i}$ are the forward and reverse stoichiometric coefficients of the k^{th} species in the i^{th} reaction.

The heat capacity quantifies the amount of heat needed to increase the temperature of the mixture by a given amount. As temperature is arguably the most important parameter in combustion, the heat capacity of the mixture is an important quantity and must be known to a high degree of accuracy. The heat capacity of the mixture, is given as

$$C_p^0 = \sum_{k=1}^{N_s} (X_k C_{p,k}^0) \quad (2.15)$$

where $C_{p,k}^0$ is the molar heat capacity at constant pressure of species k .

The enthalpy of a system is the sum of its internal energy and the product of its pressure and volume. Hence, enthalpy dictates the heat release of a reaction, as given in Equation 2.14. The molar enthalpy, H_k^0 , of species k at temperature T_k is given as,

$$H_k^0 = \int_{T^0}^{T_k} C_{p,k}^0 dT + \Delta h_k^0 \quad (2.16)$$

where Δh_k^0 is the standard-state molar enthalpy of formation of species k (i.e., at T^0 equals 298 Kelvin). The entropy of a system represents the degree of disorder in the system. As the entropy of a closed system must always increase or stay constant, it is an important parameter in computing the direction of reactions. The molar entropy, S_k^0 , of species k at temperature T_k is given as,

$$S_k^0 = \int_{T^0}^{T_k} \frac{C_{p,k}^0}{T} dT + \Delta s_k^0 \quad (2.17)$$

where Δs_k^0 is the standard-state molar entropy of species k .

From these quantities, other important species properties are easily obtained, such as the molar heat capacity at constant volume,

$$C_{v,k}^0 = C_{p,k}^0 - R \quad (2.18)$$

the internal energy,

$$U_k^0 = H_k^0 - RT_k \quad (2.19)$$

and the standard-state Gibbs free energy,

$$G_k^0 = H_k^0 - T_k S_k^0 \quad (2.20)$$

The molar thermodynamic properties of the mixture are then determined from the individual properties of the species using the following mixing laws,

$$H = \sum_{k=1}^{N_s} H_k^0 X_k \quad (2.22)$$

$$S = \sum_{k=1}^{N_s} X_k \left(S_k^o - R \ln (X_k) - R \ln \left(\frac{p}{p^o} \right) \right) \quad (2.23)$$

$$G = \sum_{k=1}^{N_s} X_k \left(H_k^o - T_k \left(S_k^o - R \ln (X_k) - R \ln \left(\frac{p}{p^o} \right) \right) \right) \quad (2.24)$$

Typically, in numerical solvers used by the combustion community, these terms are input using the NASA polynomials fit [8] to describe the temperature dependence of these properties. The value of these properties for species k at a temperature T ,

$$\frac{C_{p,k}^0}{R} = a_{1,k} + a_{2,k}T_k + a_{3,k}T_k^2 + a_{4,k}T_k^3 + a_{5,k}T_k^4 \quad (2.25)$$

$$\frac{H_k^0}{R} = a_{1,k}T_k + \frac{a_{2,k}T_k^2}{2} + \frac{a_{3,k}T_k^3}{3} + \frac{a_{4,k}T_k^4}{4} + \frac{a_{5,k}T_k^5}{5} + a_{6,k} \quad (2.26)$$

$$\frac{S_k^0}{R} = a_{1,k} \ln T_k + a_{2,k}T_k + \frac{a_{3,k}T_k^2}{2} + \frac{a_{4,k}T_k^3}{3} + \frac{a_{5,k}T_k^4}{4} + a_{7,k} \quad (2.27)$$

where $a_{x,k}$ denotes the NASA polynomial coefficients for the species k . The coefficients are found by fitting values at fixed temperatures across a temperature range. Given the broad temperature range encountered in combustion there exists two sets of coefficients, one valid for low temperatures (e.g., 200 K – 1000 K) and one for high temperatures (e.g., 1000 K – 5000 K).

2.3 Chemical Kinetics

Chemical kinetics is the study of the rates of chemical reactions and the variables that affect them. Gas phase chemical kinetics is a mature research field that is concerned with understanding, and expressing mathematically, the dependence of the rate of a chemical reaction on the properties of the participating species and the local thermodynamic properties under which the reaction occurs.

Chemical reactions occurring in a reacting flow are expressed in the form of elementary reactions. Consider an elementary reaction, i , involving $N_{s,i}$ chemical species. This can be written in the general form of,

$$\sum_{k=1}^{N_{s,i}} v'_{k,i} \chi_k \Leftrightarrow \sum_{k=1}^{N_{s,i}} v''_{k,i} \chi_k \quad (2.28)$$

where χ_k is the chemical symbol of the k^{th} species in the i^{th} reaction.

The rate of a reaction is defined in terms of the rate of change of the given reactants as,

$$K_i = k_{f,i} \prod_{k=1}^{N_s} [X_k]^{v'_{k,i}} - k_{r,i} \prod_{k=1}^{N_s} [X_k]^{v''_{k,i}} \quad (2.29)$$

where $k_{f,i}$ and $k_{r,i}$ are the forward and reverse reaction rate constants of reaction i , which encapsulate the energy and frequency of the collisions. Hence, the rate of reaction is proportional to the number of collisions occurring, the energy of the collisions and the concentration of the reactant molecules.

The production rate of species k , $\dot{\omega}_k$ is the summation of the reaction rates of all reactions the species participates in,

$$\dot{\omega}_k = \sum_{i=1}^I v_{k,i} K_i \quad (2.30)$$

where $v_{k,i}$ is the net stoichiometric coefficient, $v_{k,i} = v''_{k,j} - v'_{k,j}$.

2.3.1 Arrhenius Formulism

The reaction rate constants, k_f and k_r have been found experimentally to be strongly temperature dependent. In combustion studies these constants are conventionally expressed in a modified Arrhenius form,

$$k_{f,i} = A_i T^{n_i} e^{\left(-\frac{E_{A,i}}{RT}\right)} \quad (2.31)$$

where A is the pre-exponential factor, n is the temperature exponent and E_A is the activation energy (J mol^{-1}). Note, the units of A_i depend on the reaction order of the i^{th} reaction ($\sum_{k=1}^{N_s} v'_{ki}$) as $\text{mol}^{(1-\text{order})} \text{cm}^{-3(1-\text{order})} \text{s}^{-1} \text{K}^{-1}$.

The activation energy is the minimum amount of energy required to rearrange the geometries of the reactants to reach a transition state, to allow the bonds to be broken. The path linking the products, transition state and reactant is referred to as the minimum energy path, which is characterised by the *intrinsic reaction coordinate*. As illustrated in Figure 2.1, an activation energy is required even in the case of a reaction having a negative Gibbs free energy (i.e., exothermic).

The velocity, and hence the energy, of particles in the gas mixture are strongly dependent on temperature, and follow a Boltzmann distribution. Therefore, Equation 2.31 uses Boltzmann statistics to assess the probability that a collision between the reactants has the required energy to exceed the activation energy, resulting in the reaction occurring. It follows therefore that as the temperature increases, the velocity and energy of the particles in the gas mixture also increase. This in turn leads to a higher probability that collisions will have sufficient energy to break the reactant bonds, resulting in a larger reaction rate.

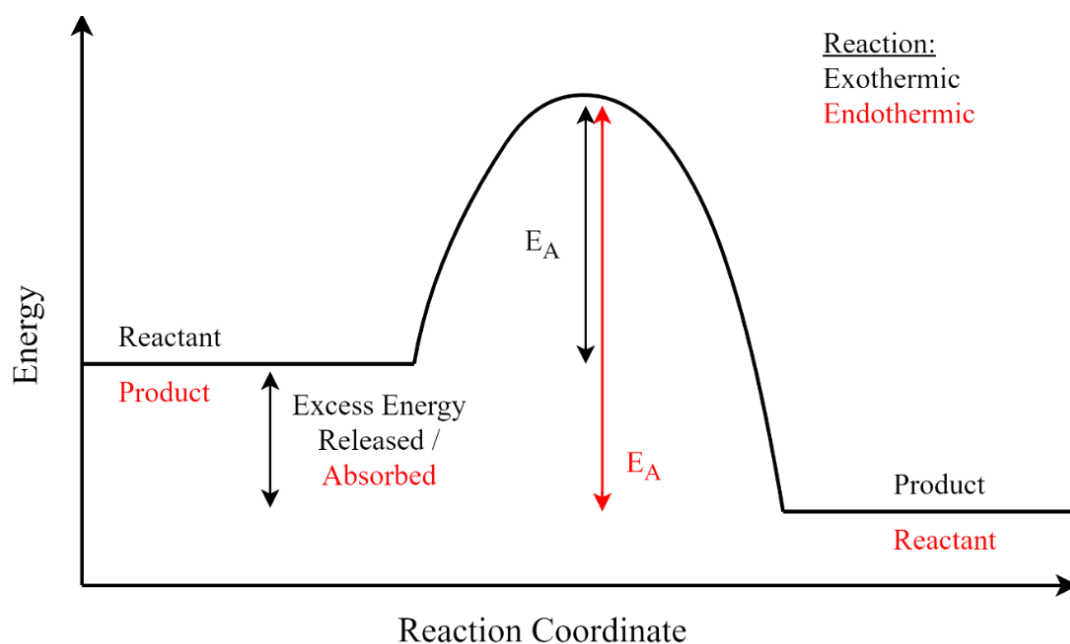


Figure 2.1. Energy diagram of an exothermic and endothermic reaction.

2.3.2 Three-Body Reactions

Three-body reactions typically involve the presence of an inert third reactant that acts as a stabiliser in highly exothermic reactions, such as radical-radical recombination reactions, by carrying away excess energy and momentum. The reaction rate (Equation 2.29) of a three-body reaction is a function of the concentration of the collision partner, $[M]$.

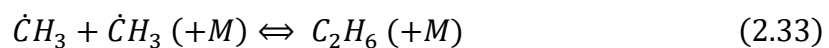
The effectiveness of a species as a collider depends on its mass, with larger molecules having greater collisional cross sections. This makes them better suited for dissipating reaction energy and carrying away momentum. Conversely, in decomposition reactions, larger molecules can provide additional energy more easily than smaller molecules. In numerical modelling, third-body efficiencies α_k , are a way of quantifying the effectiveness of species k as a collider. These efficiencies are multiplied by $[M]$ to calculate the *effective concentration* of the colliders in the reaction rate calculation.

2.4 Pressure Dependent Rate Constants

As well as a dependence on temperature, some reactions, such as unimolecular decomposition and radical-radical recombination reactions, are dependent also on pressure. For example, consider the example of methyl recombination. At very high pressures, the concentration of the collision partners is high and as such the reaction rate does not become dependent on their concentration. Therefore, the reaction can be written as,



Conversely, at the low-pressure limit, the concentration of the collision partners is low, and the rate of the reaction becomes dependent on the concentration of the collision partner. At this limit, the reaction can be expressed as,



However, at pressures in-between these limits, termed the “fall-off region”, the dependence on the concentration of the collisional partner is not as easily expressed. There are various empirical methods to express the reaction rate of such a reaction, most derived from the Lindemann [9] approach. In this approach, two sets of Arrhenius parameters are provided for the reaction. One for the low pressure limit, k_0 , and one for the high pressure limit, k_∞ ,

$$k_0 = A_0 T^{n_0} e^{\left(-\frac{E_{A,0}}{RT}\right)} \quad (2.34)$$

$$k_\infty = A_\infty T^{n_\infty} e^{\left(-\frac{E_{A,\infty}}{RT}\right)} \quad (2.35)$$

The reaction rate constant at pressure, p , is expressed as,

$$k = k_{\infty} \left(\frac{p_r}{1 + p_r} \right) F \quad (2.36)$$

where p_r is the reduced pressure,

$$p_r = \frac{k_0[M]}{k_{\infty}} \quad (2.37)$$

In the Lindemann method, the term F is equal to 1. However, in the Troe formalism [10], the most commonly used method in numerical combustion to represent the rate of pressure dependent reactions, F is given by,

$$\log(F) = \left[1 + \left[\frac{\log(p_r) + c}{n - d(\log(p_r) + c)} \right]^2 \right]^{-1} \log(F_{cent}) \quad (2.38)$$

where the constants are estimated as,

$$c = -0.4 - 0.67 \log(F_{cent}) \quad (2.39)$$

$$n = 0.75 - 1.27 \log(F_{cent}) \quad (2.40)$$

$$d = 0.14 \quad (2.41)$$

$$F_{cent} = (1 - \alpha)e^{\left(\frac{-T}{T^3}\right)} + \alpha e^{\left(\frac{-T}{T^1}\right)} + e^{\left(\frac{-T^2}{T}\right)} \quad (2.42)$$

where the parameters α , T^1 , T^2 and T^3 must be provided for the reaction. Figure 2.2 shows an example of the Troe formalism for pressure dependence of the exemplar $CH_3 + CH_3 (+M) \rightleftharpoons C_2H_6 (+M)$ reaction using Arrhenius and Troe parameter values from the NUIGMECH1.0 [11] kinetic model for hydrocarbon combustion.

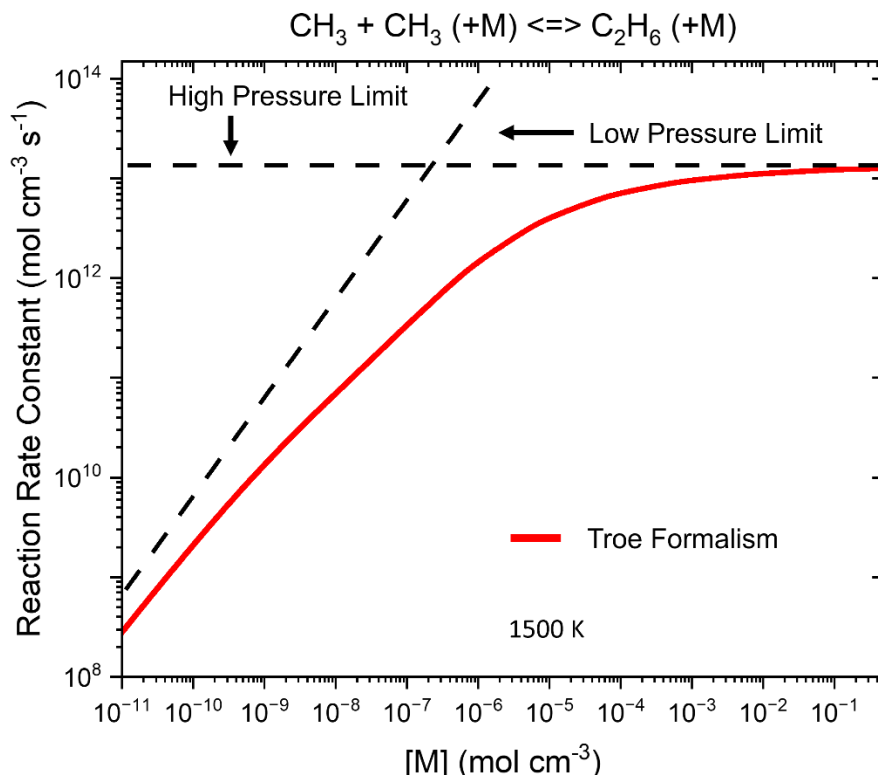


Figure 2.2. Reaction rate constant of reaction $\text{CH}_3 + \text{CH}_3 (+\text{M}) \rightleftharpoons \text{C}_2\text{H}_6 (+\text{M})$ as a function of collision partner concentration computed by the Troe formalism. Reaction rate descriptors taken from the NUIGMECH1.0 detailed model.

Another method for the expression of the pressure dependence of a reaction, and one that is often deployed unphysically, is the PLOG format. This allows for the explicit expression of a set of Arrhenius parameters for discrete pressures. If the pressure is between the pressure points provided in the PLOG expression, the reaction rate constant is obtained by logarithmic interpolation of the specified Arrhenius parameters. Therefore, the pressure dependence of the reaction rate constant is based on direct interpolation of reaction rate constants at specified pressures. For a pressure p , between p_i and p_{i+1} , the reaction rate constant is calculated by,

$$\ln k = \ln k_i + (\ln k_{i+1} - \ln k_i) \frac{\ln p - \ln p_i}{\ln p_{i+1} - \ln p_i} \quad (3.43)$$

An example of this is shown in Figure 2.3 for a PLOG description of the reaction $\text{C}_2\text{H}_5 + \text{OH} \rightleftharpoons \text{CH}_3 + \text{CH}_2\text{OH}$ (values from NUIGMECH1.0).

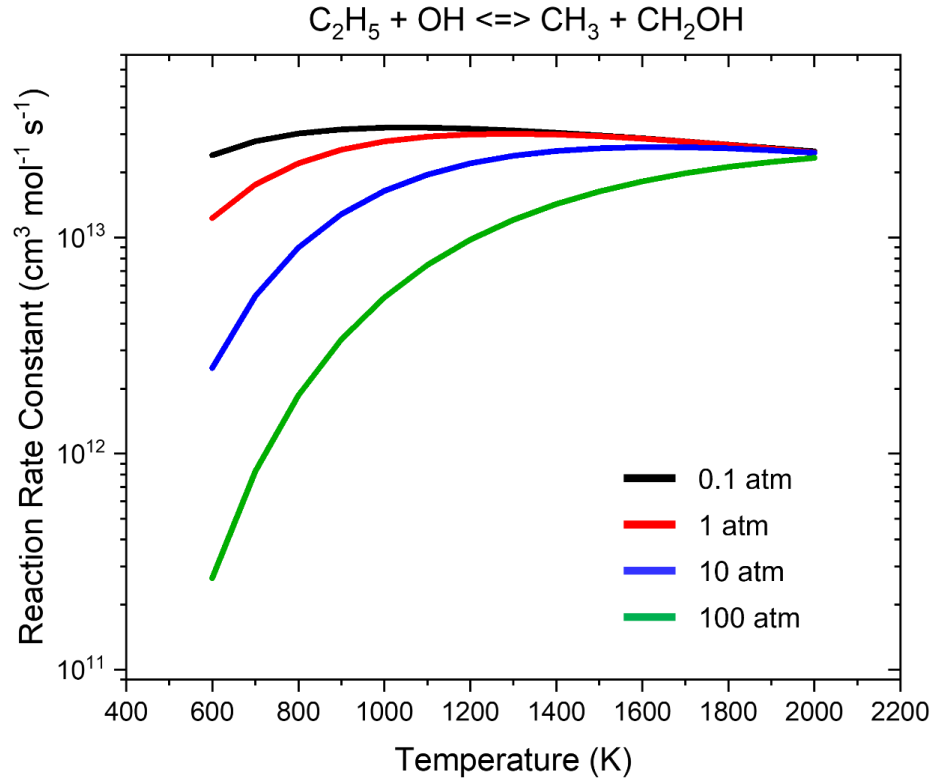


Figure 2.3. Reaction rate constant of reaction $\text{C}_2\text{H}_5 + \text{OH} \rightleftharpoons \text{CH}_3 + \text{CH}_2\text{OH}$ as a function of temperature for various pressures as given by NUIGMECH1.0 detailed model using the PLOG form of reaction rate description.

2.5 Chemical Equilibrium

When the forward and reverse reaction rates are equal, the system is in chemical equilibrium. This can be written as,

$$k_{f,i} \prod_{k=1}^{N_s} [X_k]^{v'_{k,i}} = k_{r,i} \prod_{k=1}^{N_s} [X_k]^{v''_{k,i}} \quad (2.44)$$

From this, the equilibrium constant, $K_{eq,i}$ can be expressed,

$$K_{eq,i} = \prod_{k=1}^{N_s} [X_k]^{v_{ki}} = \frac{k_{f,i}}{k_{r,i}} \quad (2.45)$$

The equilibrium constant for the i^{th} reaction is calculated by computing the change in the standard Gibbs free energy, ΔG_i^o , which is the difference in the free energy of formation of the reactants and products at standard state. It can be written as,

$$K_{eq,i} = e^{\left(\frac{\Delta G_i^0}{RT}\right)} \left(\frac{p^0}{RT}\right)^{\left(\sum_{k=1}^{N_s} \nu_{ki}\right)} \quad (2.46)$$

By substituting in Equation 2.20, this can be expressed as the change in enthalpy and entropy in the i^{th} reaction, which are obtained from the NASA polynomials of Equations 2.26 and 2.27,

$$K_{eq,i} = e^{\left(\frac{\Delta S_i^0}{R} - \frac{\Delta H_i^0}{RT}\right)} \left(\frac{p^0}{RT}\right)^{\left(\sum_{k=1}^{N_s} \nu_{ki}\right)} \quad (2.47)$$

Hence, it is readily seen how the thermodynamic properties of the species are linked to the kinetics of the system.

At chemical equilibrium however, the Gibbs free energy of the mixture is at a minimum and the temperature of the mixture is referred to as the adiabatic temperature, T_{ad} . At chemical equilibrium, the state of the gas can be solved using only thermodynamic relations, by minimising the Gibbs free energy and solving for the concentrations of the species in the mixture. Hence, the chemical equilibrium is independent of the kinetics of the system.

2.6 Mixture Stoichiometry

Stoichiometry defines the relationship between reactants and products in a chemical reaction in a quantitative manner. In the context of combustion, *equivalence ratio* is a term used to express the ratio of fuel-to-oxidiser in the combustion reaction. The equivalence ratio, ϕ , can be expressed as,

$$\phi = \frac{\text{fuel-to-oxidiser ratio}}{\text{stoichiometric fuel-to-oxidiser ratio}} \quad (2.48)$$

where the *stoichiometric fuel-to-oxidiser ratio* is the ratio which results in complete combustion of the fuel (i.e., $\left(n + \frac{m}{4}\right)$ in Equation 2.1). Conditions at which there is excess oxygen have $\phi < 1.0$ and are termed *fuel-lean*, whereas *fuel-rich* denotes the case of excess fuel and where $\phi > 1.0$. The equivalence ratio of any combustion system is a key parameter as it dictates not only the thermodynamic properties of the mixture, but also the kinetics through the concentration of chemical species at the inlet (or at time equals zero).

At fuel-lean conditions, the total enthalpy of the fuel-mixture is lower due to less fuel present. As a result, a lower adiabatic temperature is reached. Nitrogen can be oxidised during combustion to form nitrogen oxides (NO_x), however, due to the large activation energy of the cleavage of the triple bond, this only occurs at extreme temperatures. Therefore, a lower adiabatic flame temperature means lower nitrogen oxides (NO_x) emissions. Additionally, less high-carbon chemistry occurs due to the abundance of oxygen, leading to less polyaromatic production and thus, less soot production. For these reasons most modern combustion devices operate in a fuel-lean regime.

2.7 Numerical Solvers

There are several numerical solvers used to model combustion systems within the combustion community, depending on the purpose of the task. In the combustor design stage, computational fluid dynamics (CFD) software such as Ansys Fluent [12], STAR-CCM+ [13] and OpenFOAM [14] are used to model combustion inside the combustor. These software can model fluid flow, chemical reactions, and heat and mass transfer of a multi-dimensional chemically reacting flow under a set of operating conditions. These software provide a high level of detail on the combustion event and the property of the gas mixture as it evolves inside the reactor.

In the fuel research and kinetic model development stage of research, ChemKin Pro [7] and Cantera [15] are the most commonly used numerical solver software. ChemKin Pro is the industry-standard tool for the simulation of 0-D and 1-D combustion cases. Cantera has gained attention in recent years as an open-source alternative to ChemKin Pro that offers additional flexibility and user control. Cantera, which uses the CVODES [16] solver to solve the system of differential equations, is used in this thesis to perform combustion calculations.

Next, reactor physics that are used for combustion calculations performed in this thesis are presented.

2.8 Reactor Physics: Zero-Dimensional Simulations

Due to the complexity of multi-species reacting flow simulations, it is often not possible, or not needed, to model combustion in multi-dimensional simulations. Therefore, lower

dimensioned simulations are routinely used to simplify the numerical complexity to better understand the combustion phenomena for specific purposes.

Zero-dimensional (0-D) reactors are one such category of simulations. These simulations assume infinitely fast mixing of the chemical species, resulting in a homogeneous mixture where species diffusion and transport effects are negligible. As a result, the rate of conversion of reactants to products is solely determined by the chemical reaction rates, and not influenced by the mixing processes. These calculations enable the study of the temporal evolution of a spatially uniform mixture under a defined set of operating conditions (temperature, pressure, equivalence ratio). 0-D reactors are useful in studying kinetically-controlled properties such as the propensity of the fuel to auto-ignite (or commonly ignition delay time). Due to their computational efficiency, 0-D simulations are commonly employed in the gas-turbine design process to provide insights into the kinetics of the system.

Experiments can be conducted using reactors that are designed to have near-zero spatial dimensions by ensuring thorough mixing of the reactants. Analytical chemistry techniques such as gas chromatography can be used to quantify the concentration of various species by sampling the reactor outlet gas. Studying the change in species concentration as the experimental parameters (residence time, temperature, pressure, equivalence ratio) change provides an insight into the underlying chemical processes. This type of speciation data is frequently used to validate numerical simulations.

At the start of a 0-D simulation ($t = 0$), the mixture is at the defined operating conditions. From this initial state, the transient energy equation is solved at each time step to compute the mixture temperature, which in turn is used to solve for the reaction rates and thermodynamics of the mixture. The energy equation is computed under the constraint of three conservation equations: conservation of mass, energy, and chemical species. The time-dependent mass conservation equation states that the total rate of change of mass in the reactor is equal to the difference between the mass flow into, $\dot{m}_{in}$, and out, $\dot{m}$, of the reactor, plus any mass added to, or removed from, the reactor walls, $\dot{m}_{wall}$,

$$\frac{d(\rho V)}{dt} = \dot{m}_{in} - \dot{m} + \dot{m}_{wall} \quad (2.49)$$

where, V is the volume of the reactor.

The time-dependent species conservation equation states that the rate of change of the mass of species k is equal to the difference between the mass flow of species k into and out of the reactor, plus the mass production rate of species k inside the reactor, $\dot{m}_{k,gen}$, which can be expressed as,

$$\frac{d(Y_k(\rho V))}{dt} = \dot{m}_{in}Y_{k,in} - \dot{m}Y_k + \dot{m}_{k,gen} \quad (2.50)$$

where,

$$\dot{m}_{k,gen} = V\dot{\omega}_k W_k + \dot{m}_{k,wall} \quad (2.51)$$

Rearranging Equation 2.50 leads to,

$$(\rho V) \frac{dY_k}{dt} = \dot{m}_{in}(Y_{k,in} - Y_k) - Y_k \dot{m}_{k,wall} + V\dot{\omega}_k W_k + \dot{m}_{k,wall} \quad (2.52)$$

where Y_k are the mass fractions of species k .

The conservation of energy means that the rate of change of internal energy within the system is equal to the difference between the enthalpy flow of gas entering and exiting the reactor, minus the heat flux out of the reactor, plus the net rate of heat addition to the reactor, $\dot{Q}$, minus the work done by the volume on the external world,

$$\frac{dU}{dt} = \dot{m}_{in} \sum_{k=1}^{N_s} Y_{k,in} h_{k,in} - \dot{m} \sum_{k=1}^{N_s} Y_k h_k + \dot{Q} - p \frac{dV}{dt} \quad (2.53)$$

where h_k denotes the specific enthalpy of species k . To solve for the mixture temperature, Equation 2.53 can be rearranged to be expressed as a function of T . First, the internal energy of the gas can be written as,

$$U = \rho V \sum_{k=1}^{N_s} Y_k u_k \quad (2.54)$$

where u_k is the specific internal energy of species k . From this,

$$\frac{dU}{dt} = \rho c_v \frac{dT}{dt} + \rho \sum_{k=1}^{N_s} Y_k u_k \frac{dY_k}{dt} + \rho u \frac{d(\rho V)}{dt} \quad (2.55)$$

Subbing in Equations 2.49, 2.52 and 2.53 one arrives at the transient energy equation for solving the gas temperature,

$$\rho V c_v \frac{dT}{dt} = \dot{m}_{in} \left(h_{in} - \sum_{k=1}^{N_s} Y_{k,in} u_k \right) - \frac{pV\dot{m}}{m} - \sum_{k=1}^{N_s} u_k \dot{m}_{k,gen} + \dot{Q} - p \frac{dV}{dt} \quad (2.56)$$

Note, reactors may have many inlets and outlets. If such is the case, $\dot{m}_{in}$ and $\dot{m}$ in the conservation equations are replaced with $\sum_{j=1}^J \dot{m}_{in,j}$ and $\sum_{g=1}^G \dot{m}_g$ where j and g are the number of inlets and outlets respectively. A network may be created of such reactors with the outlet of one reactor being the inlet of another, in techniques such as chemical reacting networks (CRN). Here, a network of 0-D reactors is used in-place of dimensional reacting flow simulations to model a gas-turbine combustor, as the simulation is considerably quicker to run due to the lack of spatial axes, as discussed later.

2.8.1 Canonical Case: Perfectly Stirred Reactor

A perfectly stirred reactor (PSR), sometimes called a continuously stirred tank reactor or well-stirred reactor, is a commonly used 0-D constant volume reactor. This reactor assumes that as the contents enter the reactor at the inlet, they are instantly mixed into the contents inside the chamber such that the mixture is perfectly homogenous, creating an idealised kinetically-limited regime. The gas leaving the reactor at the outlet has the same composition as that of the gas inside the reactor. An important parameter in PSR simulations is the residence time, which defines the time the contents spend inside the reactor. For combustion to occur, this residence time must be long enough for ignition to occur under the set of operating conditions. Residence time is given by,

$$\tau = \frac{m}{\dot{m}} \quad (2.57)$$

Although a PSR is a steady-state problem, many solvers use transient solvers to solve the system. For instance, Cantera does not have a true steady-state solver. Instead, it uses a transient solver to integrate to steady-state. To model a PSR in Cantera, an ideal gas constant volume reactor with an inlet and outlet is used, with a valve and mass controller to control the mass flow rate (and hence the residence time).

Figure 2.5 shows a typical result from PSR simulations. These simulations are performed using a methane/air fuel mixture at 10 atmospheres (atm) with an initial temperature of 1500 Kelvin (K). Figure 2.5 (a) and (b) show the effect of residence time on the mixture temperature and the mole fraction of some important species. These simulations are performed using a mixture with an equivalence ratio of one (i.e., stoichiometric). This shows that ignition occurs when the residence time is 0.33 ms. If a residence time less than this is used, no ignition of the fuel will occur.

Figure 2.5 (c) and (d) show the effect of equivalence ratio on the temperature and mole fractions of important species. The residence time of the reactor is 10 ms. These show that the maximum temperature, and thus the maximum enthalpy of combustion, occurs when the equivalence ratio is slightly rich. At lean conditions the enthalpy is lower as there is excess oxygen, whereas at very rich conditions there is excess fuel, resulting in incomplete combustion and hence, unreleased energy. Additionally, the maximum carbon dioxide (CO_2) occurs at slightly lean conditions whereas the amount of carbon monoxide (CO) at steady state increases as the equivalence ratio increases. This is because the rate of oxidation of CO to CO_2 decreases as the amount of oxygen in the mixture decreases.

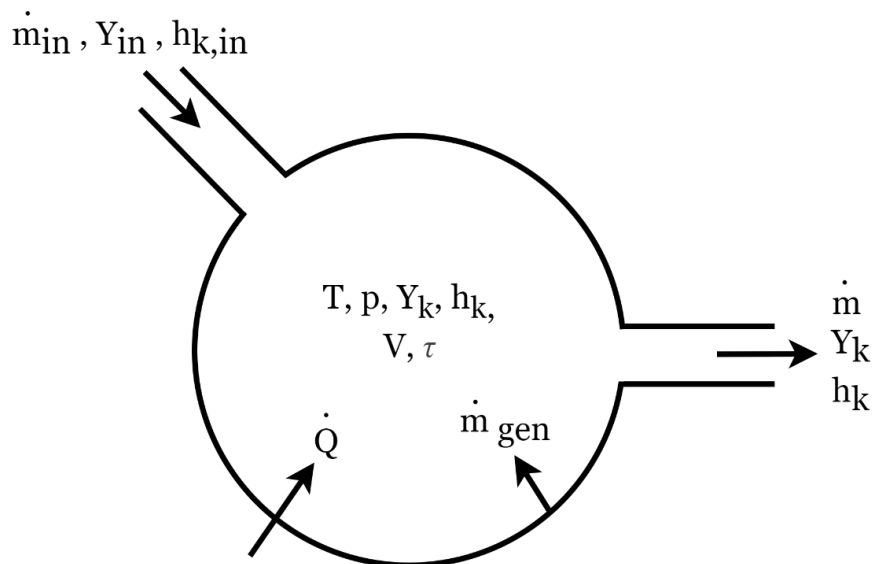


Figure 2.4. Schematic showing mass flow in and out of a perfectly stirred reactor (PSR).

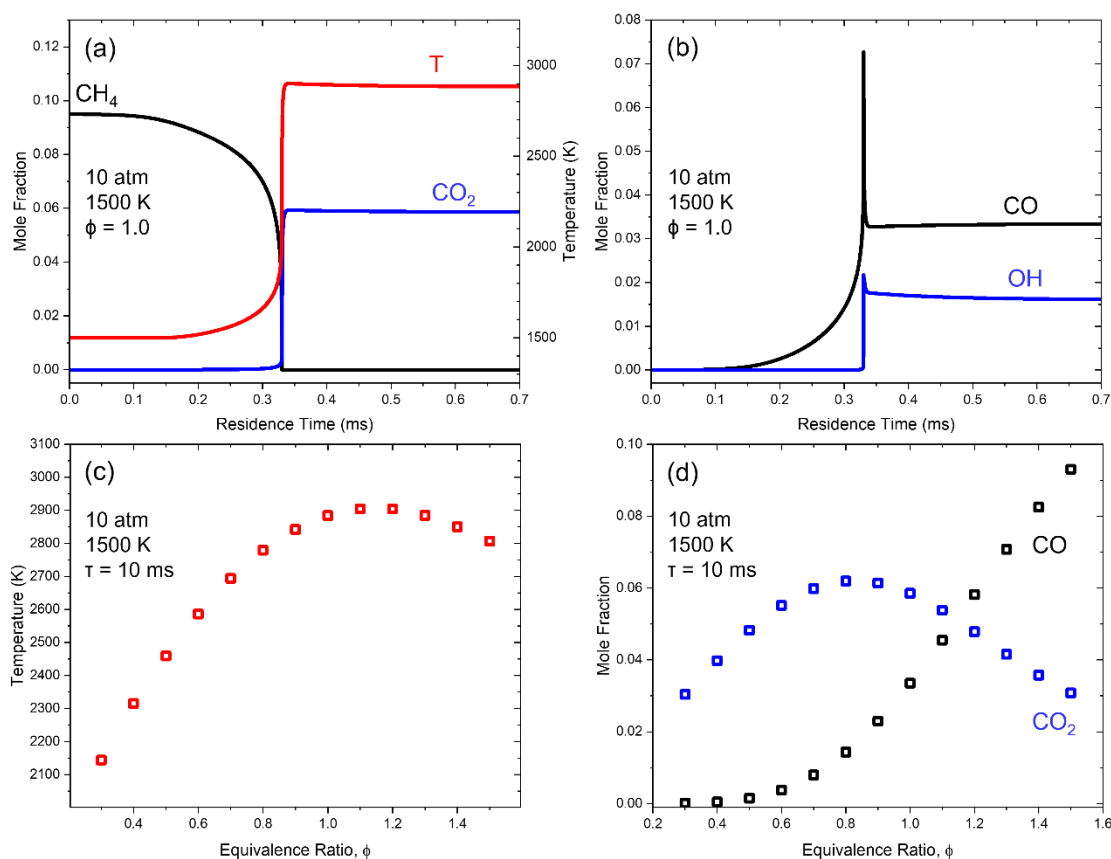


Figure 2.5. Results from perfectly stirred reactor (PSR) simulations using methane/air mixtures at 1500 K and 10 atm. (a) and (b) show the effect of residence time on the temperature and mole fractions of selected important species. (c) and (d) show the effect of fuel/air equivalence ratio at a fixed residence time.

2.8.2 Canonical Case: Constant Volume Constant Internal Energy Reactor

A constant volume constant internal energy (constant UV) reactor is a common reactor geometry used in combustion modelling. This reactor is a closed system, meaning the volume remains constant throughout the calculation and there is no inlet or outlet flow of mass. At the initial state ($t=0$), the fuel and oxidiser are perfectly mixed, thereby assuming a homogenous mixture (0-D). The system advances through the solving of the transient conservation equations until the user-defined end time. These reactors are commonly used to model autoignition (ignition delay time), which is the time taken for a certain fuel mixture to ignite at a certain set of initial temperature and pressure conditions. In Cantera, this is modelled using a constant volume ideal gas reactor.

Figure 2.6 shows the result of a series of autoignition results using a constant UV reactor using a methane/air fuel mixture at lean conditions (equivalence ratio of 0.5). The effect of both initial temperature and pressure of the reactor is readily seen. The higher the temperature, the more thermal energy in the system, resulting in faster rates of reactions. Similarly, higher pressure results in a faster ignition delay time (IDT) as the mean free path of the molecules is shorter, resulting in a greater frequency of collisions which increases the rate of reaction. In this thesis, the IDT is defined as the point at which $\frac{dT}{dt}$ is a maximum. Other definitions routinely used in literature include the time taken for the temperature to increase by 400 K and the time at which $\frac{dp}{dt}$ is a maximum. The difference between these definitions is minimal in the vast majority of cases.

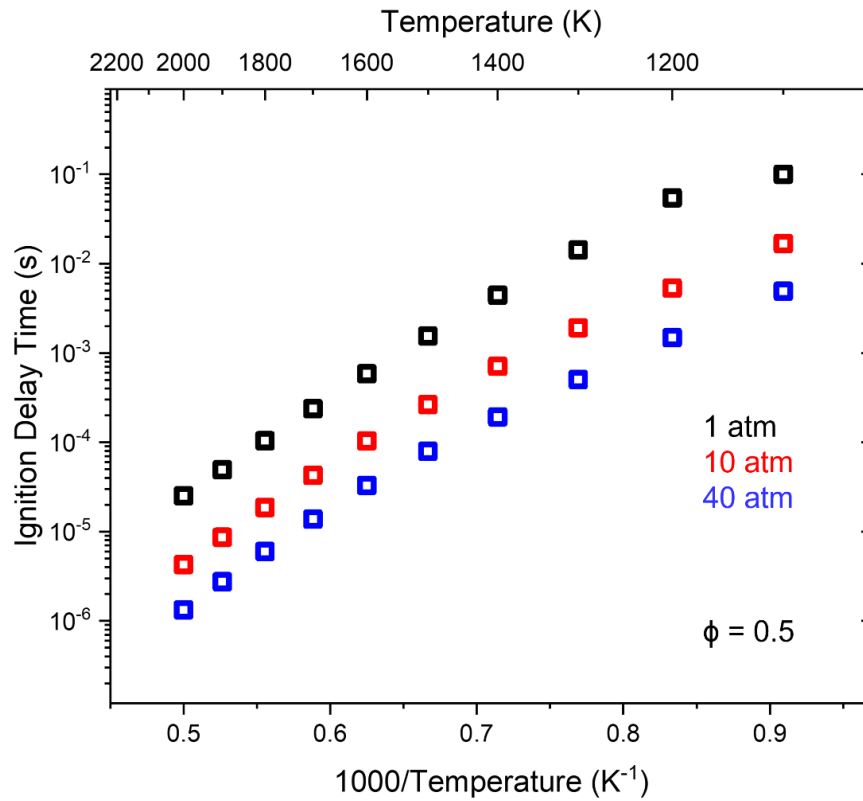


Figure 2.6. Results from ignition delay time calculations, using a constant UV reactor, for a methane/air mixture at lean conditions. A range of initial pressures and temperatures are evaluated.

2.9 Reactor Physics: One-Dimensional Simulations

One-dimensional (1-D) simulations allow for the study of the spatial evolution of a mixture along one plane. As a spatial axis now exists, species transport must be considered. This requires the mathematical solver to solve the transport equations which govern fluid flow.

In reality, combustion occurs under the coupling influences of chemical kinetics, thermodynamics, heat transfer and mass transfer. Therefore, one-dimensional (1-D) simulations provide a more realistic description of the physically occurring combustion event than 0-D simulations, however, the computational time to solve these calculations is considerably larger due to the consideration of species transport.

2.9.1 Transport Modelling

In dimensional reacting flow problems, the transport of species and energy has a considerable effect on the net production rate of species and in some cases can be rate-limiting, thus necessitating consideration.

There are two main methods to describe species transport in a mixture: multi-component transport and mixture-averaged transport. Numerical description of species transport is a non-trivial task, a brief explanation of which is provided here with comprehensive accounting found in [17-19].

In *multi-component transport* [20], the diffusion of each species relative to every other species is calculated. This is a rigorous following of kinetic theory and hence provides an accurate description of the mixture's diffusion properties. The velocity at which a species moves relative to other species in a mixture in the i^{th} direction is defined as the species diffusion velocity, $V_{k,i}$ and is composed of two terms: the velocity from ordinary diffusion and the velocity from thermal diffusion. To compute this, the diffusion of each species pair through each other must be computed. It can be written as,

$$V_{k,i} = \frac{1}{X_k W} \sum_{l=1}^{N_s} W_k D_{k,l} d_{l,i} - \frac{D_k^T}{\rho Y_k T} \frac{dT}{dx_i} \quad (2.58)$$

where the diffusion driving force term of species l in direction i is,

$$d_{l,i} = \frac{dX_l}{dx_i} + \frac{(X_l - Y_l)}{p} \frac{dp}{dx_i} \quad (2.59)$$

In these equations, D_k^T denotes the thermal diffusion coefficients and $D_{k,l}$ denotes the ordinary multicomponent diffusion coefficient of species k diffusing in species l which are determined from the binary diffusion coefficients $\mathcal{D}_{k,l}$,

$$\mathcal{D}_{k,l} = \frac{3 \sqrt{\frac{2\pi k_B^3 T^3}{m_{k,l}}}}{16\pi p \sigma_{k,l}^2 \Omega^{(1,1)*}} \quad (2.60)$$

where k_B is the Boltzmann constant, $m_{k,l}$ is the reduced mass for the (k, l) species pair (product of masses divided by sum), $\sigma_{k,l}$ is the Lennard-Jones collision diameter for the (k, l) pair and $\Omega^{(1,1)*}$ is the collision integral.

Calculation of the diffusion coefficients involves the computation of the inverse of a $N_s \times N_s$ matrix which contains the mole fractions of each species and their binary diffusion coefficients. Additionally, the thermal diffusion coefficients, D_k^T , require solving a $3N_s \times 3N_s$ set of algebraic equations.

As this calculation must be performed at each axial point, the computational cost of using the multi-component transport model is considerable, especially when modelling complex fuels, and hence, can not be afforded in multi-dimensional simulations (e.g., CFD). Moreover, in many circumstances this level of accuracy is not needed. Hence, the *mixture-averaged transport* model is routinely used. In this method, the diffusion coefficients for each species are calculated by considering the diffusion of the species through the mixture. Therefore, instead of computing the diffusion coefficients for each species pair, only one diffusion coefficient is computed for each species, and hence, no inversion of a $N_s \times N_s$ matrix is needed. Applying the Curtiss-Hirschfelder approximation [21], the species diffusion velocity of species k moving through the mixture in direction i is now,

$$V_{k,i} = - \frac{D_k}{X_k} \frac{dX_k}{dx_i} + V_{c,i} \quad (2.61)$$

where $V_{c,i}$ is a correction velocity which ensures mass is conserved in this approximation,

$$V_{c,i} = \sum_{k=1}^{N_s} \frac{W_k D_k}{W} \frac{dX_k}{dx_i} \quad (2.62)$$

Using this formulism, the diffusion coefficients, D_k , are express as,

$$D_k = \frac{1 - Y_k}{\sum_{l \neq k}^{N_s} \frac{X_l}{\mathcal{D}_{k,l}}} \quad (2.63)$$

Note, in 1-D simulations, $i = 1$.

2.9.2 Canonical Case: Premixed Freely Propagating Flame

A freely propagating premixed flame is a simulation of a steady, adiabatic, premixed laminar flame. This canonical case is a powerful model used to describe and understand a combustion system. A premixed laminar flame is characterised by a mixture of fresh gas (perfectly mixed fuel and oxidiser) and burned gas separated by a flame front that propagates towards the fresh gas mixture. The structure of this flame, as shown in Figure 2.7, can be characterised as consisting of three zones.

- 1) Preheat zone: The fresh gas mixture is heated by the thermal diffusion of radicals from the reaction zone. These radicals participate in low activation energy reactions, with the products carried into the reaction zone by convection. In hydrocarbon combustion this thermal diffusion is dominated by the H atom which has a large diffusion length owing to its size. This leads to the production of the hydroperoxyl radical, $\dot{H}O_2$, which is then converted to hydrogen peroxide, H_2O_2 . Due to the low temperatures, H_2O_2 decomposition does not occur here but instead is transported into the reaction zone by convection.
- 2) Reaction zone: This is the visible part of a flame and is characterised by high temperatures and high concentration of radicals and intermediate species. In the early reaction zone, fuel decomposition occurs due to the high concentration of radicals. Chain branching and propagation reactions dominate leading to an increase in temperature and production of fuel intermediate species. The decomposition of H_2O_2 to two hydroxyl ($\dot{O}H$) radicals is a key chain branching pathway in this region.
- 3) Post-flame Zone: Intermediate species and remaining radicals recombine to produce the major combustion products (CO_2 and H_2O in hydrocarbon combustion). The composition of the burned gas approaches chemical equilibrium with the Gibbs free energy of the system approaching a minimum.

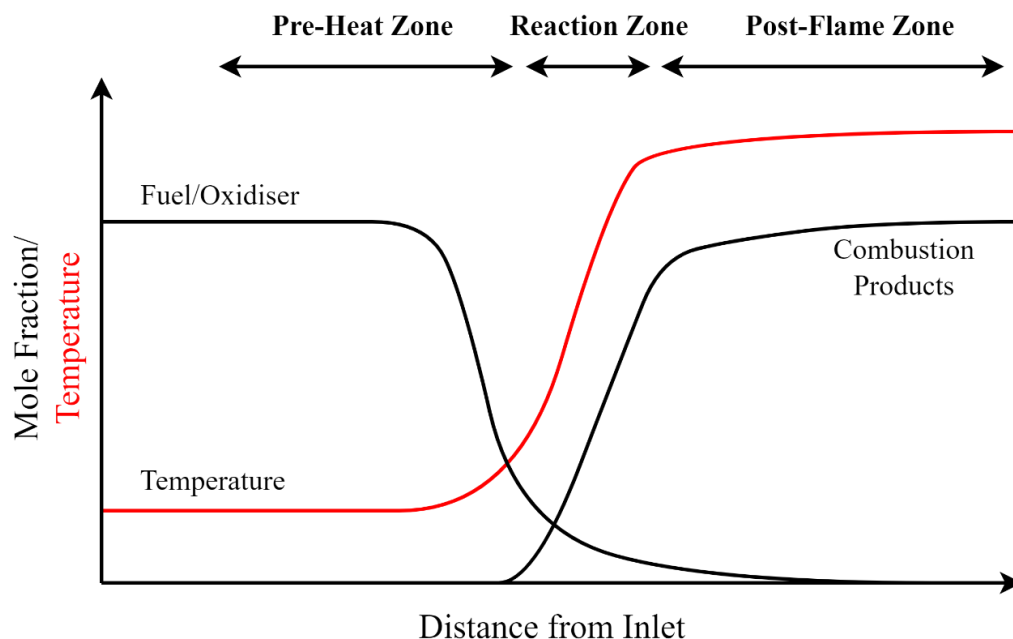


Figure 2.7. Structure of a 1-D laminar premixed flame showing species mole fraction and temperature across the pre-heat, reaction, and post-flame zones.

When simulating a 1-D laminar flame, a high level of resolution is necessary in the reaction zone due to the strong temperature and species concentration gradients. Additionally, due to the large number of species present in considerable concentrations, this zone is the root of computational “stiffness”. Computational stiffness refers to cases where the numerical method for solving a set of differential equations is numerically unstable. In the context of this work, this refers to calculations whereby finding the solution of the differential system proves difficult and results in an increased time for computation. This is partly due to the range in chemical timescales associated with each species varying by orders of magnitude, leading to a difficulty in finding a suitable solution.

The mass, energy, and species conservation equations are now expressed in spatial terms and are solved at each axial position (“grid point”). The derivation of these conservation equations in dimensional cases is non-trivial and reported in detail in many publications such as [18, 21-23]. As this is a one dimension steady-state problem, the equations simplify considerably.

The conservation of mass now states that the mass of a fluid passing through a point, a , in time t , must equal the mass of the same fluid passing through a second point, b , in time t ,

$$\rho_a A_a v_a = \rho_b A_b v_b \quad (2.64)$$

where v is the velocity of the fluid and A is the cross-sectional area at each point. Hence, the mass flow rate of a fluid in one-dimension is constant and can be defined as,

$$\dot{M} = \rho A v \quad (2.65)$$

Similarly, the conservation of species now reads,

$$\dot{M} \frac{dY_k}{dx} + \frac{d}{dx}(\rho A V_k Y_k) = A \dot{\omega}_k W_k \quad (2.66)$$

where x denotes the spatial axis and V_k is the diffusion velocity of species k . The conservation of energy for a 1-D system can be written as,

$$\dot{M} \frac{dT}{dx} + \frac{1}{C_p} \frac{d}{dx} \left(\lambda A \frac{dT}{dx} \right) + \frac{A}{C_p} \sum_{k=1}^{N_s} \rho Y_k V_k C_{p,k} \frac{dT}{dx} + \frac{A}{C_p} \sum_{k=1}^{N_s} \dot{\omega}_k W_k h_k = 0 \quad (2.67)$$

where λ is the thermal conductivity of the mixture. This energy equation now accounts for the energy flow coming from heat conduction (second term in the equation) and the energy flow from species diffusion (third term in the equation).

The laminar burning velocity (or laminar flame speed), S_u , defined as the velocity at which the flame propagates towards the unburned gases, is an important property of a flame providing insight into the global reactivity of the fuel, encapsulating the rate of reaction and overall energy of the flame. It is a fundamental characteristic of the mixture's combustion behaviour, providing an insight into the reaction mechanism, diffusion rate and heat release rate [24, 25]. Computationally, the laminar burning velocity is defined as the inlet burning velocity in a 1-D freely propagating flame calculation. As this property considers the effect of both kinetics and species transport, it is a commonly used metric to evaluate the accuracy of a simulation to experiment.

In Cantera, a freely propagating flame is modelled using the *FreeFlame* class. Figure 2.8 shows a typical result from freely propagating flame calculations. A freely propagating flame is solved using a grid-refinement approach. The solution is first solved on a coarse grid to get an approximate solution. The grid is subsequently refined by inserting additional points between the previous grid points. This continues until the resolution is below a pre-defined threshold. These thresholds are the maximum allowed variation in the solution between grid

points. In Cantera, these thresholds are called *Slope* and *Curve*. Therefore, the curves shown in Figure 2.8 (a), (b), and (f) represent a fit to a large number of closely spaced data points. In this thesis, slope and curve values of 0.02 are used to produce a fully resolved and converged solution. It is important that these values are set adequately small to ensure a converged solution and an independence between the number of grid points and the solution. Both mixture-averaged and multicomponent transport are used, depending on the fuel.

Figure 2.8 (a) and (b) show the flame temperature and mole fraction of important species as a function of the distance from the gas inlet. These simulations are performed using a mixture with an equivalence ratio of one (i.e., stoichiometric). The pre-heat, reaction and post-flame zones are readily seen here. Figure 2.8 (c) and (d) show the effect of the equivalence ratio on the temperature and maximum mole fraction of selected important species. Similar to PSR calculations, the maximum enthalpy of the flame occurs at slightly rich conditions, and as the fuel/air mixture becomes more fuel-rich, the concentration of CO increases. Figure 2.8 (e) show the laminar burning velocity (S_u) as a function of equivalence ratio and pressure. A similar trend is observed here to that observed of the flame temperature, with the maximum S_u occurring at slightly rich conditions. An increase in pressure results in a decrease in S_u due to a reduction in flame thickness (distance between unburned and burned gas) caused by an increase in gas density and viscosity. As a result, the diffusivity lengths of radicals decrease, which limits their penetration into the burned gas region, leading to a smaller preheat and reaction zone. This results in a decrease in the velocity at which the flame front propagates towards the unburned gas. This can be readily seen in Figure 2.8 (f) where the fuel and CO_2 mole fraction in a flame at 1 atm (solid line) and 10 atm (dashed line) is plotted.

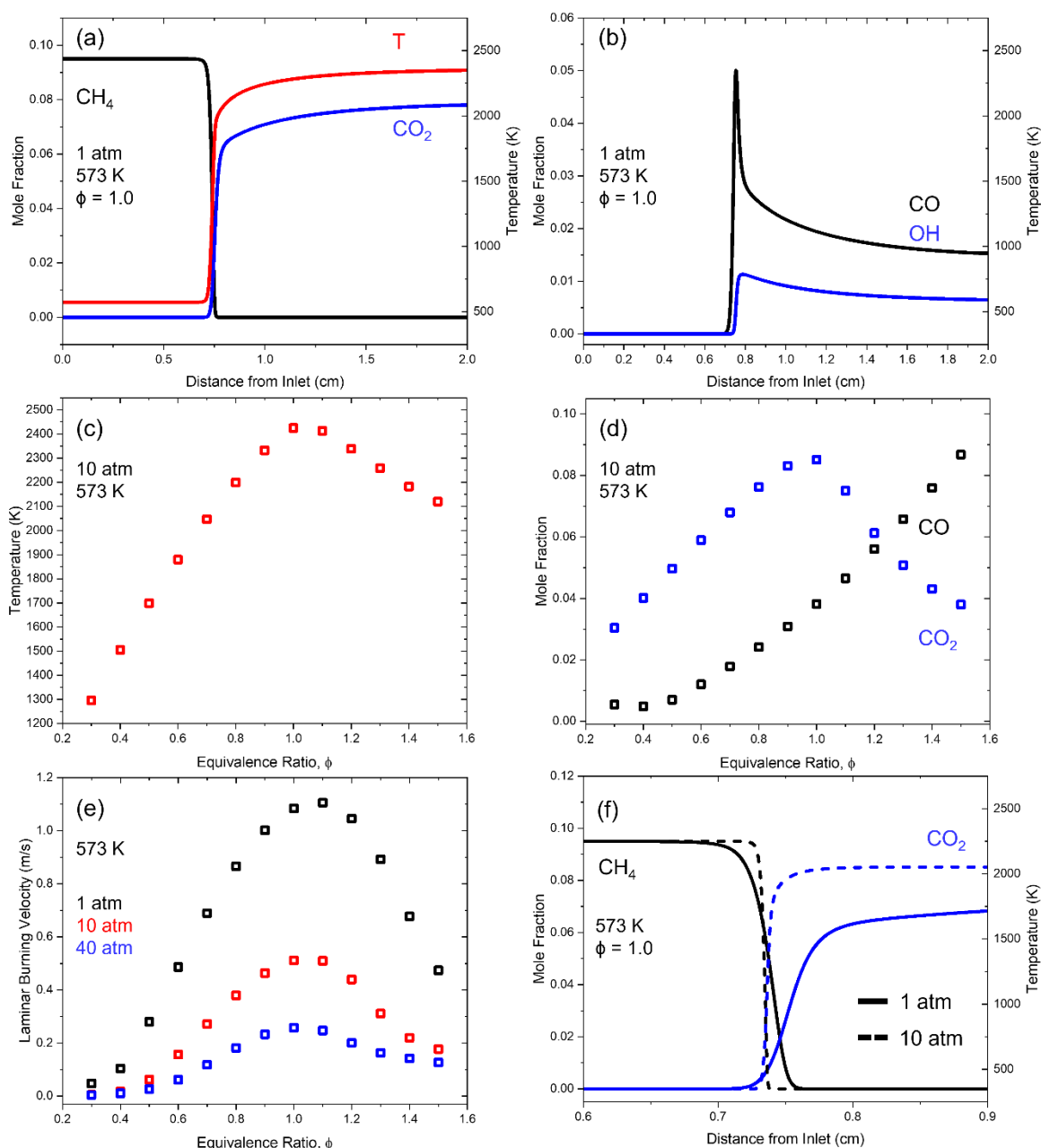


Figure 2.8. Results from freely propagating flame simulations using methane/air mixtures at unburned gas temperature of 573 K. (a) and (b) show the flame structure at 1 atm and stoichiometric conditions. (c) and (d) show the effect of fuel/air equivalence ratio at 10 atm on the temperature and the maximum mole fraction of CO and OH. (e) shows the effect of fuel/air equivalence ratio and pressure on the laminar burning velocity. (f) shows the difference in fuel and CO_2 between a flame at 1 atm (solid line) and 10 atm. This shows the decrease in flame thickness as pressure increases due to the reduced radical diffusion lengths into the unburned gas.

Chapter 3

Chemical Kinetic Models for Combustion

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3.1 Introduction

To perform a numerical combustion simulation on a specified fuel mixture, a description of the reaction mechanism of the fuel molecule(s) as it undergoes combustion is needed. This must include a list of each reaction occurring in the process, along with the corresponding

rate at which the reaction proceeds as a function of reactant concentration and temperature of the mixture. This information is provided in the form of a chemical kinetic model.

A chemical kinetic model is a mathematical representation of the underlying chemical reaction mechanism, which is the fundamental phenomenon underpinning combustion and emission properties. It provides a path from global reactants to products, using a collection of reactions for the specific fuel molecule. Over the years, the ChemKin [7] format of kinetic model has grown to become the community standard format compatible with the computational methods of both developers and users in commercial computational fluid dynamic (CFD) codes. In this format, the kinetic model comprises four components:

- 1) A reaction mechanism (or reaction network) which lists the elements, chemical species and reactions to be considered.
- 2) A reaction kinetics component containing Arrhenius reaction rate constant parameters (A , n , and E_A) for each reaction which are used to calculate the rate at which each reaction proceeds as a function of temperature, pressure, and reactant concentration.
- 3) Molecular thermodynamics descriptors for each species with which the changing thermodynamic state of the reacting gas and reaction equilibria can be calculated. This includes the NASA polynomial coefficients for each chemical species, from which the heat capacity, enthalpy, and entropy can be computed.
- 4) Molecular transport descriptors for each species which describe the transport of mass and energy across the changing state of the gas. This includes the definition of the Lewis-Jones collision diameter, potential energy well depth, and molecular weight for each chemical species.

3.2 Detailed Kinetic Models

Detailed chemical kinetic models describe the actual reaction mechanism of a molecule at a fundamental level. The inputs in the kinetics, molecular thermodynamics and molecular transport components are obtained from careful experimentation and/or complex theoretical calculations. Detailed chemical kinetic models are conceptually attractive, as they are almost completely condensable to chemical reaction and molecular thermodynamic theories. Their

elaboration over the past few decades has been encouraged by the maturation of computational tools that implement electronic structure (e.g., density functional theories) and other chemical theories (e.g., transition state theory) to determine much of the reaction mechanism and reaction kinetic components of a model to close to quantitative accuracy (e.g., [26-30]). Additionally, the development of automatic tools for reaction mechanism generation (e.g., MOMOX [31], EXGAS [32], RMG [33]) and the increase in the number of species that can be efficiently resolved in the reacting flow, has led to an acceleration in the production of detailed models for heavy molecular weight molecules from research groups such as Combustion Chemistry Centre Galway [34], CRECK Modelling Group [35], and Lawrence Livermore National Lab [36], to name but a few. These models contain thousands of discrete chemical species. A detailed description of the construction of detailed kinetic models can be found in the paper by Curran [5].

However, a lesson from this dramatic progress has been a questioning of the cost-benefit trade-off between the human time taken to gather this detail and the computational time needed to solve it, versus the knowledge value offered to combustor design. Lu and Law [37] demonstrated that the computational cost, C , of performing a transient dimensional simulation scales with the number of chemical species in the kinetic model, N_s as,

$$C \propto \alpha N_s + \beta N_s^2 + \gamma N_s^3 \quad (3.1)$$

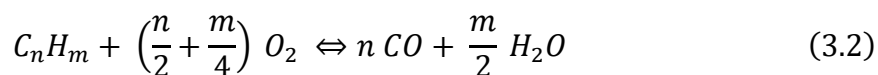
where α , β , and γ are coefficients for the rate evaluation, species diffusion and Jacobian factorisation respectively. This non-linearity between number of species and computational cost presents difficulties when performing simulations using detailed chemical kinetic models, which for real fuel compositions can detail thousands of discrete species.

Hence, due to the complexity involved in reacting flow simulations, kinetic models in excess of approximately one hundred species are of limited utility for engine design purposes. Thus, to allow for rapid iterative deployment of multi-dimensional reacting flow simulations in combustor design process, much smaller kinetic models are needed. However, these must retain a predictive fidelity in the computation of key performance quantities of interest relative to a fully detailed description. Several methods have been developed with this aim.

3.3 Global Mechanisms

Global mechanisms are *ad hoc* kinetic models that provide a description of the combustion event typically using a two-, three- or four-step reaction scheme containing less than ten chemical species (e.g., [38-43]). They are constructed with the aim of recovering specific macroscopic properties, such as the laminar burning velocity, the temperature profile of a flame, and/or the adiabatic flame temperature, across narrow ranges of operating conditions.

A global mechanism typically consists of a fuel oxidation reaction which produces one or more intermediates, followed by a reaction in which the intermediate reacts to form a global combustion product. In the example of a hydrocarbon,



The complexity can be increased by the production of more intermediates in Equation 3.2, which can in turn participate in additional reactions. The Arrhenius parameters of these mechanisms are typically fitted to reproduce the limited target set of calculations, using manual adjustment or optimisation algorithms, which will be discussed later in this Chapter. A major downside of global mechanisms is that speciation data is not obtainable, as the intermediate species do not intend to replicate the actual real species behaviour. Due to the lack of complexity in the reaction network, these mechanisms are only valid for a small set of calculations.

3.4 Virtual Chemistry

A revised global reaction description method, and one similar in philosophy to the approach undertaken in this thesis, is the *Virtual Chemistry* methodology proposed by Cailler et al. [44]. This method aims to address the inability of global mechanisms to recover speciation data.

In this approach, a mathematical architecture is constructed to reproduce user-specified properties using *virtual* species. These species are connected by *virtual* reactions, which do not represent physical chemical processes. The concept, as shown in Figure 3.1, is to have a

core reaction mechanism that can accurately retrieve macroscopic properties such as adiabatic flame temperatures using two or three reactions involving the fuel, oxidiser, and *virtual species*, similar to a global mechanism. This scheme typically takes the form of fuel oxidation to produce an intermediate virtual species, I , which then converts to a combination of N_P virtual products, P , as,



A virtual scheme of this type, containing eight virtual species, has been demonstrated to accurately capture adiabatic flame temperature and heat release for a range of hydrocarbon fuels [45]. Additional satellite mechanisms, containing additional virtual species and reactions can be created and appended to this core reaction mechanism to retrieve speciation data such as CO [45], NO [46] and soot [47] concentrations in a premixed laminar flame.

The thermodynamic properties for the virtual species are obtained by optimising the NASA polynomial coefficients to mixture-averaged thermodynamic properties from a reference database, typically detailed model calculations, using a genetic algorithm. The chemical reaction rates used in this scheme are in an Arrhenius-type formulation. Correction functions, f_i^v , which are functions of mixture fraction, are employed to improve the accuracy of the model. For example, the reaction rates for reactions in Equations 3.4 and 3.5 are generally expressed as,

$$K_1 = f_1^v A_1^v e^{\left(-\frac{E_{A,1}^v}{RT}\right)} [Fuel]^{F_{Fuel,1}} \quad (3.6)$$

$$K_2 = A_2^v e^{\left(-\frac{E_{A,2}^v}{RT}\right)} [I]^{F_{I,2}} f_2^v \quad (3.7)$$

where superscript v denotes that the term is virtual and $F_{k,r}$ denotes the forward reaction order of the k^{th} species in the r^{th} reaction. The use of correction functions enables the accuracy of the model to be maintained across wide equivalence ratios which would otherwise not be possible using such a simplified reaction scheme. Despite the encouraging results shown by this methodology, the use of such correction functions means that the

kinetic models are unable to be used in industry-standard software, such as ChemKin and Cantera, without the modification of the solvers, which is a non-trivial task.

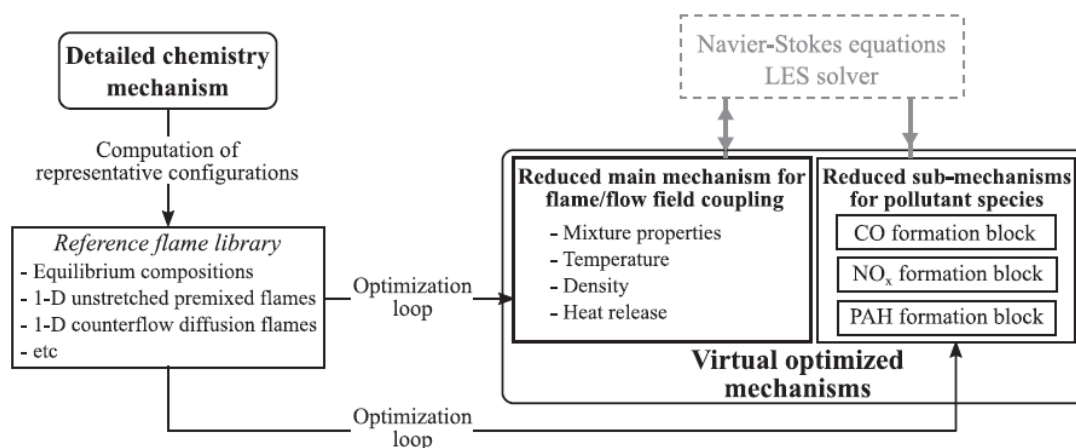


Figure 3.1. The architecture of a Virtual Chemistry mechanism consists of a core mechanism that replicates macroscopic properties and additional satellite mechanisms that may retrieve speciation data. Extracted from Cailler et al. [45].

3.5 Reduced and Skeletal Models

An alternative approach is the use of *reduced* and *skeletal* models. These are produced by applying model reduction algorithms to a detailed model to remove chemical species and reactions which are not necessary in the computation of a set of detailed model calculations to a desired accuracy.

There are two categories of reduced models, depending on the degree of reduction performed on the parent detailed model. Definitions for such models vary, however generally they can be defined as,

1. **Skeletal models/mechanisms** are produced through a conservative reduction on a detailed model, meaning only species and reactions with very low importance to the pertinent calculations are removed from the reaction mechanism. As these models still contain a considerable number of intermediate species, a realistic description of the physically occurring reaction mechanism is provided and hence an accurate replication of the detailed model calculations. However, due to the considerable number of species retained in the model and transported in the flow, these models

are typically not suitable for efficient use in multi-dimensional simulations such as CFD.

2. **Reduced models** are produced through aggressive application of model reduction algorithms. Only species whose removal would incur a significant perturbation on the target calculations are retained in the reaction network component. Due to the removal of important intermediate species, these models are only valid to a specific set of calculations. The greater the number of species removed from the reaction mechanism component of the detailed model, the more limited the set of calculations these models are valid for, and the lower the overall fidelity of model calculations to the detailed model. This simplification means that these models typically require optimisation of the Arrhenius parameters to regain fidelity that is lost in the removal of important reaction pathways.

As the work in this thesis involves reduced models, a more detailed discussion of model reduction techniques is now presented.

3.6 Model Reduction Techniques

Model reduction is the science of removal of low importance species and reactions from the reaction network of a detailed kinetic model, whilst not significantly diminishing the fidelity of the resulting model calculations. Methodologies to achieve this have received significant attention and are a mature field being reviewed several times (e.g., [37, 48, 49]). Common techniques used to reduce a detailed model are given below, categorised by the type of approach on which they are based.

1. Reaction Flux Based Methods:

- Elemental flux analysis [50-53] quantifies the elemental flux through each species during a calculation. Species with a low elemental flux are removed.
- The direct relation graph (DRG) technique, developed by Lu and Law [54], calculates the importance of each species on the net reaction flux of a set of

important (“*target*”) species, displaying the results graphically. Weakly coupled species to the target species are removed.

- Direct relation graph aided sensitivity analysis (DRG-ASA) [55] includes measurements of the error induced by the removal of each species.
- Direct relation graph with error propagation (DRGEP), developed by Pepiot and Pitsch [56, 57], measures the effect of the error induced by the removal of one species on every other species and captures how that error propagates to the target species, capturing indirect relationships between species.
- Path flux analysis (PFA), developed by Sun et al. [58, 59], quantifies the importance of each species on the production and consumption fluxes of every other species and how this affects the production/consumption fluxes of the target species.
- Global Pathway Selection (GPS), developed by Gao et al. [60], computes the elemental flux through each species, identifies important species (“*hub species*”) through which considerable elemental flux passes, and retains all species that participate in reactions that contribute considerably to the production and consumption rates of the hub species.

2. Chemical Lumping:

- Chemical species with similar reactivity and structure are combined to create a new *lumped* species whose concentration is a mathematical function of the species that make it up. e.g., [31, 61-67].
- Lumping of fuel pyrolysis products [68-72] and large carbon number species [73, 74] whilst retaining a detailed reaction mechanism of low carbon number and low molecular weight species.

3. Jacobian and Time Scale Analysis Based Methods:

- The study of rate sensitivities to deduce *redundant species* whose removal from the system will not significantly affect the production or consumption of an *important* species or target calculation e.g., [48, 75-77].
- Principal component analysis [78-81], a machine learning technique, performed on the sensitivity matrix to extract meaningful kinetic information from an array of

concentration sensitivity coefficients for species in a reacting system at various time points, to identify unimportant reactions and species.

- Computational singular perturbation (CSP) approach [82-85] groups together reactions with similar time-scales and represents them with a single characteristic time scale and group reaction rate. Modes that contain no important species can be eliminated.
- Intrinsic low-dimensional manifolds (ILDM), proposed by Maas and Pope [86], decouples the slow and fast consumed species through Jacobian analysis, similar to CSP. Low-dimensional manifolds are found that represent the slow timescale reactions which is used as an approximation for the behaviour of the system, under the assumption that fast-moving dynamics are less important as they average out over longer time scales.
- Quasi-steady state approximation (QSSA) [87-90] approach identifies species with very short chemical time-scales such that their rate of formation is much slower than their rate of consumption and places them in *steady state*. The concentration of a species in QSS is a function of one or more transported species' concentrations.

4. Optimisation Based Methods:

- The use of optimisation algorithms, to deduce the optimum subset of reactions or species e.g., [91-101]. Machine learning algorithms are most commonly deployed such as genetic algorithms and the application of neural networks.

Model reduction algorithms pertinent to the work in this thesis are now discussed in more detail.

3.6.1 Direct Relation Graph with Error Propagation (DRGEP)

The direct relation graph method (DRG) was developed by Lu and Law [54] to identify species that are unimportant in the calculation of the concentration of a set of important species, with the results displayed graphically as a network. There have been many variations

and improvements to this method over the years to improve the performance and efficiency of the method. One such adaptation is the direct relation graph with error propagation (DRGEP) method [56, 57], which has been implemented in this work.

For each species ‘A’ in the kinetic model, the strength of the interaction between ‘A’ and every species that appears in a reaction involving ‘A’ is calculated. This is called the primary dependent set of ‘A’. The strength of the primary interaction between species ‘A’ and ‘B’ is quantified by the primary interaction coefficient, r_{AB} , as,

$$r_{AB} = \frac{\sum_{i=1}^I |v_{A,i} \dot{\omega}_i \delta_{B,i}|}{\sum_{i=1}^I |v_{A,i} \dot{\omega}_i|} \quad (3.8)$$

where subscript i denotes the i^{th} reaction and $\delta_{B,i}$ is the Kronecker symbol, which equals 1 if ‘B’ participates in the i^{th} reaction and 0 otherwise.

In reaction mechanisms, it is common that a species may have an influence on another species despite not explicitly participating together in a reaction, for example ‘C’ with ‘A’ on Figure 3.2. Therefore, if ‘C’ is removed, the error will propagate to ‘A’ through ‘B’. To capture this propagation of error, path dependent coefficients are defined as,

$$r_{AC,i} = r_{AC} r_{BC} \quad (3.9)$$

Additionally, a species can be coupled to another species through multiple pathways, for example ‘D’ to ‘A’ in Figure 3.2. Therefore, to quantify the total influence of a species on another, the generalised interaction coefficient is defined as,

$$R_{AB} = \max_{all\ i} \{r_{AB,i}\} \quad (3.10)$$

For the example of ‘D’ to ‘A’,

$$R_{AD} = \max\{r_{AB} r_{BD}, r_{AD}\} \quad (3.11)$$

To perform a DRGEP reduction, a set of important species, whose production rate must be accurately replicated, is defined as the target set. The above procedure is then performed to quantify the coupling between each species in the model and the target species. An error threshold, ϵ , is set and all species with a generalised coefficient less than ϵ are removed from the model. This is performed for each target species and the final reduced model is the union of all these subsets. The larger the value of ϵ , the more species that are removed. Using the

example of Figure 3.2, if ϵ is set equal to 0.05, species ‘B’ ($R_{AB} = 0.15$) and species ‘D’ ($R_{AD} = 0.06$) would be retained, however species ‘C’ ($R_{AC} = 0.03$) would be removed. In the original DRG method, the propagation of error isn’t evaluated, and all species would be retained, as $r_{BC} > \epsilon$ and $r_{BD} > \epsilon$.

Next, reactions that do not contribute considerably to the chemical rate of the retained species are removed from the reaction network to further decrease the computational cost of the reduced model. The normalised rates of production and consumption for each species k through each reaction i is calculated as,

$$P_{k,i} = \frac{|\max(0, v_{k,i})\dot{\omega}_i|}{\sum_{i=1}^I |\max(0, v_{k,i})\dot{\omega}_i|} \quad (3.12)$$

$$C_{k,i} = \frac{|\min(0, v_{k,i})\dot{\omega}_i|}{\sum_{i=1}^I |\min(0, v_{k,i})\dot{\omega}_i|} \quad (3.13)$$

These values are then sorted and for a threshold ϵ_r , there exists an index J such that,

$$\frac{\sum_{i=1}^J (P_{k,i})}{\sum_{i=1}^I (P_{k,i})} \text{ and } \frac{\sum_{i=1}^J (C_{k,i})}{\sum_{i=1}^I (C_{k,i})} > \epsilon_r \quad (3.14)$$

Reactions 1 to J are retained in the reduced model.

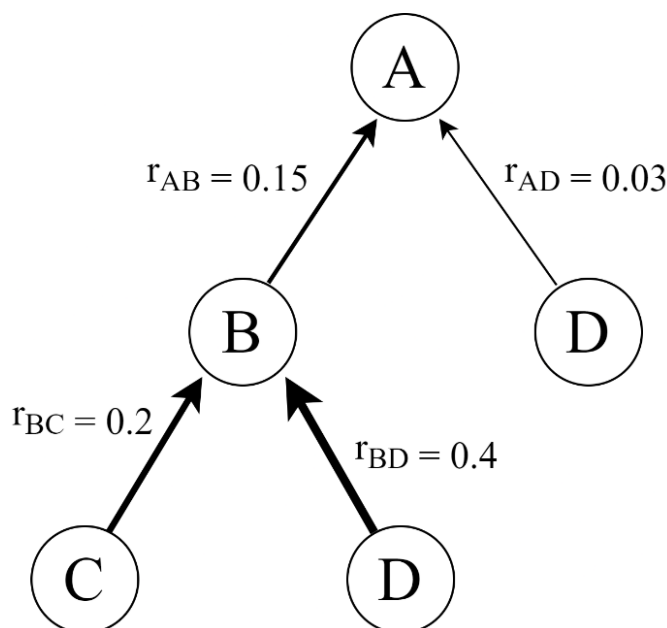


Figure 3.2. A direct relation graph for four species, where species A is the target. If an error threshold value of 0.05 is set, species C is removed by DRGEP while species B and D are retained.

3.6.2 Path Flux Analysis (PFA)

Path flux analysis, developed by Sun et al. [58], is similar in approach to DRG methods, using *interaction coefficients* to quantify the importance of each species. In PFA however, production and consumption fluxes are used in the calculation of interaction coefficients rather than net reaction rates. This provides a more accurate depiction of the flow of flux through the system, primarily by capturing the effect of intermediates, especially those with a large production and consumption rates, typical of catalysts. In DRG these would not be detected as the net reaction rate is close to zero, however, by considering both production and consumption fluxes, the effect of these types of species is easily detected. Additionally, similar to the concept of DRGEP, PFA considers the effect of species that have an impact on the target species despite not directly participating in reactions together.

To obtain the interaction coefficients, the production and consumption fluxes of species ‘A’ due to the presence of species ‘B’, P_{AB} and C_{AB} , are defined as,

$$P_{AB} = \sum_{i=1}^I \max(v_{A,i} \omega_i \delta_{B,i}, 0) \quad (3.15)$$

$$C_{AB} = \sum_{i=1}^I \max(-\nu_{A,i} \omega_i \delta_{B,i}, 0) \quad (3.16)$$

where similar to DRG, $\delta_{B,i}$ represents the Kronecker symbol. The first-generation “primary” production $r^{pro-1st}$ and consumption $r^{con-1st}$ interaction coefficients are given as,

$$r_{AB}^{pro-1st} = \frac{P_{AB}}{\max(P_A, C_A)} \quad (3.17)$$

$$r_{AB}^{con-1st} = \frac{C_{AB}}{\max(P_A, C_A)} \quad (3.18)$$

The second-generation fluxes which quantify the relationship between species ‘A’ and ‘B’ via an intermediate ‘ M_n ’ are given as,

$$r_{AB}^{pro-2nd} = \sum_{M_n \neq A, B} (r_{AM_n}^{pro-1st} r_{M_n B}^{pro-1st}) \quad (3.19)$$

$$r_{AB}^{con-2nd} = \sum_{M_n \neq A, B} (r_{AM_n}^{con-1st} r_{M_n B}^{con-1st}) \quad (3.20)$$

Although this can be extended to higher order generations, the computational cost scales as (species number)^{generation} and as such second-generation fluxes are deemed adequate in most cases. The net interaction coefficient r_{AB} , is then a simple summation of first and second-generation production and consumption interaction coefficients, providing a quantification of the importance of species ‘B’ on species ‘A’,

$$R_{AB} = r_{AB}^{pro-1st} + r_{AB}^{con-1st} + r_{AB}^{pro-2nd} + r_{AB}^{con-2nd} \quad (3.21)$$

Similar to DRG, a set of target species is selected and an error threshold, ϵ , is set. Species with a net interaction coefficient with a target species greater than ϵ are retained in the reduced model. Hence, the larger the value of ϵ , the more species that are removed from the model.

An interaction graph is shown in Figure 3.3, which has been adapted from [58] with the aim of highlighting the difference between DRG, DRGEP and PFA. Consider a scenario where one is aiming to produce a model with five (or less) species. In the case of DRG, ϵ should be set to equal 0.395. First, species ‘ M_4 ’ is selected due to its strong coupling to ‘A’ ($r_{AM_4} = 0.4$). From this, ‘ M_5 ’ is selected due to its strong coupling to ‘ M_4 ’ ($r_{M_4 M_5} = 0.9$)

and finally ‘C’ is selected due to its strong coupling to ‘M₅’ ($r_{M_5C} = 1$). In DRGEP ε should be set to equal 0.355 and the same species will be selected. Firstly, ‘M₄’ is selected ($R_{AM_4} = 0.4$), then ‘M₅’ ($R_{M_4M_5} = 0.36$), followed by ‘C’ ($R_{M_5C} = 0.36$). Species ‘B’ would not be selected however, as despite DRGEP considering indirect coupling, the flux is not summed between channels ($R_{AB} = 0.14$). In the case of PFA, ε should be set to equal 0.41. First ‘B’ is selected ($R_{AB} = 0.42$), due to the summing of the first and second generational fluxes through ‘M₁’, ‘M₂’, ‘M₃’, which are also selected. Therefore, in this hypothetical and simplified scenario, DRG and DRGEP both fail to identify the large contribution of species ‘B’ through the intermediates ‘M₁’, ‘M₂’, ‘M₃’.

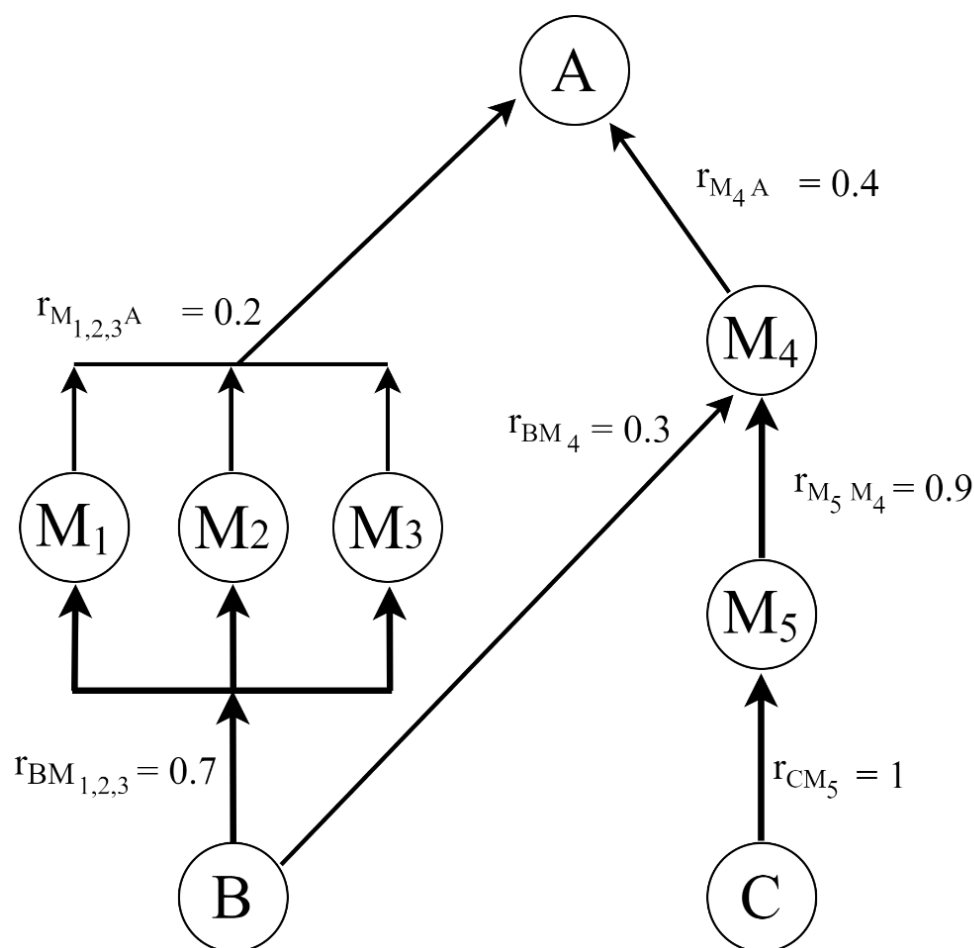


Figure 3.3. An interaction graph showing the flux relation between eight chemical species.

3.6.3 Hybrid Chemistry (HyChem)

Decades of experimentation and theory (e.g., [102-105]) have revealed that the formation of intermediate species with distinct chemical functionalities plays a crucial role in the combustion behaviour of large hydrocarbon molecules commonly found in liquid transportation fuels, such as diesel and kerosene. These intermediates contribute to the formation of important radical species, which, in turn, determine the combustion behaviour of the fuel molecule [106, 107]. For example, Ranzi et al. [108] found that the laminar flame speed of a large range of fuels is dominated by the reactivity of small molecular weight species and radicals. A similar conclusion was reached by Ji et al. [109] in terms of the extinction strain rate.

Following this logic, if one can accurately describe the formation and decomposition rate of the intermediate species, a good replication of the radical pool will be produced. the high-carbon fuel oxidation chemistry is not entirely needed resulting in an accurate replication of combustion kinetic behaviour of the large hydrocarbon fuel. Hence, a detailed description of the higher-carbon fuel oxidation chemistry is not strictly needed.

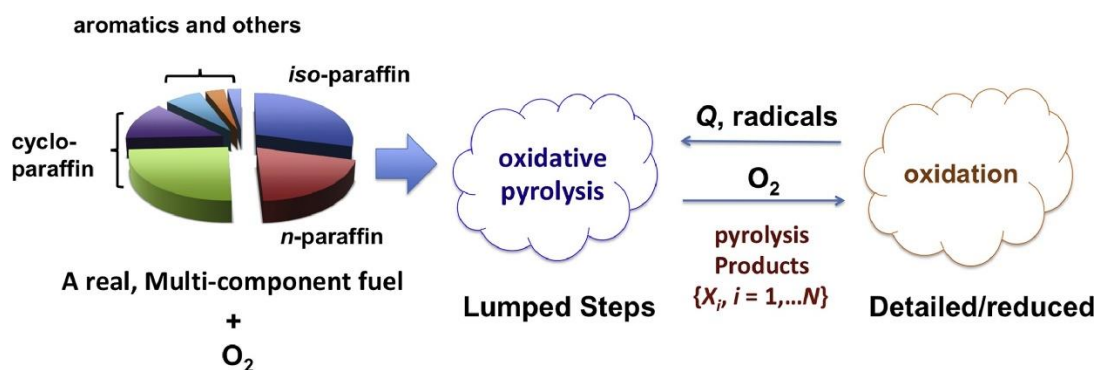
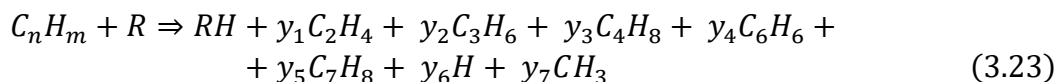
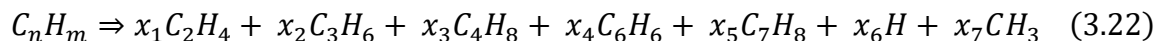


Figure 3.4. Schematic diagram of HyChem methodology. In this approach, a lumped description of fuel thermal decomposition and oxidative pyrolysis is utilised. From Wang et al. [70].

In recent years several methods have been emerged building on this idea [74, 106, 107]. One such method is the Hybrid Chemistry (HyChem) methodology by Wang et al. [69-72]. This method, as shown in Figure 3.4, combines a lumped description of fuel thermal decomposition and oxidative pyrolysis with a fully detailed description of the pyrolysis and oxidation of the fuel decomposition products. This leverages the knowledge that at high

temperatures, large hydrocarbons undergo pyrolysis first, followed by oxidation of the fuel pyrolysis products with the aforementioned knowledge that the kinetic behaviour of the fuel is driven by the radical pool. The pyrolysis process for a large hydrocarbon is described using a small number of reactions in the form of,



where R is (H, O, OH, HO₂, CH₃, O₂) and x_{1-7} and y_{1-7} are coefficients, dependent on fuel-type that ensure elemental conservation and stoichiometry.

The reaction mechanism of the pyrolysis products is described using a core mechanism, which is a detailed model typically for C₀-C₄ chemistry. Hence, one can significantly reduce the number of species needed to accurately describe high temperature chemistry for complex real fuel mixtures from the order of a few thousand to the order of hundreds.

3.6.4 Quasi-Steady State Approximation (QSSA)

Quasi-steady state has been employed to simplify kinetic systems for over a century, first proposed by Bodenstein in 1913 [87], however, it was only 30 years ago that a systematic methodology was proposed by Peters and Key [90] to apply the technique to reaction mechanisms.

In kinetic models there is significant variation in chemical timescales associated with different species, with some species reaching equilibrium orders of magnitude quicker than others, leading to numerical stiffness in calculations. The root of this problem is the existence of fast depleting radicals that reach equilibrium quasi-steady state (QSS) quickly. This problem is particularly evident in detailed models where there are a large number of species participating in a complex reaction network. As a solution, the *quasi-steady state approximation* (QSSA) method was developed. This method relies on the identification of QSS species characterised by fast destruction timescales, meaning the production rate of the species is balanced by the fast consumption rate, and hence, the species is in effect present

in low concentrations. In other words, at realistic timescales the production rate of the QSS species can be approximated as,

$$\frac{dX_k}{dt} = \dot{\omega} \approx 0 \quad (3.24)$$

The concentration of these species can thus be approximated algebraically in relation to the concentration and reaction rate of other resolved species, thereby removing said species from the transport equations.

For example, consider the simple reversible reaction, $A + B \rightleftharpoons C$. The forward, K_f and reverse, K_r reaction rates can be expressed as,

$$K_f = k_f[A][B] \quad (3.25)$$

$$K_r = k_r[C] \quad (3.26)$$

If species ‘C’ is a fast-depleting radical with a balanced rate of formation and consumption, that reaches this steady-state much faster than ‘A’ or ‘B’, we can use the QSSA to make the approximation that $K_f = K_r$. Hence, the concentration of ‘C’ can be expressed as,

$$[C] = \frac{k_f}{k_r}[A][B] \quad (3.27)$$

Therefore, species ‘C’ can be removed from the conservation equations and the rates of reactions in which ‘C’ participates in are solved using the approximation in Equation 3.27. This removes computational stiffness and results in a lower computational cost of the calculations, whilst still retaining the species in the reaction mechanism. However, kinetic models that use this approximation are unusable in ChemKin or Cantera without modification of the solvers.

3.7 Problem Statement

Model reduction methodologies are intrinsically limited however, because as species are removed from the reaction network, the fidelity of the calculations decreases until a critical point of necessary detail is reached. After this point, further removal of species leads to a deterioration in the model performance. This is due to what I refer to as the “*over-reduction*” of the reaction network component, removing species that are important in mediating the

reaction flux through the system from reactants to products. The removal of too many of these species eliminates key reaction pathways which results in a severe compromising of the computed reaction flux to the authentic reality. I refer to this threshold as the “*limit of physical authenticity*”. Kinetic models produced by applying fundamental chemical and physical theories and processed through conventional model reduction techniques will show this limit.

For example, Figure 3.5 shows this limit to be approximately twenty-seven species for the methane system across a specific performance envelope. Fidelity is calculated based on the average relative error in calculations to the detailed model (NUIGMECH1.0 [11]), with a value of 100% indicating perfect replication of detailed model calculations. Ignition delay time is the time needed for a specific fuel mixture to ignite at a specific set of operating (temperature, pressure, fuel/oxidiser equivalence ratio) conditions. Computationally, this is defined as the maximum derivative temperature derivative time $\left(\frac{dT}{dt}\right)$ in a 0-D constant internal energy and volume reactor simulation.

This behaviour is observed using a series of kinetic models resulting from two separate reduction methodologies, demonstrating that the coupling is not unique to a specific model reduction technique but has its origin in the mechanics of the model construction. It can also be expected that the more complex the target set, over the wider range of conditions, the larger the number of species required to retain an accurate fundamental description of the reaction mechanism. However, kinetic models of the order of 20-50 species in size are still too large for efficient implementation in reacting flow CFD. There is, therefore, an Industry-driven need for kinetic models below this threshold that somehow still maintain high fidelity to the target combustion property set.

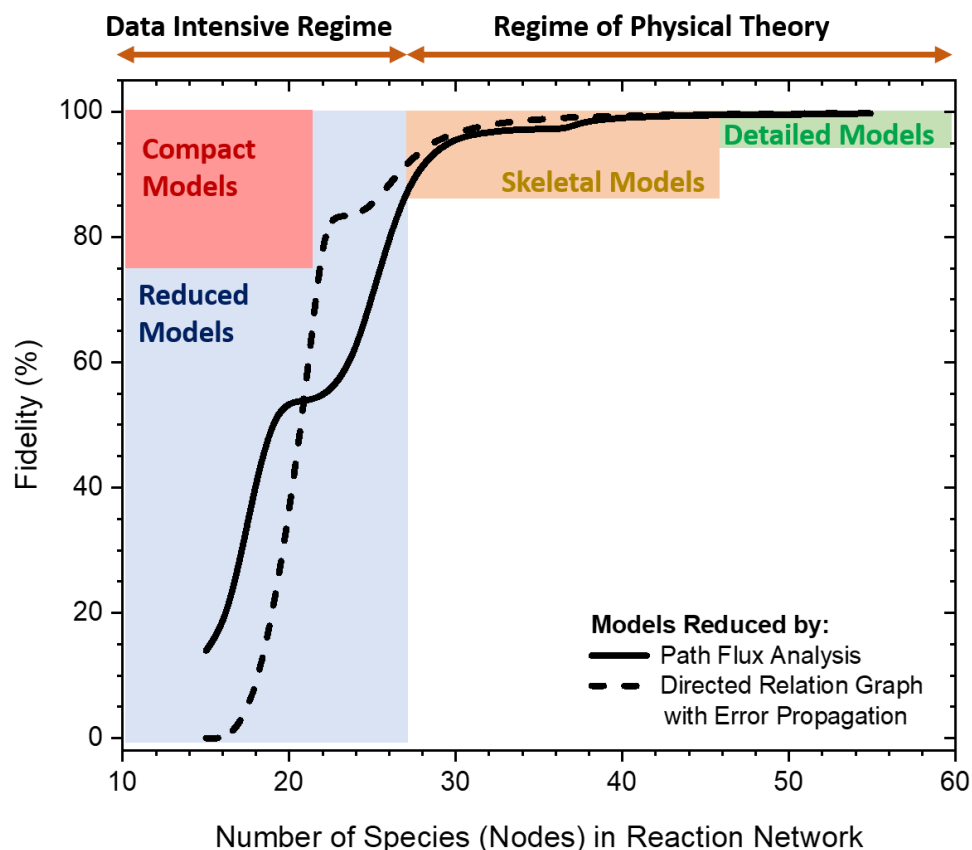


Figure 3.5. Dependence of fidelity of model calculation for methane/air combustion on complexity of reaction network, as indicated by number of species, where Detailed, Skeletal, Reduced and Compact Models occupy different regions of detail-fidelity space. A series of skeletal and reduced models are produced by the Directed Relation Graph with Error Propagation reduction method via DoctorSMOKE++ [110, 111], and by the Path Flux Analysis method from the same detailed model [11]. The reduction and fidelity assessment were performed at: 1-40 atm, 1100-2000 K, methane/air equivalence ratios 0.5 – 1.5.

3.7.1 Potential Solutions

The most common approach in the literature to produce an accurate kinetic model below this threshold is to apply analytical techniques to a reduced/skeletal model, such as the QSSA method, to solve specific species in the reacting flow via algebraic equations related to other species. This removes said species from the transport equations whilst retaining the degrees of freedom from their retention in the reaction network. This treatment can meaningfully reduce computational cost to a certain extent at the expense of the departure from the ChemKin format of reaction description. For instance, in the context of methane/air combustion, Lu and Law [112] employed DRG and DRGASA to reduce the GRI 3.0 [113] detailed model. This led to a skeletal mechanism consisting of 30 species, which was further simplified to 19 species by the application of QSSA to 11 species. Similarly, Cazères et al.

[114] reduced the GRI 3.0 detailed model to a skeletal mechanism comprised of 26 species using DRGEP. This was followed by the application QSSA to 10 species.

The challenge of balancing the complexity of reaction mechanism description with computational cost can be addressed through two distinct methods. The first, which is the focus of this thesis, involves reducing the complexity of the reaction mechanism description through the use of model reduction techniques. The second approach is to decrease the computational cost associated with a reaction mechanism of a particular complexity by modifying the solvers in industry-standard CFD codes to adjust the mathematical computations. This enables models with large numbers of species to be employed in CFD codes at a reduced computational expense. It is important to note that these two approaches are not mutually exclusive.

One such method is the use of machine learning techniques, commonly neural networks, to calculate chemical source terms at each time/axial step in place of solving the complex system of differential equations. Machine learning, a branch of artificial intelligence, encapsulates algorithms that can progressively improve in performance by processing data and information, such as linear regression, logistic regression, genetic algorithms, principal component analysis, random forests, and neural networks. A comprehensive review of machine learning for combustion can be found at [115-118]. A growing research area is the application of neural networks to accelerate the computation of combustion calculations through the prediction of chemical source terms (e.g., [119-131]).

In works of these types, neural networks are constructed, with the thermochemical state of the mixture used as the input and the chemical source terms or species concentration given as the output. Figure 3.6 shows an example of such a method taken from Wang et al. [129]. In this, the species mole fractions, and the temperature of the mixture is used as the inputs. There exist five hidden layers, each containing a number of *neurons* that are connected to neurons in the previous layer by *weights*. These weights are found by optimisation to a training set, typically detailed model calculations. This neural network outputs the rate of production for each species and the heat release rate. This application of neural networks can considerably reduce the computational cost of a simulation, especially in multidimensional cases, however, a number of challenges exist.

Neural networks are notorious for their unreliability when applied to test cases outside the scope of the training set, therefore, care has to be given to the composition of the training

set and the intended use of the model. Additionally, the computational cost in the construction of the data and validation sets is considerable.

Furthermore, the use of methods such as QSSA and neural networks produce a model that is no longer compliant to the ChemKin format. This makes the deployment of the model more difficult due to the requirement for additional sub-routines to be employed, or the otherwise modification of solvers in Industry-standard packages.

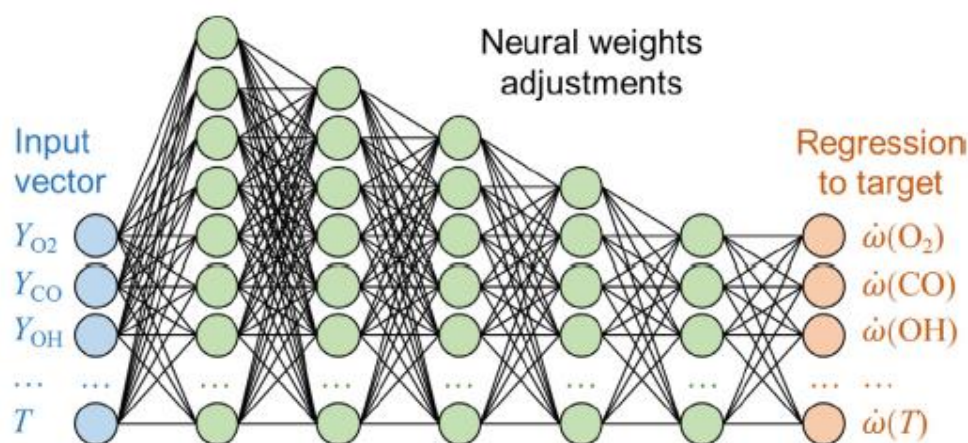


Figure 3.6. Illustration of an artificial neural network (ANN) with 5 hidden layers, that predicts the rate of species production and heat release rate using species mole fractions and temperature as the input. Extracted from Wan et al. [129].

3.8 Compact Models

Methods that would break the coupling between detail (species number) and accuracy of kinetic model calculations, whilst retaining the use of the standard ChemKin form of reaction description would be ideal. The retention of the standard ChemKin format is desirable to allow for easy and widespread use of such a model. This would enable straightforward implementation of highly-accurate, minimally-sized, kinetic models into multi-dimensional reacting flow simulations, thereby increasing their efficiency and utility in the combustor design process. The concept of a *Compact Model* is an attractive alternative concept that has the potential to meet this challenge.

In a compact model, only the minimum level of detail that is absolutely necessary to accurately reproduce the defined set of performance calculations is included in the reaction network. The errors that result, owing to the lack of detail in the model, are compensated for by optimisation of any of the reaction kinetic, molecular thermodynamic or mass/energy

transport descriptors comprising the model, which are each coupled determinators of the computed reaction kinetic combustion phenomena as outlined previously. In the next Chapter a more rigorous definition of a compact model than that found in the literature is proposed.

3.9 Kinetic Model Optimisation

Optimisation is a branch of mathematics that deals with algorithms that are constructed to find the optimal solution to a given problem. Optimisation algorithms evaluate sets of solutions and quantifies their goodness through the use of objective error functions.

An error function is a mathematical equation that calculates the error between the trial solution and the user-defined “*Optimisation Targets*”. The goal of the optimisation algorithm is to minimise this error function. Optimisation algorithms are used by the combustion community to improve the accuracy of kinetic models by the altering of the input parameters of one (or more) kinetic model components to maximise model fidelity to a given set of performance targets. Typically, this involves the optimisation of Arrhenius parameters of important reactions identified through sensitivity analysis. In other words, given a system of differential equations,

$$\frac{dy}{dt} = \mathbf{f}(y, t, \theta) \quad (3.28)$$

where y is the vector of state variables (temperature, pressure, species concentrations), t is time and θ is a set of Arrhenius parameters, and $\mathbf{f}$ is a function that describes the energy balance and mass-action law, the goal of optimisation works is to find a set of θ , such that,

$$y = \mathbf{f}(y_{t=0}, t, \theta) = y^{target} \quad (3.29)$$

where y^{target} is the optimisation targets, typically experimental data.

3.9.1 Detailed Model Optimisation

There are two distinct applications of kinetic model optimisation in literature. The first is as a method of uncertainty quantification and minimisation for detailed kinetic models. As the

Arrhenius parameters used in detailed kinetic models are either obtained through experimental or theoretical calculations, they have a sizeable associated uncertainty. Therefore, when the uncertainty of each reaction rate constant is combined, the resulting uncertainty in the kinetic model is significant and as a result, the model calculations often fail to replicate experimental observations to an acceptable degree of accuracy.

For example, Figure 3.7 shows direct rate coefficient measurements taken on the reaction $H + O_2 = O + OH$, as taken from Tomlin and Turyáni [132]. Even for this, the most important and well-studied reaction in combustion, one can see that the uncertainty range in the reaction rate constant is considerable, $\Delta \log(k) \approx 0.4$. The reaction rate constants are commonly varied within their uncertainty range to find a set of values that produce a kinetic model with a lower overall uncertainty and a better replication of experimental data. This application of kinetic model optimisation can be thought of as “fine-tuning”, meaning the reaction rate constants do not need to be significantly perturbed from the starting best-knowledge value to find the optimal set of parameters.

Most works of this type apply variants of the *solution mapping* method originated by Frenklach and Miller [133, 134]. This involves the generation of *response surfaces* for each optimisation target, whereby several simulations are performed for each optimisation target using kinetic models with different parameters. Using the results of these simulations, a relationship is developed between the result, or response of the system, η and the value of the parameters. This relationship commonly takes the form of a second order polynomial as,

$$\eta = b_0 + \sum_i b_i X_i + \sum_{i \leq j} b_{ij} X_i X_j \quad (3.30)$$

where the response surface coefficients, b , are obtained from fitting the set of simulations results to the system’s parameters and X_i is the *factorial variable* of the i^{th} reaction, which is a factorial transformation of the parameters.

There have been many developments to this method notably by Wang and co-workers [135-138], with the development of MUM-PCE and by Nagy and Turányi et al. [139] who made use of a more comprehensive range of direct and indirect experimental measurements as optimisation targets to reduce the uncertainty bounds of each Arrhenius parameter. The power of the solution mapping technique is the ability to use one-dimensional and other computationally expensive simulation results as optimisation targets for kinetic models with

large numbers of species. However, the response surface generated tends to be unable to replicate the level of complexity in the objective error function landscape and, as such, it should be noted that the response using the solution mapping technique is an approximation with a considerable uncertainty.

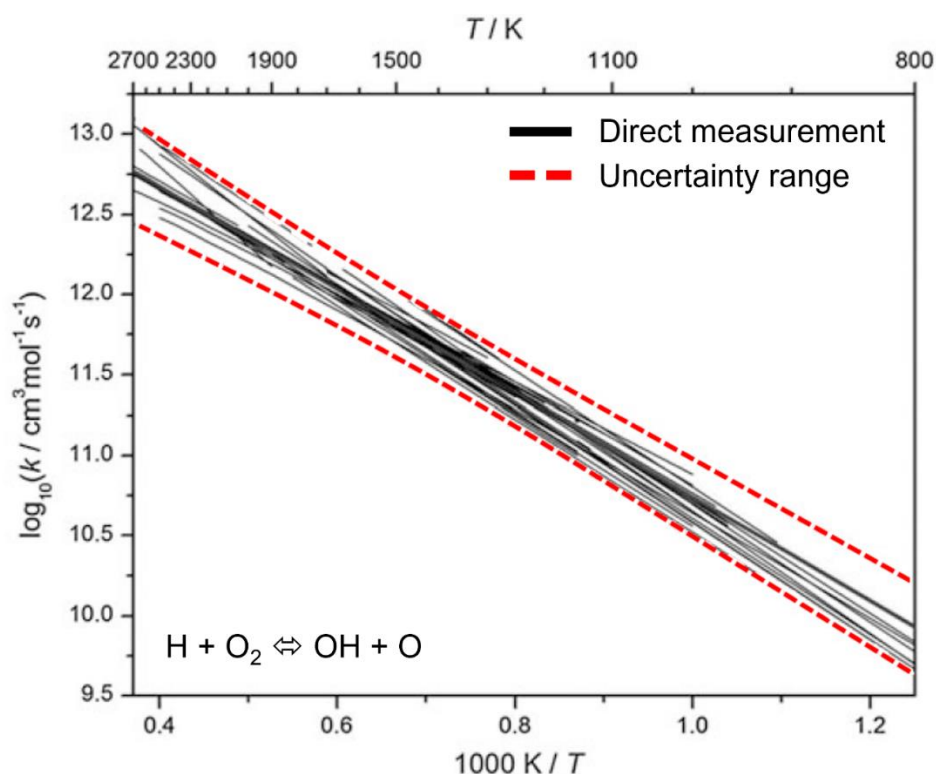


Figure 3.7. Direct measurements (solid lines) of the reaction rate constant k , of the reaction $\text{H} + \text{O}_2 = \text{OH} + \text{O}$, as a function of temperature. The uncertainty range based on this data (dashed lines) $\Delta \log(k) \approx 0.4$ for the range of temperatures under consideration. This shows that even for the most well understood reactions in combustion, there is a considerable uncertainty on the reaction rate constant, therefore necessitating optimisation. Adapted from Tomlin and Turányi [132].

3.9.2 Reduced Model Optimisation

The second application of kinetic model optimisation, and the one of interest to this work, is the optimisation of reduced kinetic models and global mechanisms to compensate for the loss in fidelity due the simplified and approximate description of the actual reaction mechanism. The optimisation task is to adjust the reaction rate constant parameters of the remaining reactions to embody the reaction flux through the more limited set of species in the reduced model, such that the same behaviours embodied in the detailed model are produced. Common optimisation targets include ignition delay time (IDT), laminar burning

velocity (S_u) and speciation data in 0-D and 1-D detailed model calculations. The hypothesis is that an accurate replication of these conventional kinetic model validation targets, leads to an accurate replication of other important detailed model calculations.

In these optimisation tasks, the uncertainty in the values of the reaction rate constants is large and for overly-reduced models (in compact model production) or for global mechanisms, this uncertainty range does not exist, as the reaction rate constants no longer intend to provide an accurate description of the physically occurring chemical reaction. The reaction rate constants can therefore take any value, resulting in a large search space.

3.9.3 Types of Optimisation Algorithms

In simple terms, the process of optimisation algorithms can be divided into three main steps:

- 1) Generation/selection of a trial solution.
- 2) Computation of the error function.
- 3) Generation/selection of a new trial solution.

The major difference between optimisation algorithms is the method of new parameter generation in step 3, i.e., whether stochastic or deterministic rules are followed, the degree to which previous solutions influence the performance of the algorithm (“self-learning”), and the required degree of user input (“automation”). Hence, the choice and suitability of an optimisation algorithm depends on the difficulty of the optimisation task. Figure 3.8 shows a categorisation of optimisation methods. Note, many optimisation algorithms combine elements of different categories, hence, incorporating them into a single category is not always easy. Optimisation algorithms that have been used for kinetic model optimisation will be discussed next.

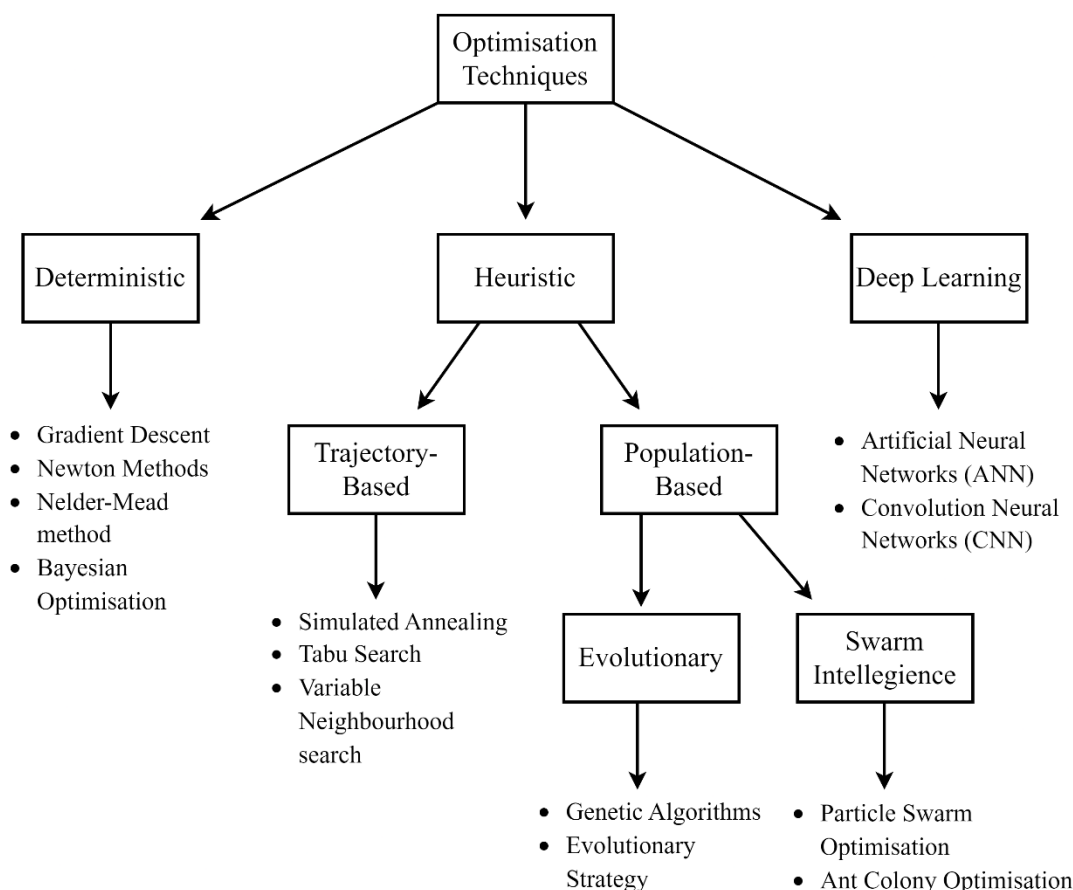


Figure 3.8. Categorisation of common optimisation algorithms. Note, some algorithms can exist in multiple categories depending on its application.

3.9.3.1 Error Function Gradient Based Methods

Early works on the optimisation of reaction mechanisms largely used algorithms that minimise the error function through computing its gradient with respect to the parameters.

Gauss-Newton:

The Gauss-Newton method is an iterative method that linearises the objective error function at each iteration and solves the linear least squares problem, using the linear approximation until the method converges on a solution that is below the acceptable error threshold. It uses the Hessian matrix, which is a square matrix of the second order partial derivatives, to obtain information on the local curvature of the objective error function. This optimisation method was used by Boch et al. [140] who proposed a boundary value problem approach to identify unknown reaction rates for a chemical reaction system.

Quasi-Newton:

The Quasi-Newton method is similar to the Gauss-Newton method, however it uses an approximation of the Hessian matrix to guide the search for the optimal solution. The Hessian matrix approximation can be updated at each iteration in different ways depending on the specific method. This method was used by Frenklach et al. [141] and later by Sheen and Wang et al. [137, 138, 142] alongside the Solution Mapping method.

Other Methods:

Davis et al. [136] developed an optimisation algorithm that uses a stochastic search of the parameter space to identify the best solution, from which a Newton search is then applied. Methling et al. [143, 144] developed a method that involved linearising the objective error function by linearising the relationship between the model parameters and the optimisation target (e.g., model calculation of laminar flame speed), followed by a gradient descent-based solver for error function minimisation.

To ensure convergence in gradient-based methods, an accurate initial guess is needed to place the algorithm in the region of the real solution which is not always possible. Even when special techniques are employed to extend the searching domain, gradient-based approaches tend to experience local minimum confinement, where the algorithm gets “stuck” in a local minimum. As such, local gradient-based approaches are usually unsuitable for complex and multimodal optimisation tasks [145, 146].

3.9.3.2 Evolutionary Algorithms

Evolutionary algorithms are a family of algorithms that are inspired by the process of evolution. Genetic algorithms (GA) [147], are heuristic algorithms that mimic the biological process of natural selection and are the most commonly used method to optimise reduced models (e.g., [95, 97, 148-150]). Elliott et al. [151] published a comprehensive review of these techniques and their effectiveness to the optimisation of kinetic models. Figure 3.9 shows the structure of the population in a genetic algorithm. A set of (A, n, E_A) Arrhenius parameters for a given reaction is called a *gene*, with the collection of these *genes* i.e., model, labelled a *chromosome*.

Although the exact procedure for each genetic algorithm varies, the general approach is similar as follows:

- 1) A population of chromosomes (i.e., kinetic models) are initially generated.
- 2) Their accuracy is computed using an error function (commonly “*fitness function*”).
- 3) From this population, the fittest chromosomes (best performing models) are selected as the “*parents*”.
- 4) Another population is then generated based on the genes of the parents.

Random perturbations of the *parent’s genes* (Arrhenius parameters), i.e., *mutations* and *crossover* events, occur to prevent the algorithm from falling into a local minimum. This process repeats until the error on the fittest model is below a predefined threshold.

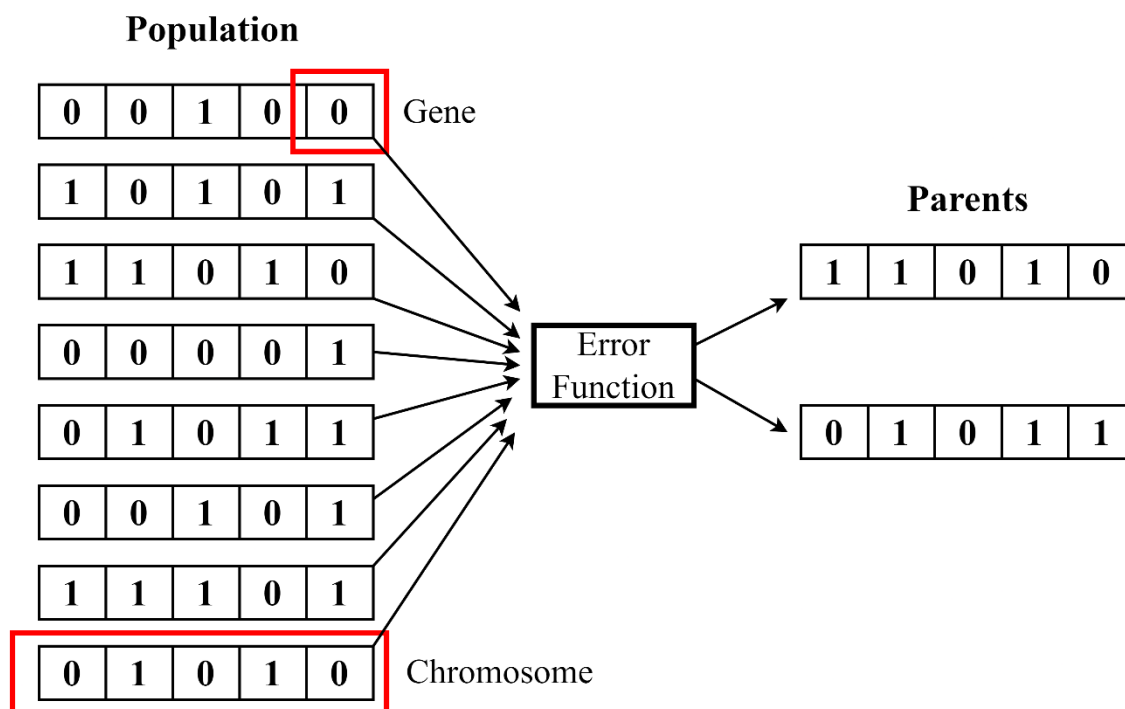


Figure 3.9. Illustration of a Genetic Algorithm. Following the selection of the parents, a crossover or mutation event occurs, followed by the generation of a new population based on the Parents.

3.9.3.3 Swarm Intelligence

Swarm algorithms are a family of optimisation algorithms that are inspired by the collective behaviour of social animals and insects. These methods generate a population of candidate solutions that interact with each other to find the optimal solution. Recently, particle swarm optimisation (PSO) [152] has been applied to combustion to optimise reaction rate constants in detailed [153, 154] and reduced [155] models. Each particle is represented by a set of parameters, called *position*, that defines its current solution. Each particle moves through the search space by adjusting its position according to both its own experience and the experience of the other particles. The general procedure is as follows,

- 1) The algorithm starts with a random initialisation of the *position* and *velocity* of each particle.
- 2) The fitness of each particle is evaluated using an objective error function.
- 3) Each particle updates its direction and velocity based on the difference between current position, its best solution, and the best solution found in the entire swarm.

This continues until convergence has been reached. PSO algorithms have been applied to many areas of science, engineering, and computer science, however, it has been shown that these algorithms tend to fall into local minima in high-dimensional space [156].

3.9.3.4 Other Methods

FOCTOPUS:

Nagy and Turányi [139] developed an iterative optimisation method that uses a continuously updating parameter space around the best model. In the first iteration of the algorithm, random sampling of the Arrhenius parameters is performed. The solutions are evaluated using an error function to compute the error in the model calculations to the optimisation targets. The best solution from this iteration is used as the centre for the parameter bounds for the next iteration. The size of the parameter space searched decreases if the best model from the iteration has a lower error function than the best model from the previous iteration. This continues until a threshold is reached. This method has been used and continuously

updated throughout literature [157-161] and has been recently shown to converge to the solutions from PSO, SA and GA methods [162].

Artificial Neural Networks:

Artificial neural networks (ANNs) are a type of machine learning technique that are inspired by the structure and function of biological neural networks. They consist of layers of interconnected *neurons* which process and transmit information. As described previously, neural networks have been applied to the task of accelerating chemical kinetics since the 1990s, however, in 2020 this technique was applied to the task of optimisation of a global mechanism [163]. In this work, the Jones and Lindstedt global mechanism for methane combustion [39] was selected and the Arrhenius parameters of all four reactions were optimised using an ANN, to produce a model for moderate or intense low-oxygen dilution (MILD) methane combustion. The ANN consisted of three hidden layers with fifteen neurons in each layer as shown in Figure 3.10.

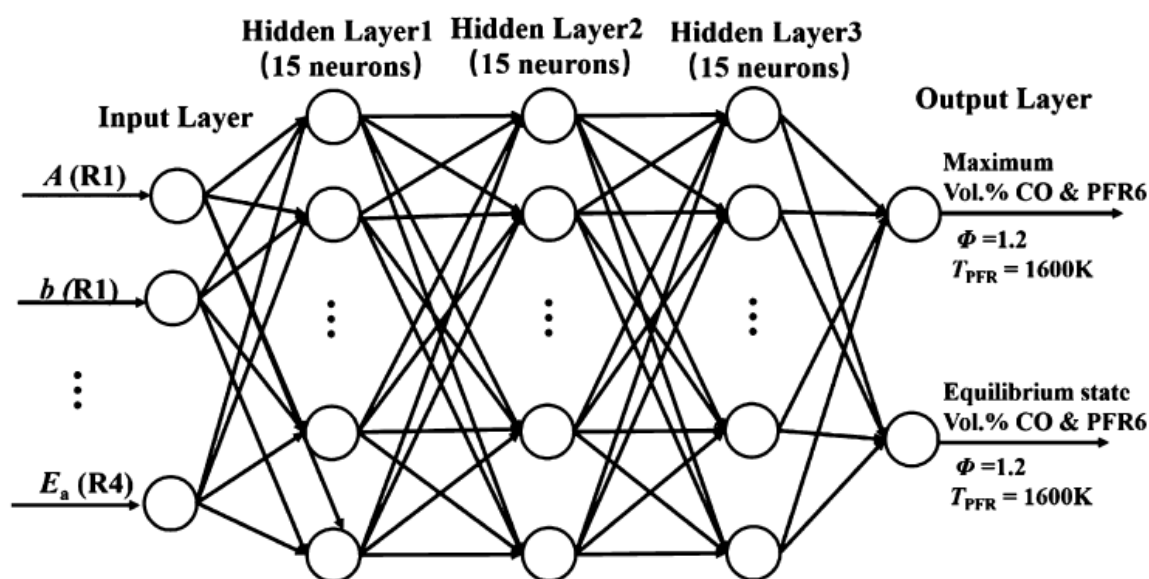


Figure 3.10. Artificial neural network (ANN) structure used. Extracted from Si et al. [163].

Figure 3.11 shows the process flow of the ANN optimisation. First, the weights of the ANN were optimised to CO concentrations in 1-D plug flow reactor calculations at 1600 K and fuel/air equivalence ratio of 1.2. 50,625 models were used as the training set and an

iterative gradient descent method was used to find the optimum set of weights. Once the weights were set, the ANN was used to optimise the Arrhenius parameters to the GRIMech3.0 [113] detailed model calculations of CO mole fractions in 1-D simulations. The suitability of new Arrhenius parameters is therefore assessed without having to perform the actual 1-D simulation, thus dramatically reducing computational cost. New sets of parameters are assessed until the ANN predicted error is below a pre-defined threshold. This method was improved by the implementation of a validation step after the training of the ANN [164] and was then applied to a skeletal model for MILD combustion by the same authors [165].

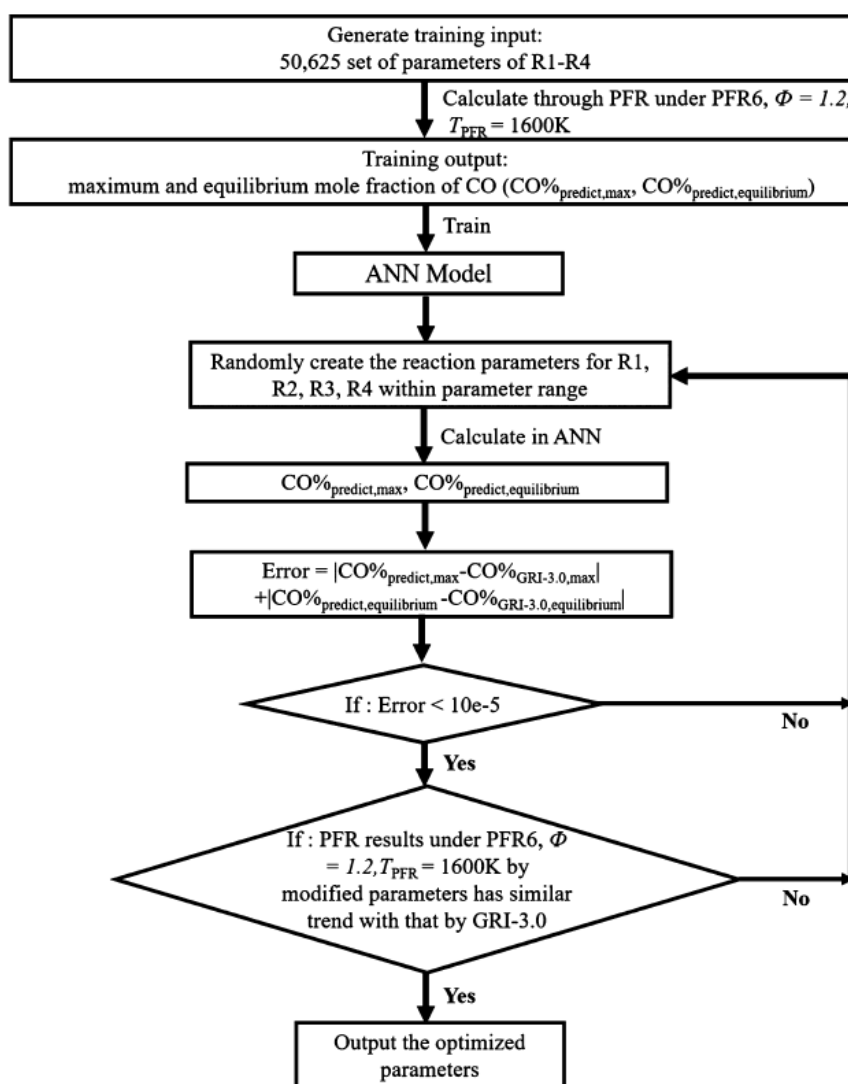


Figure 3.11. Algorithm for training of ANN and optimisation of Arrhenius parameters. Extracted from [163].

Simulated Annealing:

The simulated annealing (SA) [166] algorithm, is a stochastic search technique inspired by the annealing process used in metallurgy to purify metals and make them more resilient. It starts with an initial solution and iteratively explores the solution space by randomly generating new solutions and accepting or rejecting them based on a probability function. The probability function is based on the difference between the objective function values of the current and proposed solutions, as well as the “temperature”, which controls the probability of accepting worse solutions. As the algorithm proceeds, the temperature is gradually decreased, leading to a convergence towards a final solution. SA has been applied to kinetic model optimisation by only one author to our best knowledge. Gokularkrishnan et al. [167] used a SA algorithm to optimise a global mechanism and a reduced model for methane.

3.10 Conclusion

The advancement of supercomputing resources has facilitated a rapid growth in our comprehension of fuel combustion, offering molecular-level insights into the underlying chemical and physical processes. This progress has enabled the gas turbine industry to employ multidimensional reacting flow simulations as a rapid development tool to assess the impact of combustor design and operating conditions on gas turbine engine performance. These simulations provide a cost-effective substitute for physical experiments, permitting analysis of gas turbine operation under demanding conditions.

Despite these impressive advances, the computational cost of multidimensional simulations for turbulent reacting flows remains a significant challenge, limiting the practical use of detailed models in gas turbine design situations. This is due to the detail-computational cost coupling, where increasing the level of detail in the model results in a non-linear increase in computational cost, as shown by Equation 3.1, when using traditional industry-standard solvers.

The approaches to resolve this paradigm can be grouped into two. The first involves modifying the solvers to lessen or break the coupling in Equation 3.1. Current research in this area is focused on techniques that adjust how the set of ODEs are solved. For example,

changing how frequently the Jacobian is evaluated or the use of neural networks to calculate the chemical source terms in place of solving the set of ODEs.

The second approach, which is the focus of this thesis, is to reduce the level of detail in the kinetic model. This typically involves the use of model reduction algorithms to decrease the complexity of detailed models while maintaining sufficient accuracy to relevant calculations. Considerable progress has been made in the past few decades to develop methodologies for reducing model complexity to enable their use in simulations with a manageable computational cost. However, it should be noted that these methods strive to maintain a fundamental description of the reaction mechanisms, and as such, removing too much detail results in the loss of critical reaction pathways, leading to a deterioration in the accuracy of the model calculations, as depicted in Figure 3.5. Therefore, these models are confined to a certain size. A potential solution has been the implementation of global mechanisms, which utilise a highly simplified representation of the reaction network consisting of less than five lumped reaction steps. Although they can be useful for specific and simple calculations, their general utility is limited.

Therefore, in this Chapter, the concept of Compact Models is introduced, which has the potential to break the coupling between model detail and model accuracy. Compact Models abandon the traditional notion of preserving some physical realism in the reaction network description and instead adopt a data science approach to the problem. Despite not describing them as such, it is important to recognise that the reaction network in reduced models with reaction rate constants that have been optimised beyond their uncertainty range, are essentially virtual. As these models are no longer comprised of sufficient levels of detail to describe the reaction mechanism in a physically authentic manner, the reaction rates are optimised to embody the effect of absent pathways. Hence, in this sense, Compact Models are not new. However, the aim of this work is to formalise the definition and rather than avoiding the loss of physicality, embrace it. In the next Chapter the concept of Compact Models is further explored, and a methodology is presented to allow for the automated production of these models, i.e., *compaction*.

Chapter 4

MLOCK – An Automated Compaction Methodology

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4.1 Introduction

Compact models offer an attractive solution to break the detail-fidelity paradigm whilst retaining the ChemKin-form of reaction description, thereby allowing for their direct implementation in industry standard software. Although not an entirely new concept, this

this thesis aims to rigorize the definition of Compact Models and present a methodology leading to their production. A rigorous definition is necessary to not only ensure their proper use and interpretation, but to fully benefit from the advantages of the departure from physicality. In this Chapter, a methodology for the automated production of compact models (compaction) is presented.

Due to the availability of algorithms that automate the reduction procedure, the production of reduced models is relatively straightforward. However, one should note that when using detailed models in excess of $\sim 3,000$ species, we have found that many reduction software run into memory storage issues and as such, reduction becomes troublesome, sometimes necessitating a pre-treatment step to remove unnecessary sub-models using a-priori knowledge. This is a limitation to automated approaches to reduced/compact model generation, and as the number of species in detailed models increases over time, this is an issue that must be addressed by the model reduction community.

The optimisation of overly-reduced kinetic models is not as mature a research area as that of model reduction. It is not surprising therefore that there is currently no community-standard algorithm/software to produce compact models e.g., to over-reduce and then optimise a kinetic model in an automated procedure.

In model compaction, within the concept of model over-reduction, the optimal values of reaction rate constants may vary from the original values by orders of magnitude, necessitating parameterisation of a large bound space as routine. This results in error function landscapes that can show high levels of structure in the case of the most important reactions, to more diffuse structures that are not obvious to cursory examination in the case of other reactions. These landscapes typically consist of tens of thousands of solutions. Due to this complexity, the task of finding an optimum set of parameters using an automated methodology appears challenging. We emphasise appreciation that the suitability and effectiveness of an optimisation technique depends on the extent of the optimisation challenge. In compact model generation, two major terms define this:

- 1) The range and complexity of target property phenomena.
- 2) The complexity of the reaction network.

In the literature, it is common for compact models to be produced by apparently *ad hoc* optimisation or manual adjustment of Arrhenius parameters (e.g., [168-170]). For the most ambitious aim of high-fidelity compact model performance at a comprehensive range of conditions, one should expect high-complexity in the objective error function topologies. Here, it stands to reason that manual approaches to the task of optimisation will be severely time-limiting, and unlikely to yield solutions that are actually optimum.

In the absence of rigorous and automated compaction methodologies, a significant level of human intervention and expertise is needed to produce an accurate compact kinetic model that can be reliably used in multi-dimensional reacting flow simulations. That pursuit is a rapidly growing field of research with recent works attempting to improve the process, to yield more accurate low-dimensional ChemKin-form kinetic models with less human involvement for example the works of Kelly et al. [171-173], Perini et al. [53], Jaouen et al. [148], Leylegian et al. [174, 175] and Ji et al. [176]. Automated compaction from minimal user input would be a significant advance and is the objective of this thesis.

In this thesis, I present an automated compute intensification compaction methodology, called *Machine Learned Optimisation of Chemical Kinetics (MLOCK)*, which is a step towards the goal of a fully-automated self-learning compaction methodology. This methodology makes use of modern computing power to perform a large number of computer simulations quickly. The large data sets that are produced can be automatically analysed using machine-learning, statistical and data analysis techniques to improve the algorithm's efficiency and to learn discreet combinations of kinetic model parameters that result in one or several compact kinetic models which accurately replicate a target set of combustion kinetic data. A central tenet of the MLOCK method is that as little prior knowledge of the reaction mechanism as possible be utilised in the compaction procedure. This removes the constraint of the holding of a comprehensive scientific understanding.

The FAIR [6] principles of data science require computational models to be interoperable, meaning they can be readily used with current software infrastructure ("plug and play"). This has important implications that limit how MLOCK, or other compaction methodologies, should produce compact models. It is logical that MLOCK be constructed to operate upon the standard ChemKin format of kinetic model description. This excludes the use of such analytical techniques described earlier (e.g., QSSA), or other techniques that

result in a model that does not abide by the ChemKin format and/or requires modification of the solver to be exercised.

4.2 Compact Model Structure

As compact models do not contain the necessary level of detail in the reaction network component to describe the reaction mechanism with detailed fundamental physics, the description of the reacting flow is *virtual* rather than physically authentic. The compact model concept interfaces the fundamental physics-based description of reaction kinetics with a less physical, *virtual* perspective through data-science manipulation of the four archetypal components of the standard ChemKin format for a kinetic model:

1. A Virtual Reaction Network in place of the reaction mechanism. The purpose of the virtual reaction network is to provide minimal, but sufficient, degrees of freedom to the reacting flux such that certain combinations of virtual reaction rate constants can exist that yield models of high fidelity to the set of combustion kinetic target properties defined by the user. Formally, the virtual reaction network is comprised of nodes (species) joined together by connections (virtual reactions) of varying weights (virtual reaction rate constants). The configuration of each is adjustable to a possibly inexhaustible number of combinations with the objective of replicating some defined set of combustion kinetic performance attributes. The more complex or higher accuracy sought in performance attributes (e.g., species fractions, additional combustion phenomena), and the wider the range of performance conditions (e.g., mixture fraction, temperature, pressure, timescales), the more complex the virtual reaction network needed. Figure 4.1 provides a graphical representation of this concept, illustrating the differences between a virtual reaction network and a traditional reaction mechanism.
2. Virtual Reaction Rate Constants (or Weights), k_v , define the magnitude of the connection between the nodes of a virtual reaction network. Analogous to the elementary reaction rate constants, but not describing of a physically real chemical reaction. Units are s^{-1} , $cm^3 mol^{-1} s^{-1}$ and $cm^6 mol^{-2} s^{-1}$ for first, second, and third order virtual reactions respectively.

3. Molecular Thermodynamic Descriptors of each node including, elemental composition, standard-state molar enthalpy (H^0), entropy (S^0), and the constant pressure heat capacity (C_p^0). If perturbed, each are converted to the analogous virtual quantity, then not describing of the physical reality.
4. Mass and Energy Transport Descriptors for each node including Lennard-Jones potential well depth, collisional diameter, dipole moment, polarizability, and rotational relaxation collision number. If perturbed, each are converted to the analogous virtual quantity, then not describing of the physical reality.

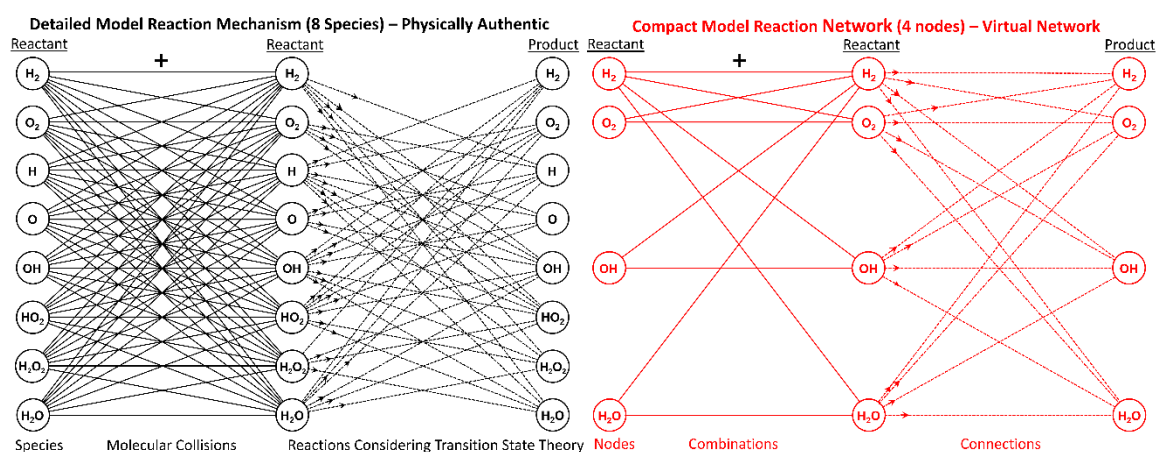


Figure 4.1. Illustration highlighting the difference between a reaction mechanism (left) and the virtual reaction network concept (right) and for the case of H_2/O_2 combustion system. Left: This is a physically accurate description of the reaction mechanism. The first panel (solid lines) represents a combinatorial model for collisions between each species in the system. The second panel (dotted lines) represents the intrinsic reaction coordinate connecting the reactants to products. Right: The first panel represents a combinatorial model linking each node in the network. The dotted lines on the second panel represent potential connections between reactant nodes and product nodes. The virtual reaction network does not require an intrinsic reaction coordinate to exist for a reactant and product to be linked. The number of nodes depends on the complexity of the performance targets. More complex targets necessitate a more complex reaction network to provide sufficient degrees of freedom to embody the detailed model behaviour. Note: The products from a collision may result in two or more products, which are represented as separate lines connecting the reactant and product.

For a compact model to be useful, the model calculations must be accurate to calculations that are pertinent to the intended use of the model. Our industry partner, Siemens Energy, specified that ignition delay time (IDT), laminar burning velocity (S_u), and speciation data of important species in zero-dimensional (0-D) and one-dimensional (1-D) simulations are required for their gas turbine design efforts and as such they act as performance calculations to which the compact model must be accurate. The specific speciation data that is required

and the exact operating conditions that these calculations must be valid at depends on the fuel.

This Chapter details the first version of MLOCK, *MLOCK1.0*, which is a five-step coded algorithm to compact a detailed chemical kinetic model to user-specified performance conditions. MLOCK1.0 serves as a framework to which minor modifications have been made in more recent algorithm versions. The MLOCK1.0 work-flow is summarised in Figure 4.2. The MLOCK algorithm is implemented through python and makes use of the Cantera suite [15] to perform reactor simulations. Although the MLOCK philosophy considers perturbation of all four kinetic model components, MLOCK1.0 perturbs only the reaction network and reaction kinetics components. A comprehensive account of the MLOCK1.0 methodology is presented below.

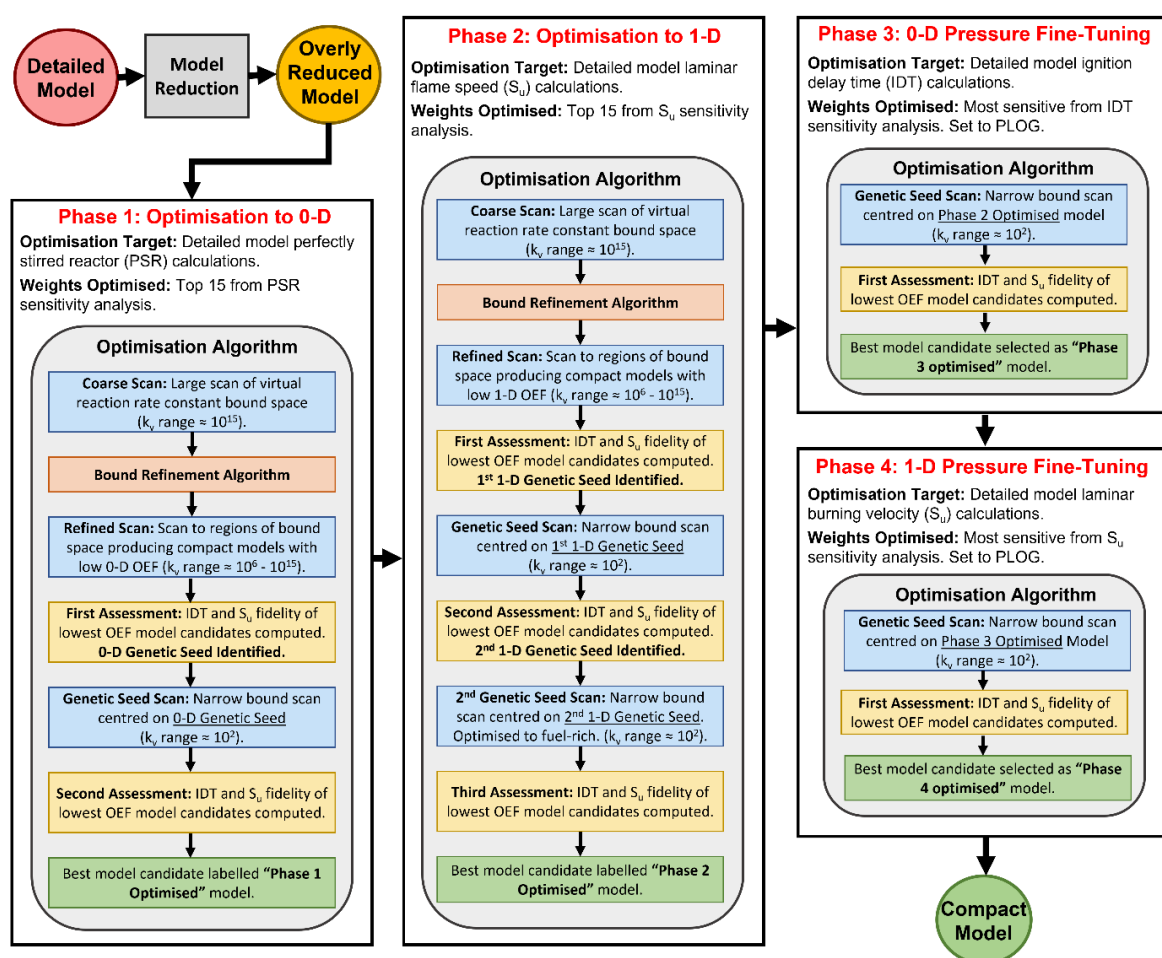


Figure 4.2. Process flow of the MLOCK1.0 algorithm. The optimisation targets comprising the Objective Error Function (OEF) in each Scan and the validation targets evaluated in each Assessment are user-defined.

4.3 Virtual Reaction Network Generation

Compact kinetic model generation (or *compaction*) first involves generating a virtual reaction network. This may be performed by applying mechanism reduction techniques to a detailed kinetic model, by practicing combinatorics, or by other approaches. In MLOCK1.0, the virtual reaction network is achieved by rigorous application of the path flux analysis (PFA) reduction procedure with the objective of producing an overly-reduced model, which will be of low fidelity. Note that the specific reduction technique used is not of principal concern. Our use of a conventional reduction algorithm serves only to produce a simplified reaction network. Any other reduction method could be employed for this purpose and would likely converge to the same or very similar set of species, e.g., Figure 3.5.

4.4 Optimisation of Weights of Virtual Reactions

The reaction kinetics component of the overly-reduced model is then optimised by perturbation of the virtual reaction rate constants, k_v , that show a major influence on the calculation of the performance targets. MLOCK1.0 performs this by simultaneous perturbation of the virtual reaction rate constant parameters (A' , n' , and E_A'). The overly-reduced model is first optimised to zero-dimensional (0-D) calculations in Phase 1, followed by optimisation to one-dimensional (1-D) calculations in Phase 2. Model performance to 0-D and 1-D calculations at the lower and upper pressure limits of the performance envelope are fine-tuned in Phases 3 and 4. Each Phase comprises one or more surveys of the virtual reaction rate constant space - *Scans*.

4.4.1 Scans

A *Scan* is a stochastic search of a defined search space. It is an automated procedure that generates a large number of model candidates by trialling new A' , n' , and E_A' for selected virtual reactions from a pre-prepared library. Simulations are subsequently performed using each model candidate and the performance is evaluated using an Objective Error Function (OEF) which quantifies the error in model calculation of the selected optimisation targets.

- A *Coarse Scan* searches a region of k_v for each connection (virtual reaction) undergoing optimisation ranging from 1 to 1×10^{15} . The purpose is to build an initial

database from which data analysis tools can be applied to deduce any dependence of the OEF on k_v and subsequently narrow the search space.

- A *Refined Scan* searches a smaller region of k_v to that of the Coarse Scan with the purpose of improving the resolution of the search space regions that produce models showing low OEFs. The k_v ranges searched vary depending on the observed dependence of OEF to k_v for each connection.
- A *Genetic Seed Scan* is a narrow-bounded search, where the bounds are given by perturbation of k_v of each connection in the *Genetic Seed* that is undergoing optimisation, by a factor of three, as described below. MLOCK1.0 operates on the assumption that the *Genetic Seed* has approximate attributes that could comprise a high-fidelity compact model.

Each *Scan* tests a user defined number of model candidates (n). In MLOCK1.0, n is 80,000.

4.4.2 Virtual Reaction Rate Constant Library

The Virtual Reaction Rate Constant Library is assembled at the start of each Scan. In Coarse and Refined Scans, a library of logarithmically uniformly distributed k_v is produced for each connection, with the bounds prescribed as above. A library of uniformly distributed n' and E_A' is produced for each connection with bounds $\pm 15\%$ and 50% respectively. These bounds were arbitrarily defined to allow suitable flexibility of the temperature dependence for each connection. The k_v , n' and E_A' terms for each connection are selected at random and the A' parameter is obtained by evaluating the k_v at a nominal reference temperature of 2000 K. In a Genetic Seed Scan, a library of A' , n' and E_A' is produced for each connection using gaussian distributions centred on the corresponding A' , n' and E_A' parameters, of the Genetic Seed, with standard deviations of $A'/3$, $n'/20$ and $E_A'/6$ for each connection.

4.4.3 Model Candidate

A Model Candidate is created by random assignment of A' , n' and E_A' terms to the connections of the virtual reaction network that were selected for optimisation.

4.4.4 Objective Error Function

An Objective Error Function (OEF) is utilised in each Scan to automatically assess the error in the calculations of each model candidate to the optimisation targets. In this study, the following OEFs are used.

4.4.4.1 Phase 1 Objective Error Function – Zero-Dimensional, Kinetic Emphasis

A purpose of the Phase 1 optimisation is to ensure the good performance of the compact model in replicating the detailed model calculations in kinetic regimes, particularly fuel/air ignition. Equation 4.1 shows the OEF used in Phase 1,

$$Phase\ 1\ OEF = \frac{1}{N_J N_K} \sum_k \sum_j \left\{ \left[\sum_i w_i \left(2 \frac{|X_{i,k}^{red}(t_j) - X_{i,k}^{det}(t_j)|}{X_{i,k}^{det}(t_j) + \max(X_{i,k}^{det})} \right) \right] \right. \\ \left. + w_{fuel} \left(X_{fuel,k}^{red}(t_j) - X_{fuel,k}^{det}(t_j) \right)^2 \right\} \quad (4.1)$$

where $X_{i,k}$ refers to the mole fraction of the i^{th} species at the k^{th} set of temperature, pressure, and equivalence ratio conditions; superscript *det* and *red* refers to detailed model and model candidate respectively; N_K and N_J refer to the total number of operating conditions and time points that are included in the evaluation; and w is a weighting term that can be used to assign a greater importance to the error in certain species mole fractions. The first term in this OEF is designed such that the error is weighted more heavily to instances where species mole fractions are close to the maximum mole fraction. This term was used by Nagy et al. [177] to evaluate the error in species concentrations during model reduction. As the fuel has a maximum mole fraction at $t = 0$, this term does not provide a suitable evaluation of its error. As such, if the mole fractions of the fuel are included as an optimisation target, the error in calculation of the fuel mole fraction is evaluated by a simple mean squared error.

4.4.4.2 Phase 2 and Phase 4 Objective Error Function – One-Dimensional Freely Propagating Flames

The Objective Error Function used in Phase 2 and Phase 4 has the purpose to ensure compact model performance in computation of the 1-D laminar burning velocity,

$$\text{Phase 2 and Phase 4 OEF} = \frac{1}{N_k} \sum_k \left(\frac{|S_{u,k}^{red} - S_{u,k}^{det}|}{S_{u,k}^{det}} \right) \quad (4.2)$$

where $S_{u,k}$ is the laminar burning velocity at the k^{th} set of temperature, pressure, and equivalence ratio conditions and N_k is the number of conditions.

4.4.4.3 Phase 3 Objective Error Function – Ignition Delay Time

The Phase 3 Objective Error Function has the purpose to ensure compact model performance in computation of the ignition delay time,

$$\text{Phase 3 OEF} = \frac{1}{N_k} \sum_k \left(\frac{|IDT_k^{red} - IDT_k^{det}|}{IDT_k^{det}} \right) \quad (4.3)$$

where IDT_k is the ignition delay time in a constant volume constant internal energy (UV) 0-D reactor at the k^{th} set of temperature, pressure, and equivalence ratio conditions and N_k is the number of conditions.

4.4.5 Bound Refinement

Bound Refinement is the process of automatic numerical analysis of the Objective Error Function versus k_v behaviour that identifies regions of the k_v bound space which show the largest densities of higher fidelity models, as apparent through low OEFs. In the MLOCK1.0 algorithm, bound refinement is performed automatically using a coded algorithm that operates on the principal of a binomial test in which the null hypothesis is that the percentage of model candidates in a region of k_v that have an OEF below a certain value, is the same as the percentage across the whole population (full k_v range). A Z-test is then performed to test the null hypothesis for each region of k_v .

First, the value of the OEF that corresponds to the 99.5th percentile of the model candidates produced in the Coarse Scan is calculated and the number of model candidates in the complete population with an OEF below this value is recorded. The k_v bound space is then divided into a series of regions, and the number of model candidates in each region that have an OEF below this threshold is counted. Each region is then scored based on the percentage of model candidates in the region with an OEF below this threshold. If the proportion of models below the OEF threshold in the full population is $\bar{p}$, and within a given region of k_v it is found to be p , then for a region of k_v with m model candidates, the Z-score for that region is,

$$Z = \frac{\bar{p} - p}{\sqrt{\frac{\bar{p}(1 - \bar{p})}{m}}} \quad (4.4)$$

Lower Z-values correspond to a greater proportion of low OEF model candidates produced in the specific k_v region. A significance value (α) of 0.05 is set and the algorithm outputs regions of k_v with a Z-score below the critical value (i.e., rejecting the null hypothesis), concluding that the greater proportion of “good” models produced in these regions is not a result of chance variation. This is performed independently for every connection undergoing optimisation. In MLOCK1.0, Bound Refinement is performed on the OEF versus k_v data generated by the Coarse Scans of Phase 1 and Phase 2, with the bounds of the subsequent Refined Scan defined by the regions of k_v bound space identified by the bound refinement algorithm.

4.4.6 Assessments

An *Assessment* identifies the best performing model candidate from the previous Scan. A fidelity index is used that quantifies the accuracy of the model candidate between 0-100%, where 100% denotes perfect replication of the target calculations. The fidelity equation that is used is defined in each Chapter. MLOCK1.0 implements the below procedure to identify the best performing model.

1. Ignition Delay Time (IDT) fidelity and laminar burning velocity (S_u) fidelity of the 100 model candidates with the lowest OEF are calculated at the validation conditions.

2. Model candidates that do not experience a maximum laminar burning velocity at fuel/air equivalence ratios 1.0 or 1.1 are removed.
3. Model candidates that compute a maximum laminar burning velocity that is $> \pm 25\%$ of the validation target maximum laminar burning velocity (S_u) are removed.
4. Of the remaining model candidates, that which computes the highest average IDT fidelity and S_u fidelity is identified as the best performing model.

Figure 4.3 shows the burning velocities of three model candidates produced in the MLOCK1.0 Phase 1 Refined Scan in the case of compaction of a detailed model for methane/air combustion. The IDT fidelity and Phase 1 OEF of the models are similar. Although the models have a similar S_u fidelity, from examination of the raw data it is clear that Model 3 is the most suitable model, as both Model 1 and Model 2 exhibit undesirable traits. Model 1 has a very large maximum S_u whilst having an underprediction of S_u at lean conditions. Whereas Model 2 has a maximum S_u that is similar to the detailed model, however this maximum occurs at lean conditions.

This highlights the necessity for a more nuanced approach to facilitate the selection of the optimal model, thereby guiding the algorithm towards the optimum solution. One possible approach is to develop a more intricate S_u fidelity definition, although this must remain universally applicable and not overfitted to this specific fuel system. Hence, an alternative, albeit more rudimentary, approach is to integrate specific criteria within the Assessment stages to prevent the algorithm from selecting an inappropriate model, i.e., Steps 2 and 3 above.

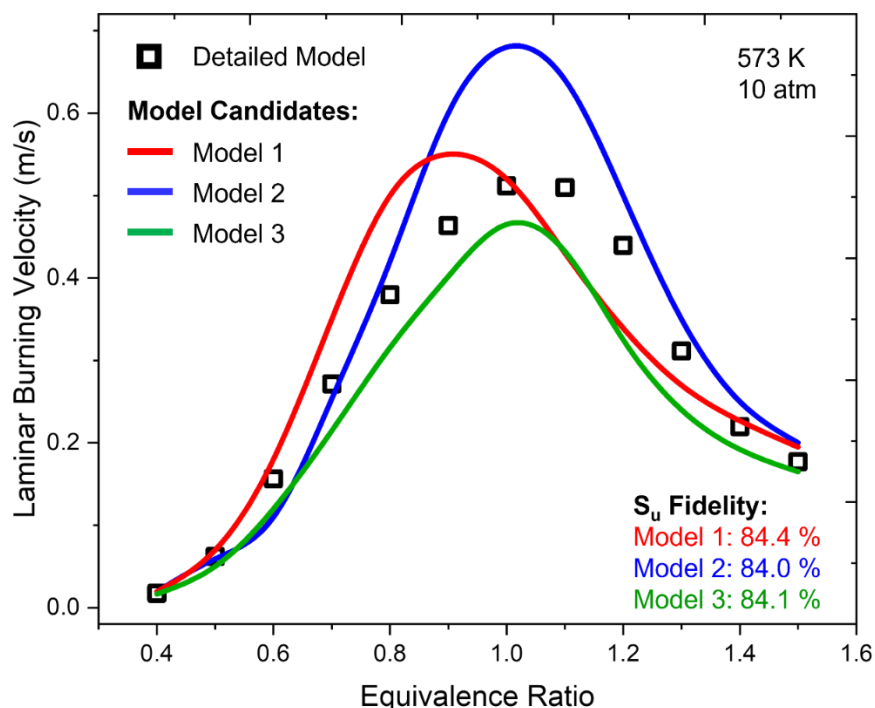


Figure 4.3. Laminar burning velocity as a function of equivalence ratio for methane/air fuel mixtures at 10 atm using NUIGMECH1.0 [11] detailed model and a series of 15-node model candidates produced in the MLOCK Phase 1 Refined Scan. This shows the need for the qualification arguments in the Assessment stage to prevent the algorithm choosing a model with undesirable burning velocity behaviour.

4.5 Particulars of Phase 1

The first optimisation module of MLOCK1.0, *Phase 1*, deals with optimisation to 0-D calculations. In Phase 1, a series of detailed model perfectly stirred reactor (PSR) calculations of mole fraction profiles of chemical species that are important to the specific fuel reaction mechanism with respect to residence time, are used as the optimisation targets. MLOCK1.0 then performs sensitivity analysis on the Overly-Reduced Model at the same PSR conditions. Sensitivity analysis is the sequential perturbation of reaction rate constants to identify connections that are important to the calculation. The sensitivity coefficient of each virtual reaction is calculated as,

$$\frac{dt_{50\%}}{dk_i} = \frac{|t_{50\%} - t_{50\%}^0|}{t_{50\%}^0 * w_{sens}} \quad (4.5)$$

where $t_{50\%}$ is the time for 50% fuel consumption in a PSR following perturbation of a weight by a factor w_{sens} and $t_{50\%}^0$ is the time for 50% fuel consumption prior to perturbation. In MLOCK1.0, w_{sens} is set to 0.1 and 10. This perturbation both increases and decreases the

rate constant by an order of magnitude to capture connections that may be at a low and high-limit. MLOCK1.0 selects the fifteen connections exhibiting the largest sensitivity coefficients as parameters for optimisation.

In Phase 1, the *First Assessment* identifies the best performing model candidate and selects this as the *0-D Genetic Seed*. The *Second Assessment* selects the best performing model candidate following the Genetic Seed Scan. This model candidate is identified as the *Phase 1 Optimised Model*.

4.6 Particulars of Phase 2

The second optimisation module of MLOCK1.0, *Phase 2*, deals with optimisation to 1-D freely propagating flame calculations. Phase 2 begins by performing laminar burning velocity sensitivity analysis on the Phase 1 Optimised model at the Phase 2 Optimisation conditions, to identify the top fifteen most sensitive virtual reactions, which are set as parameters for optimisation.

The sensitivity coefficient of each virtual reaction is calculated by computing the new laminar burning velocity, S_u , following perturbation of reaction k_i as,

$$\frac{dS_u}{dk_i} = \frac{|S_u - S_u^0|}{S_u^0 * w_{sens}} \quad (4.6)$$

where S_u^0 is the laminar burning velocity prior to perturbation. In MLOCK1.0, w_{sens} is set to 0.1 and 10.

As in Phase 1, Phase 2 employs the Coarse Scan – Bound Refinement – Refined Scan – Genetic Seed Scan procedure. However, an additional Genetic Seed scan is performed with the optimisation targets comprised of freely propagating flame calculations at rich conditions. This is to further improve model performance at rich conditions, which is more challenging to replicate.

As the computational cost in simulating a flame is much greater than that of a PSR, the number of calculations included in the Phase 2 OEF is kept at a minimum to balance the computational efficiency with the effectiveness of the algorithm. Furthermore, a pre-screening of model candidate performance against the Phase 1 OEF is performed to ensure

only model candidates with an OEF below a specified threshold advance to the calculation of the Phase 2 OEF. This significantly reduces computational cost by removing poor performing models, which also tend to be “stiff” to converge. To further lessen the computational cost of these Scans, a multiple linear regression model is trained and validated on data from the Phase 2 Refined Scan and incorporated in the following Genetic Seed Scans. The best performing model resulting from this second optimisation module is identified as the *Phase 2 Optimised* model.

4.6.1 Multiple Linear Regression

Multiple linear regression is a statistical technique that uses several explanatory variables, x_i , to predict the outcome of a response variable, Y_i ,

$$Y_i = \beta_0 + \beta_1 x_{i1} + \beta_2 x_{i2} + \cdots + \beta_n x_{in} \quad (4.7)$$

where β denotes the regression coefficients for each explanatory variable.

Multiple linear regression is employed on-the-fly in Phase 2 to predict the laminar burning velocity at each condition in the OEF using PSR calculations as the explanatory variables, making use of Scikit-learn [178] package. From this, the Phase 2 OEF can be calculated by computing and summing the error at each condition. As previously mentioned, the Phase 1 OEF is evaluated in Phase 2 to ensure that computationally costly S_u calculations are only performed on models with suitably good replication of PSR profiles. It is this 0-D data that is used to train the regression models.

A correlation matrix, which deduces the coupling between variables and quantifies the degree of coupling as a number between 0 and 1, is used to select the 40 most predictive properties to include as explanatory variables at each condition in the S_u OEF, including:

- (i) Relative error in the maximum mole fractions of selected species,
- (ii) Relative error in the steady-state mole fractions of selected species,
- (iii) Relative error in the maximum and steady-state temperature,
- (iv) Relative error in the maximum heat release rate,

at the range of initial temperatures and fuel/air equivalence ratios included in the Phase 1 OEF. The multiple linear regression models are trained and validated on a selection of model candidates from Phase 2 Refined Scan, using a 75-25 split, and employed in the Phase 2 Genetic Seed Scans.

4.7 Particulars of Phase 3

The purpose of Phase 3 is to act as a fine-tuning module, to ensure compact model performance against ignition delay time at variable pressures. Phase 3 does this by performing a sensitivity analysis on the Phase 2 Optimised model at the lower and upper pressures of the performance envelope.

The PLOG formulism is used to define and optimise a new set of Arrhenius parameters for various pressures to fine-tune the performance of the compact model at these pressures, without affecting the calculations of the compact model at a previously optimised pressure(s). As the virtual reaction network of a compact model is not intended to be physically authentic, it is permitted to impose pressure dependence on a reaction that does not depend on pressure in reality.

The most sensitive connection at the lower and upper pressures in the performance envelope is selected for optimisation. The connections are set to the PLOG pressure dependence convention within the ChemKin format, and a Genetic Seed Scan is performed using the Phase 2 Optimised model as the Genetic Seed, as this model will have a reasonable performance and acts as a good starting point. The best performing model candidate from this Scan is identified as the *Phase 3 Optimised* model.

4.8 Particulars of Phase 4

The purpose of Phase 4 is to ensure compact model performance against S_u at variable pressures. Phase 4 does this by performing a laminar burning velocity sensitivity analysis on the Phase 3 Optimised model at the lower and upper pressures of the performance envelope. The most sensitive connection at each pressure is selected for optimisation. The PLOG convention is again used, and a Genetic Seed Scan is performed using the Phase 3 Optimised model as the Genetic Seed. The best performing model candidate from this Phase is

identified as the *Phase 4 Optimised* model. In MLOCK1.0 the Phase 4 Optimised Model is deemed the *Compact Model*.

4.9 Conclusion

In this Chapter a novel compute intensification methodology to simplify the description of complex chemical reaction systems has been detailed. *Machine Learned Optimisation of Chemical Kinetics (MLOCK)* is a coded algorithm that allows for the production of minimally complex, high fidelity kinetic models, termed “Compact Models” (i.e., minimised and optimised). The advantage of this approach is that it allows the creation of models with a minimal number of species, that are not bound by the constraint of physical authenticity, and are optimised to have a high level of fidelity to detailed model calculations over a wide range of conditions. This is achieved by representing the reaction mechanism of the fuel as a network of nodes (species) interconnected through connections (virtual reactions). The strength of the connection between each node is then be optimised to replicate the desired set of calculations.

The MLOCK methodology is intentionally designed to require minimal starting information, other prior human knowledge, or human monitoring. Instead, the MLOCK methodology emphasises the leverage of modern computing resources to perform large numbers of complex simulations quickly with minimal user input. The concept of MLOCK is to produce sequential data sets, which are interrogable by objective data analysis methods to automatically search the data set to find the optimum sets of numerical terms which result in an accurate replication of the target calculations. MLOCK is designed to address a gas-turbine Industry informed brief that comprises the replication of a set of combustion performance targets by a model of specified size and to operate within the standard reaction kinetic simulation infrastructure of the day (i.e., ChemKin format).

Chapter 5

Compact Models for Methane/Air Combustion

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5.1 Introduction

As society transitions from fossil fuel to renewable energy sources, the role of gas turbines will be central to operating on a more diverse range of fuels from conventional natural gas

to biomethane to liquified natural gas. Methane is a major component in these fuels. Understanding the kinetics of methane combustion is therefore essential for optimising the performance of combustion systems and reducing their environmental impact. An essential component in this advancement is the availability of minimally-sized kinetic models for methane that are accurate at calculations pertinent to gas turbines.

Methane is a unique hydrocarbon due to its distinctive molecular structure and properties. The carbon-hydrogen (C-H) bonds in methane are highly stable, possessing a considerable bond dissociation energy of 439 kJ/mol [179], resulting in relatively low reactivity when compared to other hydrocarbons. These properties are reflected in the significant energy required for methane to undergo combustion, which is notably higher than other hydrocarbons. Additionally, methane exhibits a lack of low-temperature chemistry, which is a key feature distinguishing it from other hydrocarbons.

The GRI-Mech [113] is a renowned detailed kinetic model that has been extensively utilised for simulating methane combustion. This model is composed of 52 discrete species, 17 of which contain nitrogen and are incorporated to represent the formation of NO_x during methane combustion. Therefore, to ensure a comprehensive and fundamental understanding of the methane combustion reaction mechanism, a minimum of 35 species is required. This is essential to capture the complex interactions and reaction pathways involved in methane combustion and to provide an accurate representation of the process.

Despite the simplicity of its molecular structure, few accurate compact models exist for methane at comprehensive operating conditions and combustion phenomena. To address this challenge, the MLOCK1.0 algorithm is applied with the aim of demonstrating its potential on this archetypal combustion system.

5.2 Specifics of Compaction

In MLOCK1.0, the calculations of the detailed model that is to be compacted are used to optimise and validate the compact models. Table 5.1 shows the set of calculations that Siemens Energy provided as pertinent to their gas turbine design efforts in respect to methane/air combustion. These calculations serve as the performance criteria against which the accuracy of the compact model will be evaluated.

Table 5.1. Performance targets for methane/air combustion defined by gas-turbine Industry sponsor. These targets are defined by Industry as being required for their gas turbine design efforts and as such their accurate replication is required from compact models. Compact model performance will be benchmarked to replication of these targets.

Reactor Physics	Property	Pressure (atm)	Equivalence Ratio	Temperature (K)
Perfectly Stirred Reactor	[OH], [CO], [CO ₂], [H ₂ O]	1, 10, 20, 30, 40	0.4, 0.5,..., 1.5	1000, 1100, ..., 2000
Constant Volume Constant Internal Energy	IDT	1, 10, 20, 30, 40	0.5, 1.0, 1.5	1100, 1200, ..., 2000
Freely Propagating Flame	S _u	1, 10, 20, 30, 40	0.4, 0.5,..., 1.5	473, 573, 673

To optimise the overly-reduced model that results from path flux analysis (PFA), it is not feasible to use the full set of performance conditions. Therefore, a set of optimisation targets must be selected to serve as indicators of model performance across a range of unseen calculations. For methane/air combustion, these targets are presented in Table 5.2, and their selection and suitability will be discussed in a later section of this Chapter. Table 5.3 presents the validation conditions, which are a subset of the performance conditions and are used in the Assessment step of MLOCK1.0 to serve as indicators of overall model performance.

To quantify the accuracy of the compact models to the performance and validation conditions, fidelity indexes are used,

$$Fidelity (\%) = \frac{100}{N} \sum_k \left(1 - \frac{|X_k^{compact} - X_k^{detailed}|}{X_k^{detailed}} \right) \quad (5.1)$$

where X_k is the calculation (e.g., laminar burning velocity) at the k^{th} set of pressure, temperature, and equivalence ratio conditions and N is the number of conditions included. A value of 100% indicates a model with perfect replication of the detailed model calculations.

- For IDT fidelity, X represents the time at which derivative temperature by derivative time is at a maximum.
- For S_u fidelity, X is the laminar burning velocity.

For PSR fidelity, X is the maximum mole fraction of CO, OH, H₂O and CO₂, the time at which this maximum occurs, and the steady state concentration of CO, OH, H₂O and CO₂ at residence times of 100 ms.

Table 5.2. Optimisation targets that comprise the OEFs evaluated in the Scans of each Phase of MLOCK1.0. An optimisation target provides an indicator of model performance in 0-D and 1-D calculations at Industry relevant operating conditions. MLOCK1.0 uses these targets to optimise the model candidates.

Purpose	Reactor Physics	Property	Pressure (atm)	Equivalence Ratio	Temperature (K)
Phase 1 Optimisation Targets	Perfectly Stirred Reactor	[CH ₄], [CO], [OH], [H]	10	0.7, 0.9, 1.0, 1.1, 1.4	1000, 1500, 2000
Phase 2 Optimisation Targets	Freely Propagating Flame	S_u	10	0.8, 1.05, 1.3	573
Phase 2 Optimisation Targets (2nd Genetic Seed Scan)	Freely Propagating Flame	S_u	10	1.05, 1.3, 1.5	573
Phase 3 Optimisation Targets	Constant Volume Constant Internal Energy	IDT	1, 40	0.5, 1.0, 1.5	1200, 1400..., 2000
Phase 4 Optimisation Targets	Freely Propagating Flame	S_u	1, 40	0.8, 1.05, 1.3	573

Table 5.3. Validation targets that are evaluated in the Assessment in each Phase of MLOCK1.0. A validation target is a calculation that acts as an important indicator of overall model performance. MLOCK1.0 uses these targets to calculate model fidelity.

Purpose	Reactor Physics	Property	Pressure (atm)	Equivalence Ratio	Temperature (K)
Phase 1 Validation	Constant Volume Constant Internal Energy	IDT	10	0.5, 1.0, 1.5	1100, 1200, ..., 2000
	Freely Propagating Flame	S_u	10	0.4, 0.5, ..., 1.5	573
Phase 2 Validation	Constant Volume Constant Internal Energy	IDT	10	0.5, 1.0, 1.5	1100, 1200, ..., 2000
	Freely Propagating Flame	S_u	10	0.4, 0.5, ..., 1.5	573
Phase 3 Validation	Constant Volume Constant Internal Energy	IDT	1, 40	0.5, 1.0, 1.5	1100, 1200, ..., 2000
	Freely Propagating Flame	S_u	1, 40	0.4, 0.5, ..., 1.5	573
Phase 4 Validation	Constant Volume Constant Internal Energy	IDT	1, 40	0.5, 1.0, 1.5	1100, 1200, ..., 2000
	Freely Propagating Flame	S_u	1, 40	0.4, 0.5, ..., 1.5	573

5.3 Compact Models for Methane/Air Combustion

MLOCK1.0 was utilised to compact two distinct detailed models, namely *NUIG1817C3* [180], a developmental detailed model for hydrocarbon combustion, and the recently released *NUIGMECH1.0* [11]. The compaction results for each detailed model will be presented and their optimisation behaviours will be discussed. Note, the performance target parameter space is vast, and so we show graphical representation of model performance only at representative conditions. More detailed accounting can be found in the corresponding published papers and Appendices, as stated in each section.

5.3.1 NUIG1817C3 Detailed Model

The NUIG1817C3 detailed model, which details hydrocarbon combustion up to C₃ species, consists of 118 species and is a developmental version of the recently released NUIGMECH1.0. To produce the overly-reduced model, which is the first step in the production of a compact model (see Figure 4.2), PFA is performed. To do this a numerical database of time dependent chemical species concentration profiles in a homogenous constant volume reactor up until the point of ignition using methane/air mixtures at 1, 10, 20, 30, and 40 atmospheres (atm), 900 – 2000 K and at equivalence ratios 0.5, 1.0 and 1.5 is constructed. This resulted in two overly-reduced models, one with 15 nodes and one with 19 nodes. To produce the 15-node model, the error threshold value ε , is increased to its maximum value.

Incidental to the MLOCK1.0 process that followed, the *15-node Overly-Reduced Model* showed PSR fidelity of 71.5%, an IDT fidelity of 58.7% and a S_u fidelity of 65.1%. The *19 node Overly-Reduced Model* shows PSR fidelity of 88.2%, an IDT fidelity of 82.5% and a S_u fidelity of 88.1% at the performance conditions of Table 5.1.

The application of MLOCK1.0 yielded two compact models that accurately reproduce the calculations of the NUIG1817C3 detailed model over a wide range of conditions and phenomena. For the purpose of this thesis, these two compact models will be referred to as C3_15sOp and C3_19sOp henceforth.

C3_15sOp has a PSR fidelity of 83.9%, an IDT fidelity of 75.0% and a S_u fidelity of 83.1% and C3_19sOp has a PSR fidelity of 94.8%, an IDT fidelity of 93.6% and a S_u fidelity of 95.0% at the performance conditions of Table 5.1.

Figure 5.1 shows the laminar burning velocity (S_u) and ignition delay time (IDT) calculations of the 15- and 19-node Overly-reduced and Compact Models at representative conditions to evidence the effect of MLOCK on the accuracy of the models. The compact models accurately replicate important PSR speciation data across the performance envelope.

Figure 5.2 shows the PSR profiles of key species at a representative set of operating conditions to illustrate the typical performance of each compact model. It can be seen that at this representative condition, both compact models have good replication of the detailed model calculations, with C3_15sOp having a slight time resolution error. Additional

validation plots can be found in Appendix A or at [171]. The compact models can be found in Appendix B.

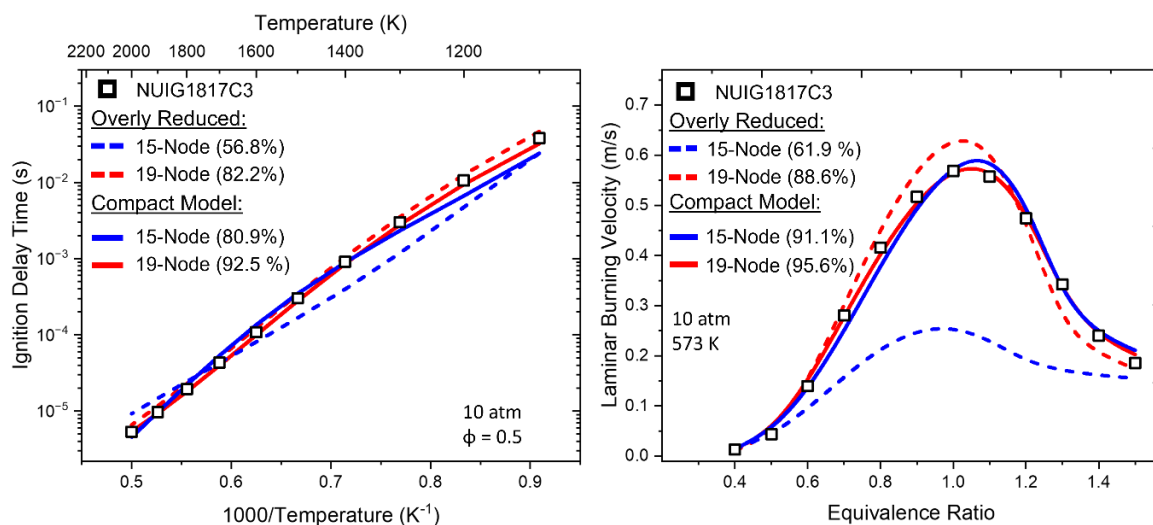


Figure 5.1. Ignition delay time as a function of temperature (left) and laminar burning velocity as a function of equivalence ratio (right) for methane/air mixtures at 10 atm using the NUIG1817C3 detailed model (symbols), Overly-Reduced Models (dashed line) and Compact Models (solid lines). Fidelity of each model shown in brackets in the legend.

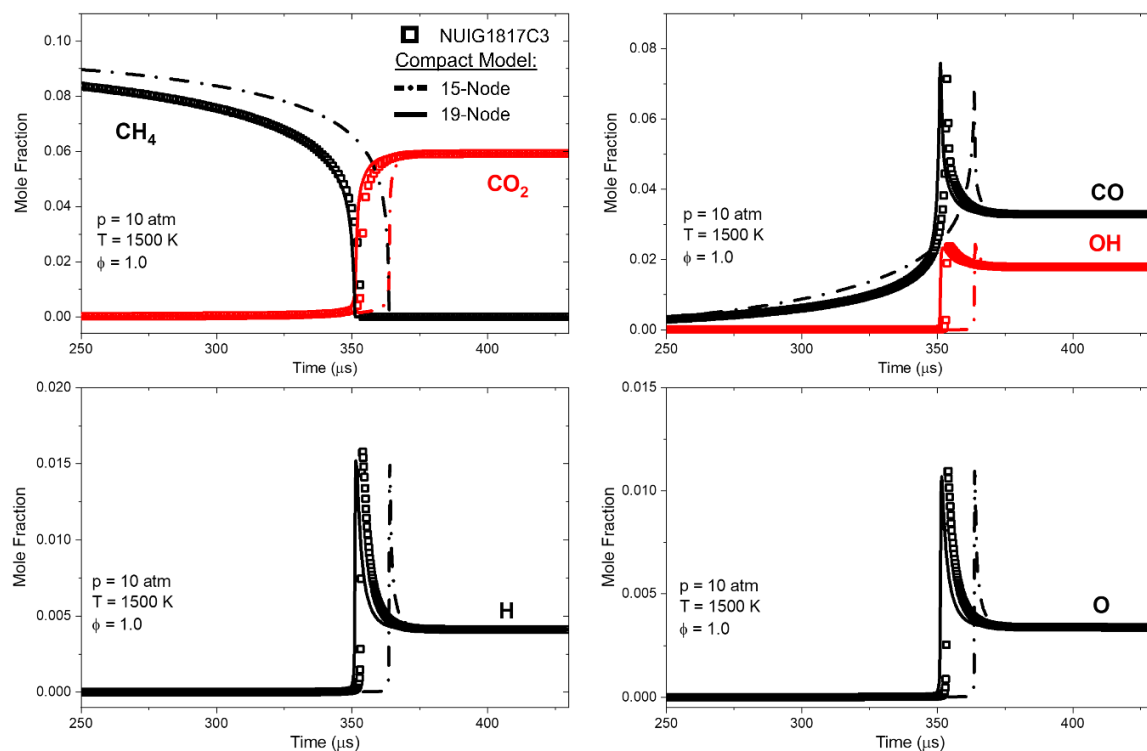


Figure 5.2. Perfectly stirred reactor (PSR) mole fraction profiles of important species at 10 atm, 1500 K for stoichiometric methane/air using the detailed model (symbol), C3_19sOp (solid line) and C3_15sOp (dashed line).

5.3.2 NUIGMECH1.0 Detailed Model

The NUIGMECH1.0 detailed chemical kinetic model for small hydrocarbon combustion comprises 2,759 species and is expected to offer a higher accuracy in modelling methane combustion than detailed models that precede it. MLOCK1.0 is applied to this construction with the task to produce a compact model for methane/air combustion with fidelity in excess of 75% against the set of Industry-defined performance calculations of Table 5.1 while limiting the model size to a virtual reaction network of 15 nodes. The overly-reduced model is obtained by application of PFA using the same procedure as with NUIG1817C3. The model is obtained by increasing the error threshold ε , to its maximum value. Incidental to the MLOCK1.0 process that follows, the *15-node Overly-Reduced Model* resulting from PFA shows PSR fidelity of 54.1%, an IDT fidelity of 39.6% and a S_u fidelity of 59.7% at the performance conditions of Table 5.1.

For the purpose of this thesis, the 15-node compact model produced by applying MLOCK1.0 to NUIGMECH1.0 will henceforth be referred to as *NUIGMECH_15sOp*. NUIGMECH_15sOp has a PSR fidelity of 79.9%, an IDT fidelity of 87.1% and a S_u fidelity of 89.8%.

Figure 5.3 shows the S_u and IDT calculations of the Overly-Reduced, Phase 1 Optimised and Phase 2 Optimised models at representative conditions to illustrate the effect of the first two optimisation modules. To illustrate the fine-tuning performance of Phases 3 and 4, Figure 5.4 shows the S_u and IDT calculations of the Phase 2 Optimised, Phase 3 Optimised, and the Phase 4 Optimised (NUIGMECH_15sOp) models at 40 atm.

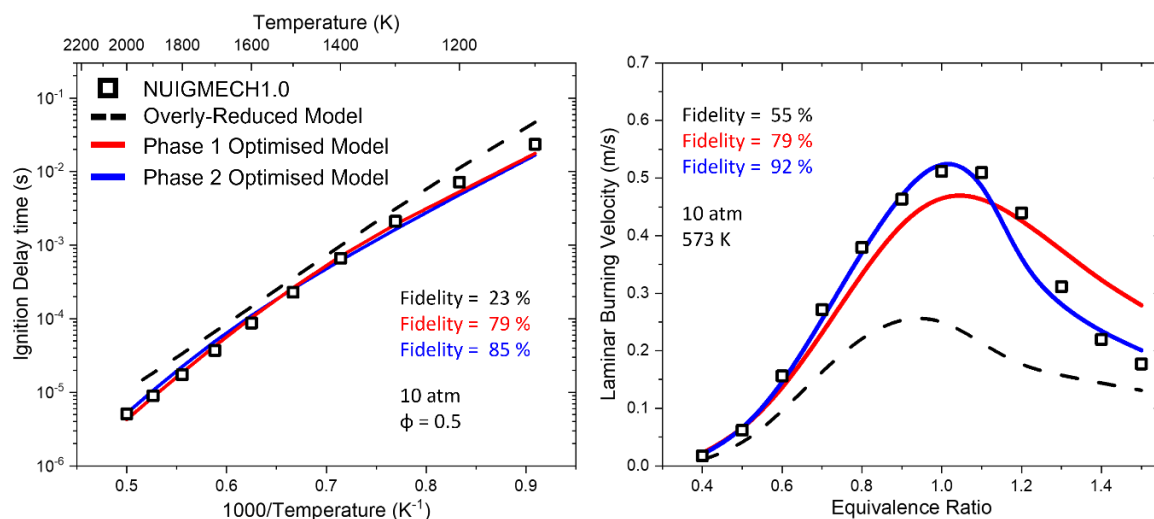


Figure 5.3. Ignition delay time as a function of temperature (left) and laminar burning velocity as a function of equivalence ratio (right) for methane/air mixtures at 10 atm using the NUIGMECH1.0 detailed model (symbols) and 15-node models (lines).

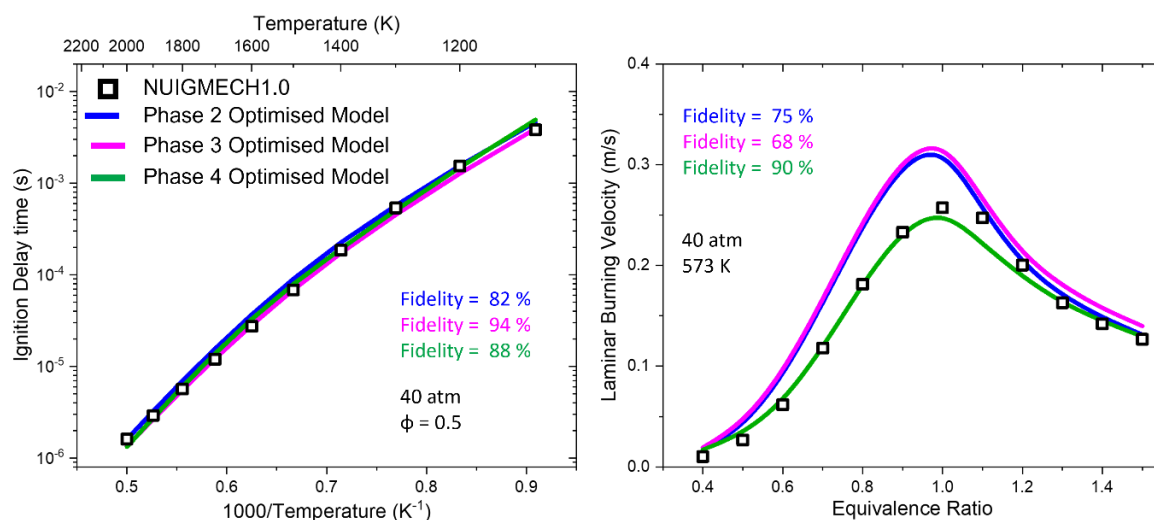


Figure 5.4. Ignition delay time as a function of temperature (left) and laminar burning velocity as a function of equivalence ratio (right) for methane/air mixtures at 40 atm using the NUIGMECH1.0 detailed model (symbols) and 15-node models (lines).

Table 5.4 makes a granular condition-by-condition, phase-by-phase, reporting of the fidelity of the best model candidate at the performance conditions given in Table 5.1 as MLOCK1.0 progresses through its methodology. Additional validation plots can be found in Appendix C, with more comprehensive validation at [173]. The compact model can be found in Appendix D.

Table 5.4. Ignition delay time and laminar burning velocity fidelity of the best 15-node model candidate at various stages during the MLOCK1.0 process. The Phase 4 Optimised model is the final Compact Model.

Performance Property	Model	1 atm	10atm	20 atm	30 atm	40 atm
Ignition Delay Time (IDT) $\phi = 0.5 - 1.5$ 1100 – 2000 K	Overly-Reduced	23.2 %	51.0 %	48.0 %	41.4 %	34.2 %
	Phase 1 Optimised	72.5 %	79.1 %	79.4 %	75.8 %	70.2 %
	Phase 2 Optimised	79.8 %	84.0 %	84.7 %	80.9 %	75.2 %
	Phase 3 Optimised	87.5 %	84.0 %	89.1 %	91.1 %	91.0 %
	Phase 4 Optimised	89.6 %	84.0 %	87.3 %	87.6 %	87.0 %
Laminar Burning Velocity (S_u) $\phi = 0.4 - 1.5$ 573 K	Overly-Reduced	64.4 %	55.8 %	57.8 %	59.8%	60.9%
	Phase 1 Optimised	65.5 %	78.5 %	77.5 %	75.4 %	69.2 %
	Phase 2 Optimised	67.7 %	91.9 %	84.8 %	78.8 %	74.9 %
	Phase 3 Optimised	67.8 %	91.9 %	83.0 %	74.9 %	68.3 %
	Phase 4 Optimised	83.9 %	91.9 %	91.9 %	91.1 %	90.2 %

5.3.3 Benchmarking to State-of-Art Compact Models

Table 5.5 compares the performance of the compact model of this thesis to the state-of-art minimally-sized models for methane/air combustion. Here, we regard the attributes of merit to be the number of nodes (species) in the virtual reaction network and the fidelity of the calculations of the compact model to those of the respective parent detailed model at the performance conditions of Table 5.1. At 24 species, DRM22 [181] is larger than the other models, however, it is included as it is a low-dimensional model familiar to Industry and as such it serves as a recognisable benchmark.

Table 5.5. Comparison of the state-of-art compact models for methane/air combustion. IDT, S_u and PSR fidelity are as defined in text and calculated relative to the respective parent detailed model calculations. The fidelity calculation was performed at the conditions of Table 5.1. The computational cost of each model relative to that of DRM22 was calculated by the time taken to calculate a set of freely propagating flames at 10 atm, 573 K and equivalence ratios 0.4 – 1.5.

Author	No. of Nodes	IDT Fidelity (%)	S_u Fidelity (%)	PSR Fidelity (%)	Parent Mechanism	Time for 1-D Calculation (% DRM22)
<i>State-of-art Models</i>						
Lytras et al. [170]	14	18.6	66.2	59.1	USC Mech II [182]	34.3
Leylegian [174]	15	39.3	83.8	72.5	USC Mech II	35.0
Leylegian et al. [175]	15	16.3	86.2	72.3	USC Mech II	46.2
Bioche et al. [183]	17	94.7	65.1	66.1	GRI 1.2 [184]	58.1
Larson et al. [168, 169]	18	0.0	81.7	5.4	GRI 3.0 [113]	52.2
DRM22 [181]	24	98.1	94.5	98.1	GRI 1.2	100
<i>MLOCK Compact Models</i>						
NUIGMECH_15sOp	15	87.1	89.8	79.3	NUIGMECH1.0	62.3
C3_15sOp	15	75.0	83.1	83.9	NUIG18_17_C3	59.9
C3_19sOp	19	93.6	95.0	94.8	NUIG18_17_C3	89.2

Both 15-node compact models produced in this work outperform the state-of-art compact models across this broad range of gas turbine relevant calculations. We note however, that not all the compact models in the literature were produced with the aim to be accurate across these comprehensive range of performance conditions. As discussed later, due to the lack of detail in the virtual reaction network of compact models, the task of producing a compact model that is valid across a wide range of conditions is challenging and demands a more complex optimisation technique. Thus, compact models tend to be produced for use in limited combustion calculations at a narrow range of operating conditions. The compact model developed by Lytras et al. [170], for example, was constructed for application to 1-D calculations at atmospheric conditions and so, as expected, the compact model performs well at such calculations (87.0%). However, the model performs poorly at elevated pressures and

at 0-D calculations. It is also important to note that the authors did not provide a description of the optimisation methodology, suggesting an ad-hoc optimisation approach. The models developed by Leylegian et al. [174, 175] predict the IDT to high fidelity at the operating conditions at which the model was developed for, however, model performance decreases outside these ranges. The models by Leylegian et al. are the state-of-art in terms of model fidelity to the set of Industry-defined performance calculations. These models were produced by applying PFA to the USC MECH II [182] detailed model, followed by optimisation of the overly-reduced models by a gradient-based optimisation algorithm coupled to the solution mapping technique (in [174]) and by a genetic algorithm (in [175]).

It is interesting to note that the MLOCK-produced compact models have a notably higher relative computational cost. By assessing the computational cost of models from conventional model reduction (i.e., pre-MLOCK), this was found to be an inherited characteristic of the parent detailed model.

5.4 Discussion

In this section, the data obtained from the compaction of NUIGMECH1.0 (unless otherwise stated) will be used to illustrate the behaviour of MLOCK1.0.

5.4.1 Data Structure in Model Error Dependence on Virtual Reaction Rate Constant

Figure 5.5 shows the Coarse Scan – Bound Refinement – Refined Scan behaviour of Phase 1 (see Figure 4.2) using the example of the connection $CH_3 + O_2 \rightleftharpoons CH_2 + O_2$. 80,000 models are produced by varying the virtual Arrhenius parameters (A' , n' , E_A') of important connections across a large range of the virtual reaction rate constant (k_v) bound space in the Coarse Scan (black symbols). Following this, the Bound Refinement algorithm is performed to identify regions of the bound space with high-density of low OEF models (blue line). The more negative the Z-score, the greater the density of models with a low OEF. 80,000 models are then produced in the Refined Scan to further resolve these regions of the bound space (red symbols). From Figure 5.5, one can see that good models are only produced when k_v for this connection is greater than $10^8 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, indicating the importance of this connection for this 15-node reaction network construct. At all k_v less than 10^8 , there is a high

concentration of model candidates with an OEF equal to 1.52, implying that ignition did not occur during any PSR simulation. The poor performance of models in these regions is reflected by the positive Z-score. Furthermore, the bound refinement algorithm identifies the region of 10^8 to 10^{12} $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$ as producing a density of low OEF models that can not be attributed to random variation.

In Figure 5.5, a large deviance in the OEF of model candidates with the same value of k_v for this connection is readily seen and exists for two reasons. Firstly, there are fourteen other connections simultaneously undergoing optimisation, with the k_v of each having an effect on model performance, ranging from negligible to significant, as shown in Figure 5.6. Secondly, two models may have the same value of k_v at 2000 K, however, the temperature dependence of each model (i.e., n' and E') is not depicted in Figure 5.5, hence a variation in model performance is expected.

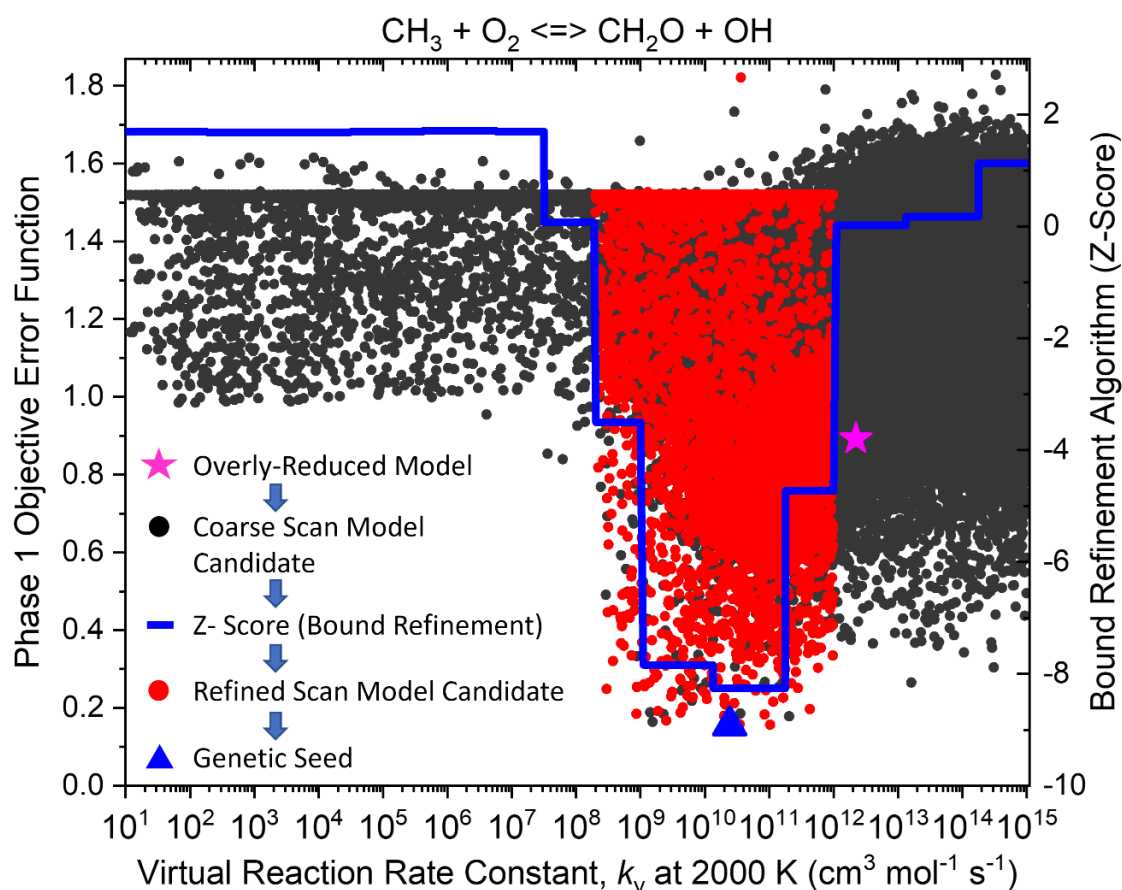


Figure 5.5. Phase 1 Objective Error Function (OEF) of model candidates produced in the Phase 1 Coarse and Refined Scans, as a function of the virtual reaction rate constant of the connection $\text{CH}_3 + \text{O}_2 \rightleftharpoons \text{CH}_2\text{O} + \text{H}$. The Z-score is calculated by the bound refinement algorithm following the Coarse Scan. 2000 K is used as a nominal reference.

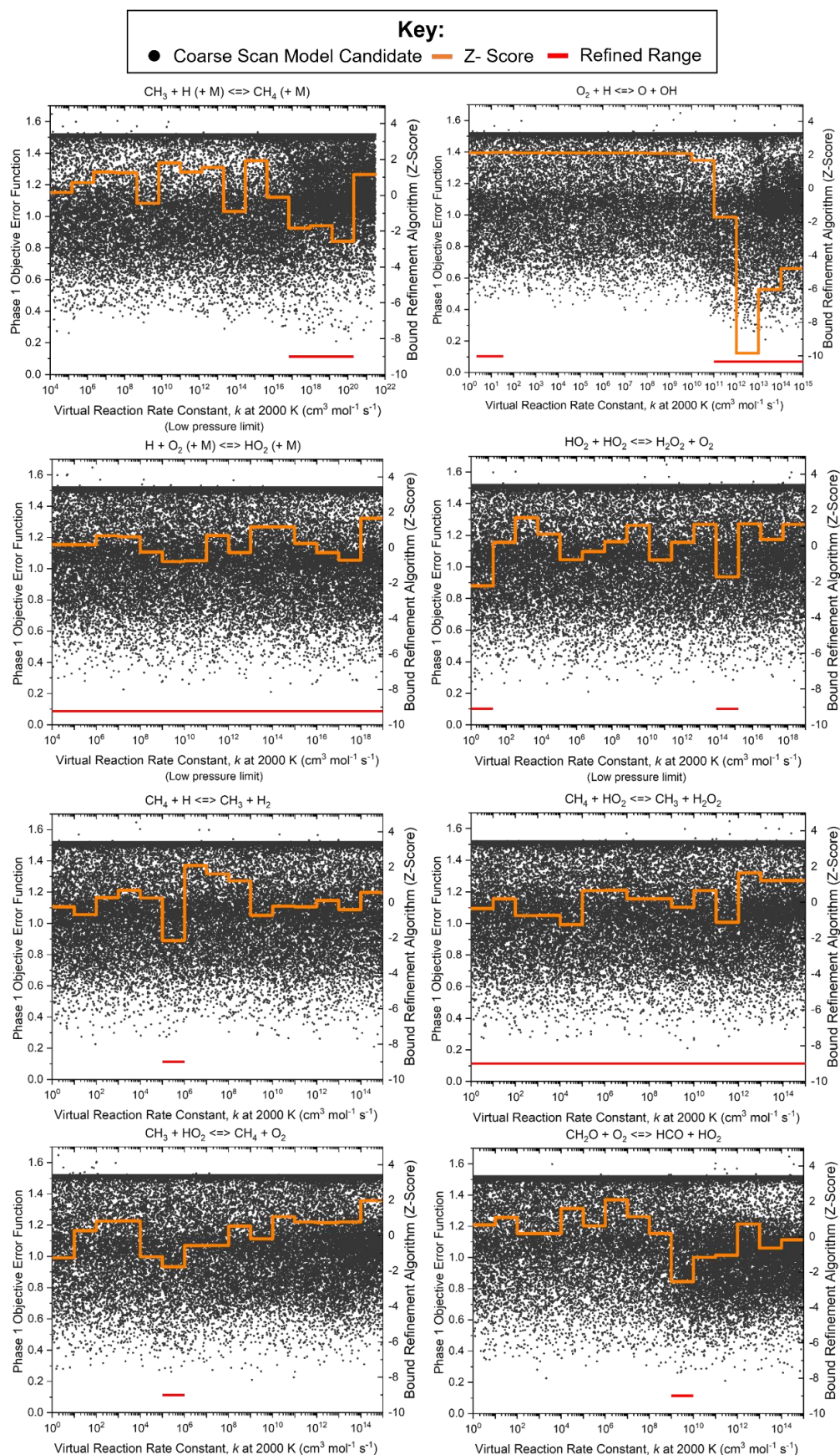


Figure 5.6. (a) Phase 1 Objective Error Function (OEF) of model candidates produced in the Phase 1 Coarse Scan as a function of the virtual reaction rate constant of each connection undergoing optimisation.

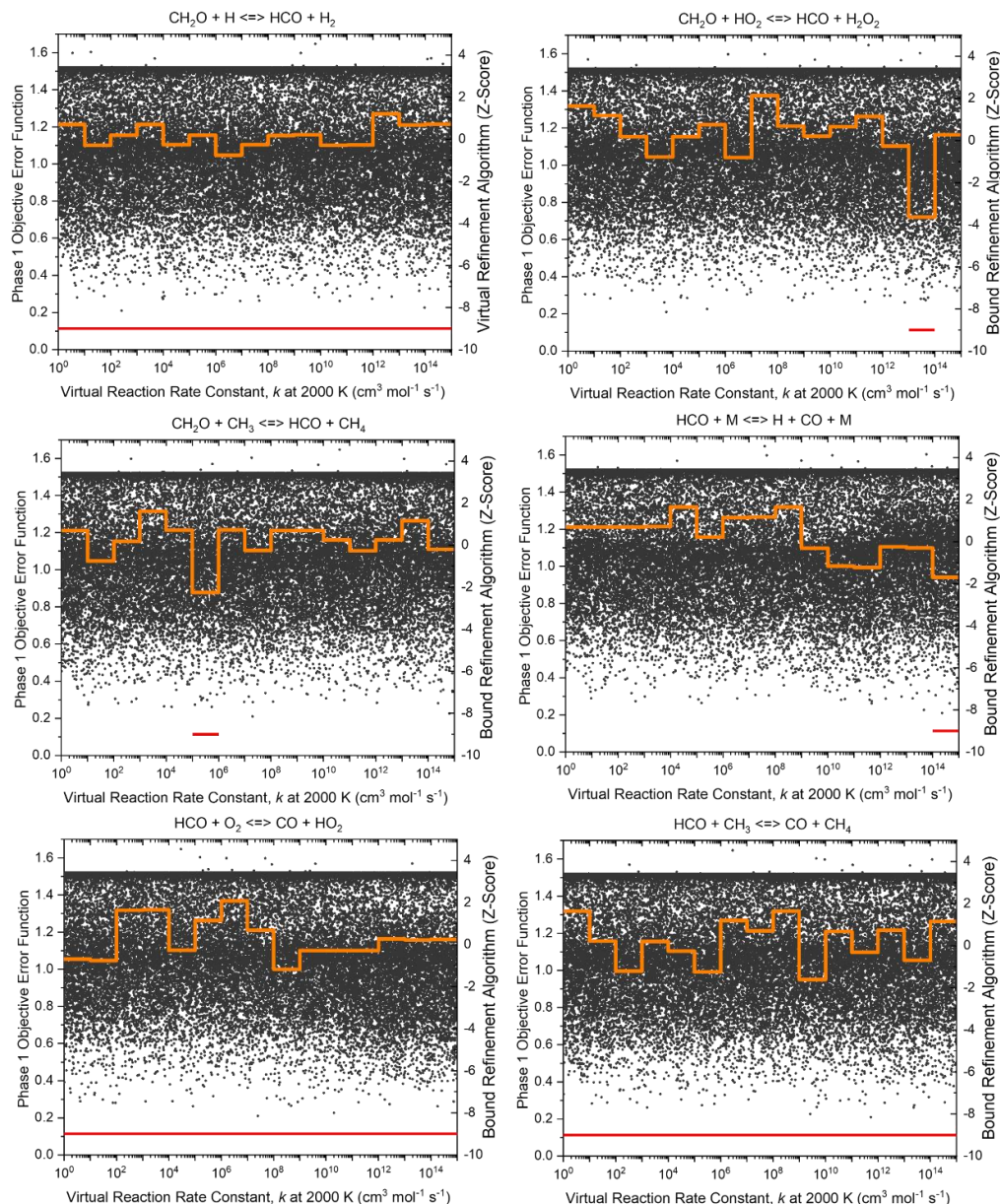


Figure 5.6. (b) Phase 1 Objective Error Function (OEF) of model candidates produced in the Phase 1 Coarse Scan as a function of the virtual reaction rate constant of each connection undergoing optimisation.

5.4.2 Effectiveness of Search Algorithm Procedure

Figure 5.7 shows the number of model candidates produced in the Phase 1 Coarse, Refined and Genetic Seed Scans in this study that have a Phase 1 OEF less than 0.3, indicating a good replication of the Phase 1 optimisation targets. Figure 5.7 demonstrates the expected trend that a larger number of model candidates generated in a Scan results in a higher number of high-fidelity models produced. Additionally, the graph illustrates the increased efficiency of each Scan as it advances through Phase 1, with a greater number of low OEF models

identified as the magnitude of the search space decreases. For 80,000 model candidates, the Coarse, Refined and Genetic Seed Scans respectively find 15, 2125 and 6091 models with 0-D OEF less than 0.3.

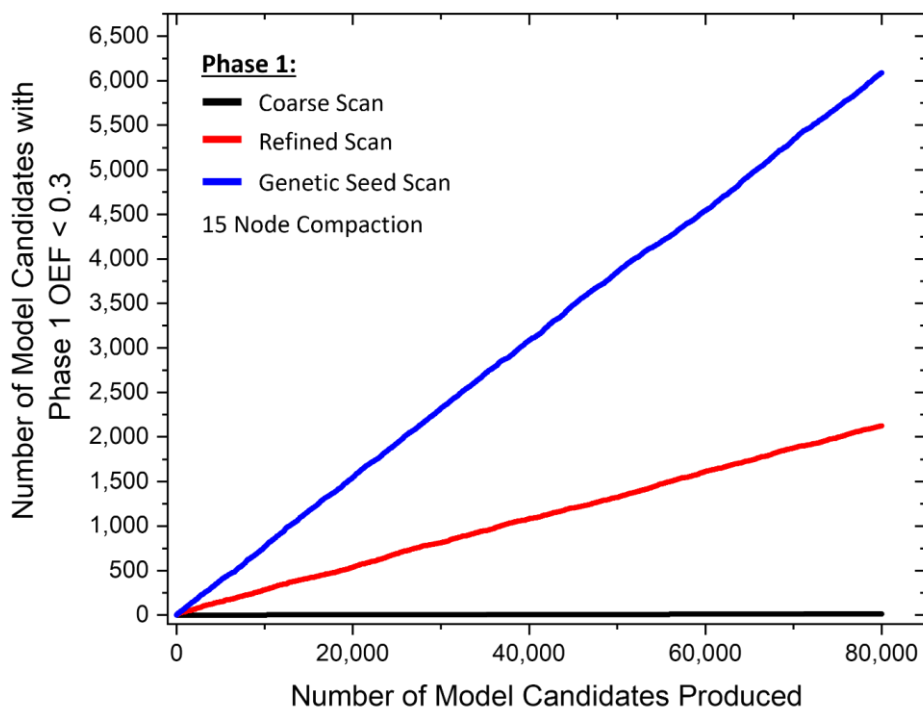


Figure 5.7. The number of model candidates produced with a Phase 1 Objective Error Function (OEF) less than 0.3 in each of the MLOCK Phase 1 scans as a function of the number of model candidates produced.

5.4.3 Analysis of Phase 1 Objective Error Function

It is a widely held hypothesis in the model reduction literature, and in this study, that an accurate replication of PSR calculations is necessary in replicating a range of other combustion phenomena. Figure 5.8 shows the ignition delay time (IDT) fidelity of model candidates produced in the Phase 1 Refined Scan as a function of their Phase 1 OEF. The lower/upper bounds on Figure 5.8 were obtained by binning the data into Phase 1 OEF intervals of size 0.02, selecting the lowest/highest IDT fidelity model in each bin, and fitting the points.

The upper bound may imply that this hypothesis is not strictly true, that some models are produced with a good replication of IDT whilst having a poor replication of CO, OH, H and CH₄ PSR mole fractions. However, the presence of the lower bound (with R^2 of 0.95) means

that the better the replication of these PSR calculations, the higher the likelihood of a more accurate IDT replication. Additionally, the convergence of the two bounds at low Phase 1 OEF infers that the more accurate the replication of PSR calculations, the lower the variation in IDT fidelity. Despite the relatively poor R^2 , denoting a large mean error between the data points and the line of best fit, the slope (denoting Phase 1 OEF) has a p-value essentially equal to zero, indicating that the Phase 1 OEF has a statistically significant effect on the IDT fidelity. Hence, whilst not being a perfect correlator to IDT fidelity, this OEF formulation is useful and provides a rich description of 0-D performance.

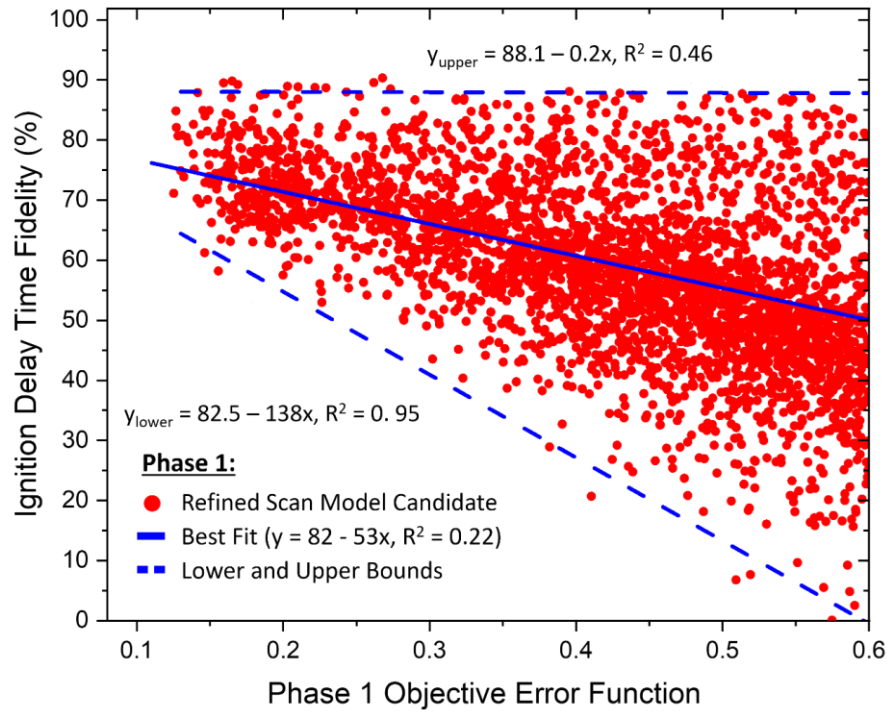


Figure 5.8. Ignition delay time (IDT) fidelity of 15-node model candidates produced in MLOCK Phase 1 Refined Scan as a function of the Phase 1 Objective Error Function (OEF). IDT fidelity was calculated at 10 atm, 1100 – 2000 K, and equivalence ratios 0.5 – 1.5, as per Table 5.3.

Figure 5.9 shows the same plot as Figure 5.8 but for the case of 19-node compaction of NUIG1817C3. Here, a more definite coupling exists between the IDT fidelity and the Phase 1 OEF, as denoted by a larger R^2 value of the line of best fit. This means that this equation better describes the data compared to the case of 15-node compaction, meaning a better coupling between the two metrics. Additionally, a larger R^2 means that there is less variation in the data, which is also observed by the smaller range between the lower and upper bounds.

As there are more nodes in the 19-node construct, a better description of the reaction mechanism is possible due to a larger number of degrees of freedom, and hence, a stronger coupling between the OEF and IDT fidelity. In this construct, the nodes will act more like their physical counterparts in a detailed (or skeletal) model and hence, the species that comprise the Phase 1 OEF will act as better indicators for overall model performance than in a more virtual construct. Furthermore, due to the additional nodes in the 19-node construct, models are produced with a better replication of PSR calculations (lower Phase 1 OEF), and a better replication of IDT calculations (higher IDT fidelity) compared to the 15-node compaction.

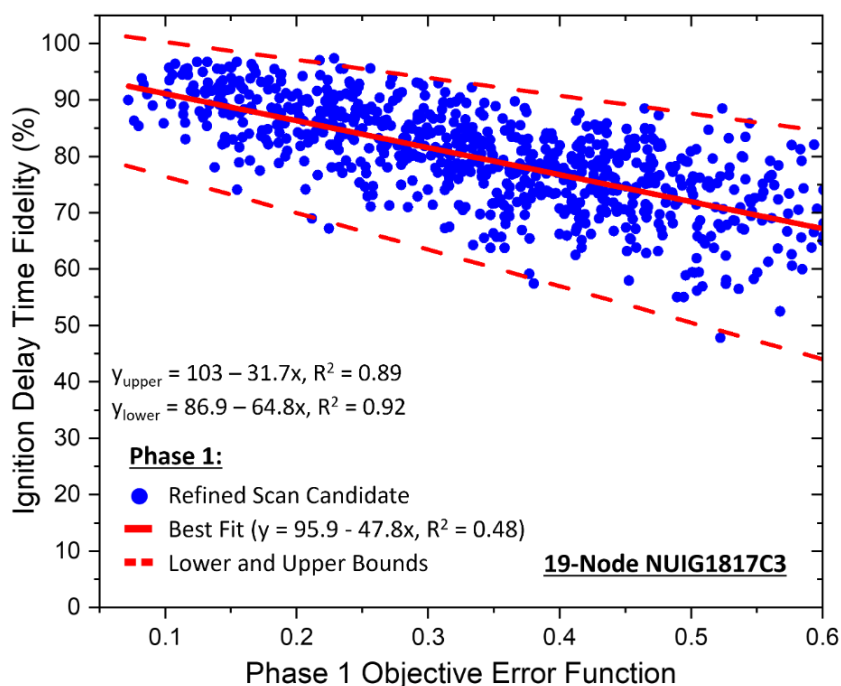


Figure 5.9. Ignition delay time (IDT) fidelity of 19-node model candidates produced in MLOCK Phase 1 Refined Scan of NUIG1817C3 compaction as a function of the Phase 1 Objective Error Function (OEF). IDT fidelity was calculated at 10 atm, 1100 – 2000 K, and equivalence ratios 0.5 – 1.5, as per Table 5.3.

However, it is also apparent from examination of Figures 5.8 and 5.9 that no model is produced with a perfect replication of NUIGMECH1.0 PSR or IDT calculations, highlighting the performance limit of the 15-node and 19-node constructs. Similar to previously reported [151], Figures 5.8 and 5.9 show that multiple sets of solutions produce an equally good replication of the optimisation target (Phase 1 OEF) but with varying performance to other validation targets (IDT fidelity). Furthermore, as discussed later, the

Phase 1 OEF provides no indication as to the S_u fidelity of the model candidate. Hence, selecting the best performing model based solely on the OEF would most likely not select the best overall model. This necessitates the Assessment steps which are crucial to the outcome of the MLOCK process.

5.4.4 Analysis of Phase 2 Objective Error Function

A significant obstacle to purposes such as this study is the apparent non-transference of PSR attributes to laminar flame attributes as shown in Figure 5.10 (a), where no meaningful relationship exists between the Phase 1 OEF and S_u fidelity of 15-node model candidates produced in the Phase 1 Refined Scan. This non-correlation necessitates direct optimisation to flame calculations, which is not a problem when dealing with models for simple fuels such as methane, however this can pose a problem when working with more complex systems e.g., liquid transportation fuels. For these fuels, flame calculations have a considerable computational cost and can be numerically stiff to converge. It is therefore highly desirable to obtain an OEF that is comprised of information from 0-D calculations that provides a good indication of the performance of a model candidate in both 0-D and 1-D simulations.

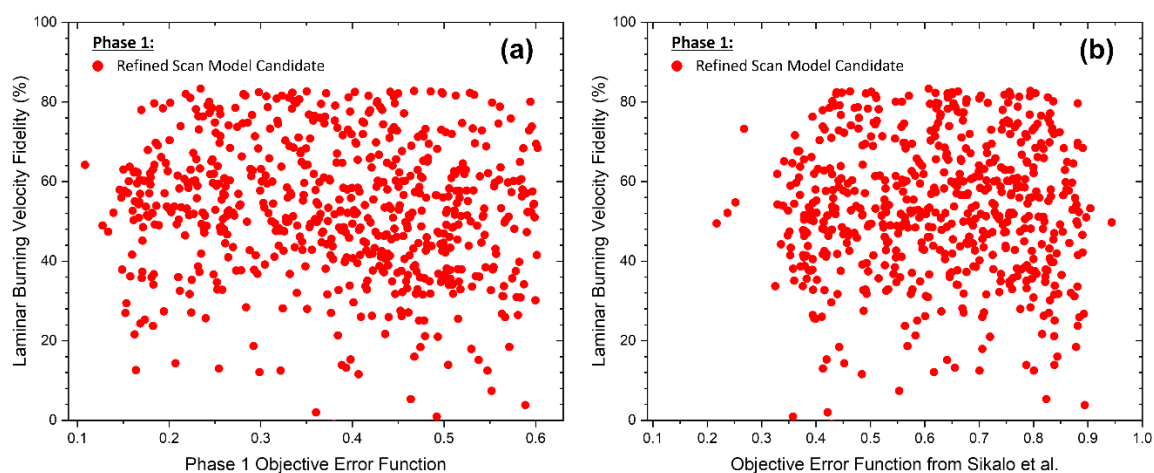


Figure 5.10. Laminar burning velocity (S_u) fidelity of a subset of 15-node model candidates produced in Phase 1 Refined Scan as a function of the: a) Phase 1 Objective Error Function (OEF). b) OEF from work of Sikalo et al. [95]. S_u fidelity calculated at 573 K, 10 atm, and equivalence ratios 0.4 – 1.5. No discernible dependence of S_u fidelity to either OEF is apparent.

Following review of the literature in this regard, given the prevalence of the use of 0-D computed data in model reduction, it is surprising that apparently no effective relationships to this purpose have been demonstrated. Sikalo et al. [95] optimised a 25 species model for methane combustion using a genetic algorithm with an OEF composed of 0-D calculations, leading to a reduction in the error in S_u calculations from 10% to 5%. Error in the mole fractions of atomic hydrogen (H) in 0-D reactor calculations was included in the OEF as an indicator for S_u performance. This OEF was applied in this work, however no discernible relationship was found between this OEF and the burning velocity fidelity for 15-node model candidates. Figure 5.10 (b) shows the result of this OEF applied to the same set of model candidates as in Figure 5.10 (a). The likely reason for this is that in a 15-node reaction network construct, the now virtual hydrogen atom will not embody the same characteristics as in a realistic reaction mechanism, and therefore it will not perform as well as an indicator for S_u model performance. This highlights that a level of precaution must be taken when using a compact model that has been optimised to 0-D calculations only. If the description of the reaction mechanism is virtual, then the accuracy of the model to 0-D calculations does not act as an indicator for model performance to 1-D calculations. It is thus necessary to test the performance of such a model on a range of 1-D calculations. Numerous OEFs containing 0-D calculations have been formulated, all reporting behaviour similar to the Phase 1 OEF, with a non-predictiveness of S_u . Thus, as an interim measure to bridge this divide, a basic hybrid OEF composed of data from a library of 0-D calculations trained by multiple linear regression to calculations of S_u was devised. It should be noted that an alternative approach to optimising the kinetics component to 1-D calculations (i.e., Phase 2) is the optimisation of the species transport component, which is a relatively unexplored area of research. Due to the lack of literature on this, the potential adverse effects of such an optimisation remains unknown and warrants careful exploration. Care must be taken to ensure that this does not affect the performance of the model in higher dimensional calculations and to ensure that laminar burning velocity remains a suitable indicator for 1-D model performance.

5.4.5 Application of Multiple Linear Regression

Only models with Phase 2 OEF less than 0.5 were included in the training and validation datasets for the multiple linear regression, as this was found to produce regression models with better predictability for high fidelity compact models. Figure 5.11 shows the predictive

capability of the regression model for model candidates produced in the 1st Genetic Seed Scan of Phase 2 for a MLOCK instance. This enabled the analytical prediction of the Phase 2 OEF for model candidates rather than simulating a series of laminar flames, significantly reducing the computational cost of the algorithm.

It was found that developing a regression model for each condition in the Phase 2 OEF and then combining their predictions of the error produced better results than making one regression model to predict the Phase 2 OEF. Additionally, training on each condition allows for easy changing and retraining of the regression model when the conditions in the Phase 2 OEF are changed.

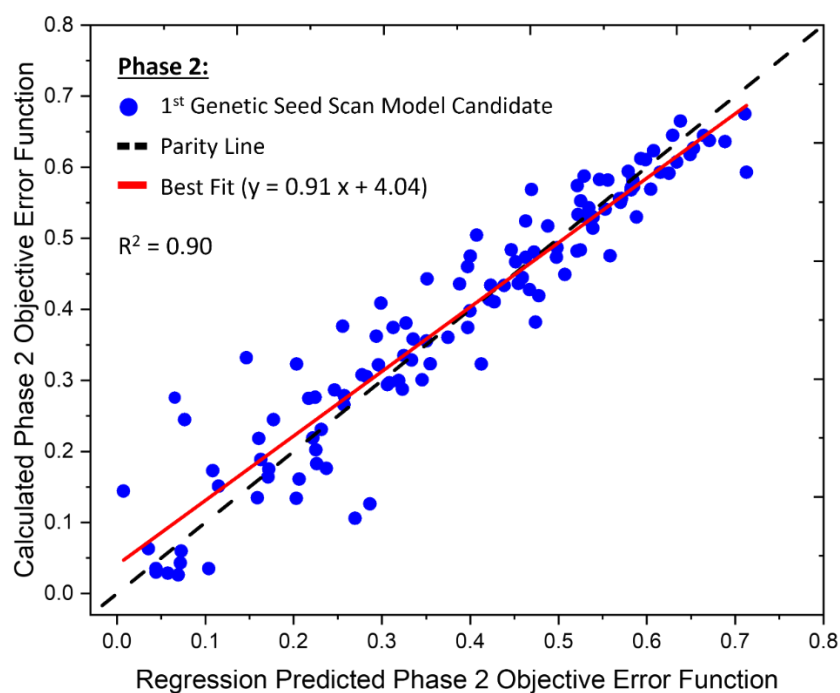


Figure 5.11. Calculated Phase 2 Objective Error Function (OEF) versus Phase 2 Objective Error Function predicted by the multiple linear regression model developed in Phase 2, of a subset of model candidates produced in the 1st Genetic Seed Scan of Phase 2.

5.4.6 Analysis of Phase 3 and 4

In this MLOCK1.0 application, only calculations at 10 atm are evaluated in Phases 1 and 2. This choice assumed that kinetic model parameters valid at 10 atm are likely to be valid at other pressures, thus significantly reducing the number of calculations performed in Phase 1

and Phase 2. As shown in Table 5.4 this assumption is somewhat valid, however, Phase 3 and Phase 4 were constructed to act as fine-tuning modules. In Phase 3, the most sensitive connection at both 1 and 40 atm was $\text{CH}_3 + \text{O}_2 \rightleftharpoons \text{CH}_2 + \text{O}_2$. The value of k_v for this connection was decreased at 1 atm by approximately 33% from the optimised value at 10 atm, whereas at 40 atm it was increased by approximately 149%, as shown in Figure 5.12. In other words, to improve replication of NUIGMECH1.0 ignition delay time calculations at 1 atm, it was found that this connection needed to be slowed down, whereas at 40 atm the connection must be sped up to increase reactivity.

In Phase 4 the connection $\text{H} + \text{O}_2 \rightleftharpoons \text{O} + \text{OH}$ was found to be the most sensitive at both 1 and 40 atm. Here, it was found that to improve fidelity to NUIGMECH1.0 burning velocity calculations at 1 atm, k_v must be increased by approximately 19% from the optimised value corresponding to 10 atm to increase chain branching, whereas at 40 atm it must be decreased by approximately 47%.

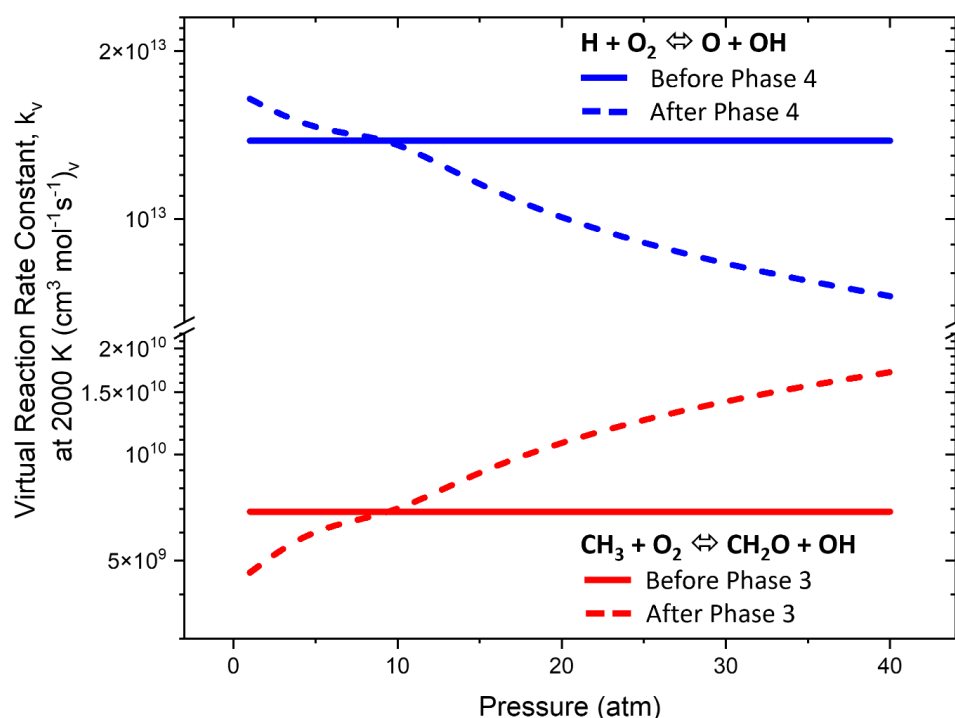


Figure 5.12. Effect of Phase 3 and Phase 4 on the virtual reaction rate constant, k_v , for the connections $\text{CH}_3 + \text{O}_2 \rightleftharpoons \text{CH}_2\text{O} + \text{OH}$ and $\text{H} + \text{O}_2 \rightleftharpoons \text{O} + \text{OH}$ respectively.

Following Phase 4, it was observed that the model candidates with the highest IDT fidelity tended to have a low S_u fidelity. This is due to a disparity in the value of k_v that corresponds to the global maxima for the S_u and IDT fidelity, as shown in Figure 5.13, thus necessitating a compromise, as can be seen by a slight decrease in the IDT fidelity of the Phase 4 optimised model compared to the Phase 2 optimised model, as shown in Table 5.4. This implies the need to either optimise more connections, or to optimise to IDT and S_u simultaneously (i.e., to combine Phases 3 and 4).

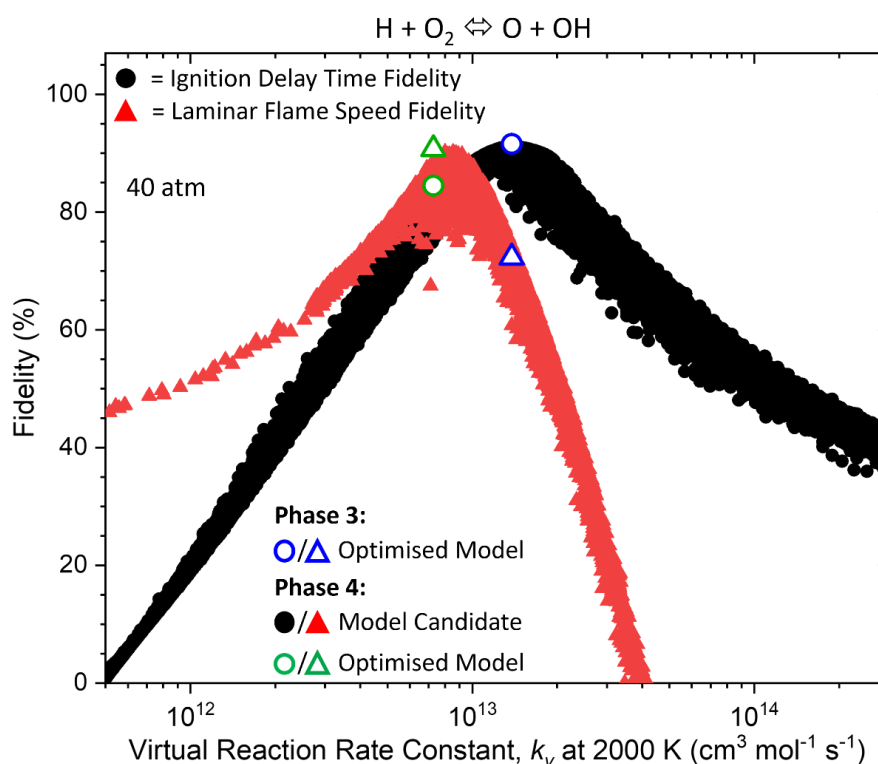


Figure 5.13. The ignition delay time (black) and laminar flame speed (red) fidelity of 15 node model candidates produced during MLOCK Phase 4 at 40 atm as a function of k_v at 2000 K for the connection $\text{H} + \text{O}_2 \rightleftharpoons \text{O} + \text{OH}$.

5.4.7 Effect of Reaction Network Complexity on Optimisation

As evidenced in Table 5.5 through examination of the *MLOCK Compact Models*, the larger the number of nodes in the virtual reaction network, the easier the optimisation task and the higher the overall fidelity of the compact model. To highlight the difference in the behaviour of MLOCK dependence on the number of nodes in the network, a Phase 1 Coarse Scan was performed on 19- and 22-node overly-reduced models. Figure 5.14 demonstrates this

difference in behaviour by counting the number of model candidates produced in this Scan with a Phase 1 OEF below 0.3. This shows that the larger the virtual reaction network, the greater the number of low OEF models produced in the Scan (15, 42 and 77 for fifteen, nineteen and twenty-two node constructs respectively). Moreover, the model candidate with the lowest OEF from the 15-, 19- and 22-node Coarse Scan had an OEF of 0.21, 0.14 and 0.12 respectively, showing that the more complex the reaction network, the higher the fidelity of the models produced. Hence, if a larger kinetic model can be computationally afforded, the optimisation task is a much simpler one. However, if a minimally-sized kinetic model is required, the optimisation task is considerably more challenging necessitating a complex optimisation technique.

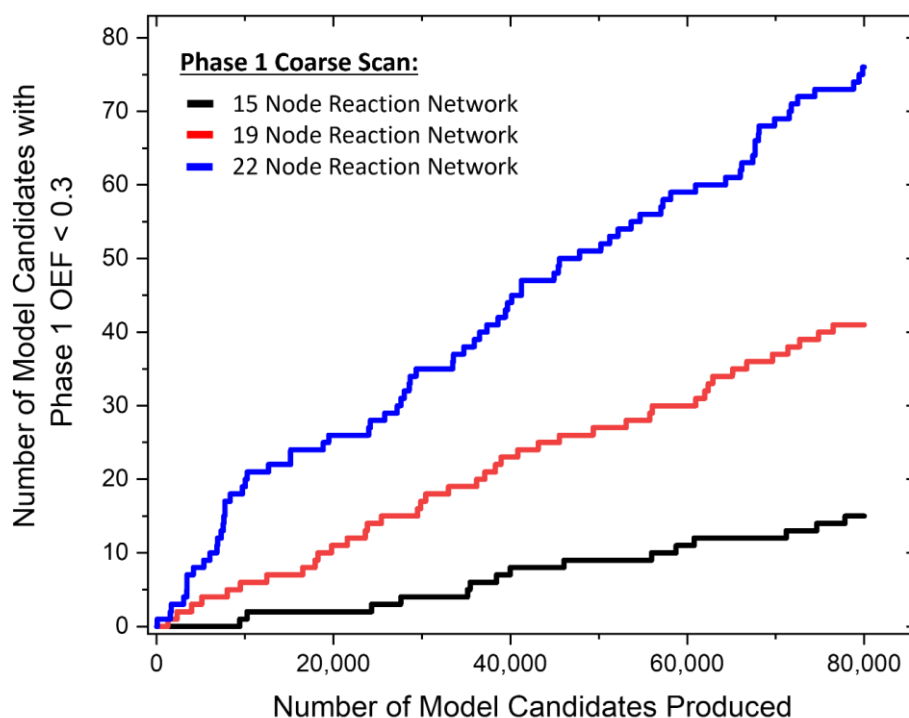


Figure 5.14. The number of model candidates produced with a Phase 1 objective error function (OEF) less than 0.3 in the Coarse Scan during 15-, 19- and 22-node compaction, as a function of the number of model candidates produced by the Scan. The model candidate with the lowest Phase 1 OEF was 0.21 for the 15-node compaction, 0.14 in the case of 19-node compaction and 0.12 in the case of 22-node compaction.

5.4.8 Effect of Number of Optimised Connections on Optimisation

To highlight the effect of the number of connections undergoing optimisation on the behaviour of MLOCK, two Phase 1 Coarse Scans were performed using the 15-node Overly-Reduced Model from NUIGMECH1.0. In the first Coarse Scan, only the connection $CH_3 +$

$O_2 \rightleftharpoons CH_2 + O_2$ was optimised and in the second Coarse Scan a second connection was also optimised. The k_v vs Phase 1 OEF for the connection $CH_3 + O_2 \rightleftharpoons CH_2 + O_2$ from these two Scans is shown in Figure 5.15. In the case of one-connection optimisation, a very clear coupling exists with a small variation at each x-axis point. This variation is solely due to the difference in the temperature dependence of each model. However, the coupling between Phase 1 OEF and k_v for this connection in the two-connection optimisation is less exact with more variation due to the additional dependence of the model performance upon the k_v of the second connection. Therefore, the more connections that are included in the optimisation, the more indistinct the minimum becomes. Thus, looking at Figure 5.6, one could easily assume that no minima exist for some connections, however, it is likely the case that the minima is less-defined due to the inclusion of fourteen other connections in the optimisation. This highlights the need for a sophisticated algorithm to detect regions at which a minimum is likely to be found.

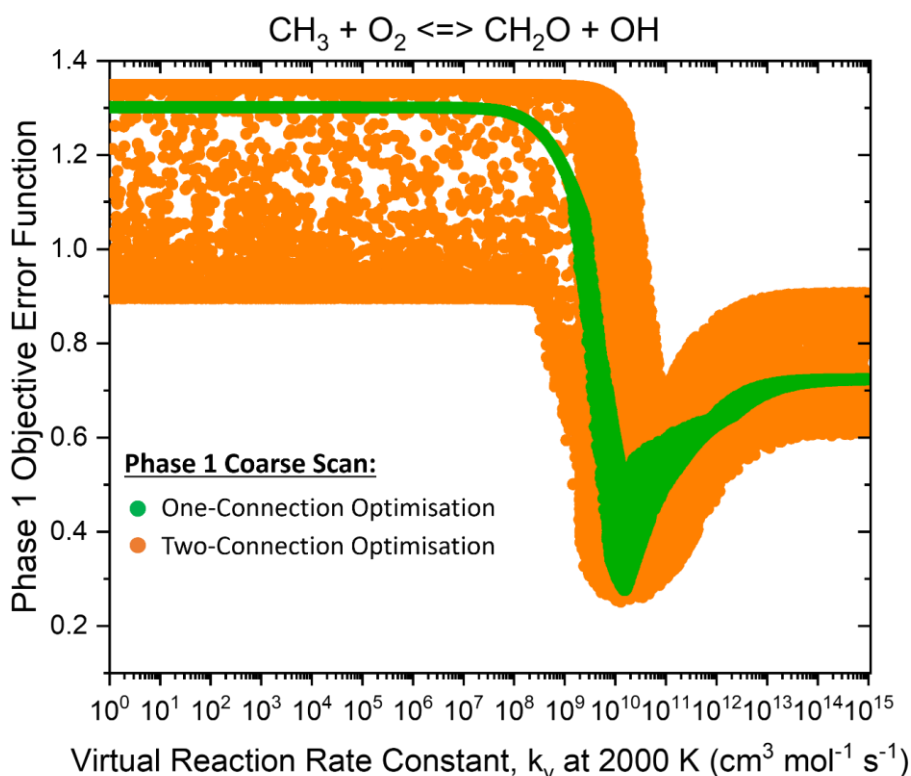


Figure 5.15. Phase 1 Objective Error Function (OEF) of model candidates produced in the Phase 1 Coarse as a function of the virtual reaction rate constant of the connection $CH_3 + O_2 \rightleftharpoons CH_2O + H$ in the case of one (green) and two (orange) connections undergoing optimisation.

Furthermore, examination of Figure 5.15 reveals that including more connections in the optimisation results in models with lower Phase 1 OEFs being found. To further study this, Phase 1 Coarse Scans were performed on the 15-node Overly-reduced Model from NUIGMECH1.0, with the number of connections undergoing optimisation set to three, six, nine and fifteen. Figure 5.16 shows the results of these Scans in terms of the number of “good” models produced and the lowest Phase 1 OEF model found during each Scan. These results highlight that by increasing the number of connections, the number of possible solutions increases, meaning that the coverage factor of the bound space decreases. Hence, the number of “good” models found decreases as the number of connections undergoing optimisation increases. Conversely, the Phase 1 OEF of the best model decreases as the number of connections undergoing optimisation increases. This is due to the increased degrees of freedom available to the optimisation algorithm in diverting the virtual reaction flux through the system resulting in the production models with better replication of the optimisation targets. Hence, it is important to use a suitably large value of n (number of model candidates produced) in each scan when optimising a large number of connections.

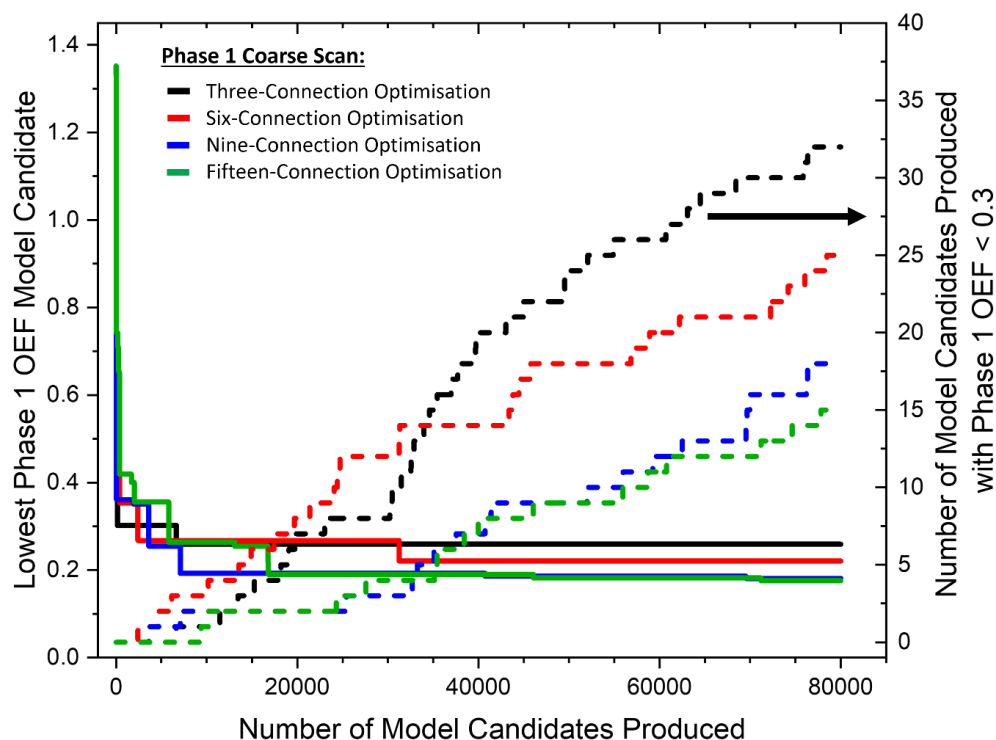


Figure 5.16. The number of model candidates produced with a Phase 1 Objective Error Function (OEF) less than 0.3 (dashed lines, right axis) and the lowest Phase 1 OEF model found (solid lines, left axis) in Phase 1

Coarse Scans with 3, 6, 9 and 15 connections undergoing optimisation in a 15-node virtual reaction network construct.

5.5 Conclusions

The MLOCK algorithm is applied to the archetypal methane combustion system. The Industry-defined performance targets for the simulation of methane/air combustion comprise ignition delay time (IDT), perfectly stirred reactor (PSR) and laminar burning velocity (S_u) calculations across a broad range of operating conditions as computed by the NUIGMECH1.0 detailed kinetic model, which is the item to be compacted.

Adherence to the ChemKin format presents obvious restrictions to the compaction process. Even with these restrictions, it is shown that MLOCK readily arrives at a large number of discreet compact model instances of 15-19 nodes (species) that show high fidelity in calculation of the Industry-defined performance targets. It is demonstrated that MLOCK readily simplifies two separate detailed kinetic models for hydrocarbon combustion, *NUIG1817C3* and *NUIGMECH1.0*, the former a developmental version of the later.

C3_19sOp outperforms both *C3_15sOp* and *NUIGMECH_15sOp* as expected, due to the greater number of nodes and therefore greater level of information and degrees of freedom contained in the virtual reaction network. *C3_15sOp* and *NUIGMECH_15sOp* were shown to outperform the current state-of-art models in terms of 0-D and 1-D validation tests across the range of Industry-defined performance calculations. The 15-node compact models have a computational time of ~60% that of DRM22 in solving 1-D laminar flames. The results of this work appear to support the concept that high-fidelity, low-dimensional “compact” models can be automatically produced using data-intensive methodologies, with the output conforming to Industry-standard (i.e., ChemKin) model formats.

Chapter 6

Compact Models for Methane/Air Combustion with NO_x Chemistry

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6.1 Introduction

Nitrogen oxides (NO_x), which are mainly composed of nitric oxide (NO) and nitrogen dioxide (NO₂), are one of the most important groups of species produced during combustion. These highly reactive molecules are major contributors to air pollution and greenhouse gas

emissions. The presence of NO_x in the atmosphere can cause respiratory problems in humans and contribute to acid rain [185]. For these reasons, stringent legislation has been introduced setting targets on the level of NO_x emissions permitted from combustion devices, thus driving the development of NO_x emission control techniques. This demand is concurrent with ongoing operational needs for gas turbines to provide clean and efficient, low NO_x combustion for a wide range of fuel choices.

6.1.1 NO_x Chemistry

The formation of NO_x during combustion is a complex phenomenon owing to multiple formation pathways occurring at different timescales and locations within the flame. A large volume of work has been devoted to better understand the NO_x formation pathways during combustion (e.g., [186-188]) and to develop technologies to control and reduce their emissions (e.g., [189, 190]). A comprehensive review of NO_x chemistry is found at [191].

The three major NO_x formation pathways in combustion are *Thermal NO*, *Prompt NO* and the *N₂O pathway*, as discussed next.

- **Thermal NO**, also known as the Zeldovich mechanism [192], is the most important formation pathway for NO at high temperatures. The principal reactions are:



Due to the triple bond in N₂, which has a bond dissociation energy of approximately 945 kJ/mol [193], the first reaction in this pathway has a very high activation energy, approximately 315 kJ/mol [194], and hence this route only proceeds at significant rates at high temperatures. Consequently, this route typically only occurs in the burned gas regions (post-flame zone) in flames. The thermal NO path is coupled to the kinetics of the system due to the participation of the radicals O, OH and H. Hence, the accuracy of a kinetic model in replicating thermal NO is dependent upon the accurate depiction of the kinetics of the particular combustion system.

- **Prompt NO**, or Fenimore NO [195, 196], is an important NO formation pathway at fuel-rich conditions. This mechanism is initiated by the attack of CH_n radicals, produced through fuel oxidation, on N_2 in the flame front, the most important of which is,



The NCN radical acts as an important cyanide radical, ultimately leading to the production of NO and NO₂ through subsequent oxidisation reactions. These reactions occur in the flame front and proceed at fast rates, hence the term *prompt*. In terms of modelling, this pathway is not as well described due to the more complex reaction mechanism, the involvement of the lesser known NCN radical and more carbon-nitrogen chemistry, which necessitates the inclusion of a larger number of hydrocarbon species in the reaction mechanism to accurately describe.

- **The N₂O pathway** involves the combination of N_2 and O through the reaction,



followed by the formation of NO by,



or,



The NH radical then may oxidise to NO or participate in further chain propagating or branching reactions. At high pressures this pathway becomes relevant due to the effect of the collision partner in the initiation reaction.

Therefore, to accurately describe NO_x chemistry, one must have an accurate replication of other kinetics of the system and the hydrocarbon species pertinent to NO_x formation reactions. To meet the demand for low NO_x combustion devices, low-dimensional kinetic models are needed that can accurately predict this complex NO_x formation chemistry using a minimal number of species, to enable the efficient coupling to multi-dimensional

simulations in the combustor design stage. Hence, MLOCK is applied to this task to produce compact models for NO_x formation.

6.2 Specifics of Compaction

In this Chapter, calculations using the NUIGMECH1.0 detailed model for hydrocarbon combustion are used for performance, optimisation, and validation targets. Table 6.1 shows the set of calculations that Siemens Energy require the compact model to be accurate to for it to be useful in their combustor design process. These include performance targets for both the base fuel and NO_x chemistry. The overall fidelity of the model to the calculations in Table 6.1 must be at least 75%, with a base fuel of methane. The 15-node compact model for methane/air combustion (NUIGMECH1.0_15sOp) that was presented in Chapter 5 is used as the base fuel model. From this, a virtual reaction network for NO_x formation will be appended and the connections optimised. MLOCK1.1, an adapted version of the MLOCK1.0 algorithm, is used for this challenge. The optimisation targets used by MLOCK1.1 in the compaction process are detailed in Table 6.2. Additionally, the set of calculations used by MLOCK1.1 in the Assessment steps are presented in Table 6.3.

Table 6.1. Gas-turbine industry defined performance targets for NO_x formation during methane combustion. Compact model performance will be benchmarked to replication of these targets. An overall model fidelity of >75% is deemed acceptable.

Reactor Physics	Property	Pressure (atm)	Equivalence Ratio	Temperature (K)
Perfectly Stirred Reactor	[OH], [CO], [CO ₂], [H ₂ O], [NO], [NO ₂]	1, 10, 20, 30, 40	0.4, 0.5,..., 1.4	1000, 1100, ..., 2000
Constant Volume Constant Internal Energy	IDT	1, 10, 20, 30, 40	0.5, 1.0, 1.4	1100, 1200, ..., 2000
Freely Propagating Flame	S _u	1, 10, 20, 30, 40	0.4, 0.5,..., 1.4	473, 573, 673

Table 6.2. Optimisation targets that comprise the OEFs evaluated in the Scans of each Phase of MLOCK1.1. An optimisation target provides an indicator of model performance in 0-D and 1-D calculations at Industry relevant operating conditions. MLOCK1.1 uses these targets to optimise the model candidates.

Purpose	Reactor Physics	Property	Pressure (atm)	Equivalence Ratio	Temperature (K)
Phase 1 Optimisation Targets	Perfectly Stirred Reactor	[NO], [NO ₂]	1, 10, 40	0.7, 0.9, 1.0, 1.1, 1.4	1100, 1500, 2000
	Freely Propagating Flame	[NO], [NO ₂]	10	0.6, 0.8, 1.0, 1.2, 1.4	573

Table 6.3. Validation targets that are evaluated in the Assessment stage of MLOCK1.1. A validation target is a calculation that acts as an important indicator of overall model performance. MLOCK1.0 uses these targets to calculate model fidelity.

Purpose	Reactor Physics	Property	Pressure (atm)	Equivalence Ratio	Temperature (K)
Phase 1 Validation	Perfectly Stirred Reactor	[NO], [NO ₂]	1, 10, 40	0.5, 0.9, 1.3	1100, 1200, ..., 2000
	Freely Propagating Flame	[NO], [NO ₂]	1, 10, 40	0.5, 0.9, 1.3	573

To quantify the accuracy of the compact models to the performance and validation conditions, fidelity indexes are used,

$$Fidelity (\%) = \frac{100}{N} \sum_k \left(1 - \frac{|X_k^{compact} - X_k^{detailed}|}{X_k^{detailed}} \right) \quad (6.8)$$

where X_k is the calculation (e.g., laminar burning velocity) at the k^{th} set of pressure, temperature, and equivalence ratio conditions and N is the number of conditions included. A value of 100% indicates a model with perfect replication of the detailed model calculations.

- For IDT fidelity, X represents the time at which derivative temperature by derivative time is at a maximum.
- For S_u fidelity, X is the laminar burning velocity.

- For PSR NO_x fidelity, X is the maximum mole fraction of NO and NO₂, the time at which this maximum occurs, and the steady state concentration of NO and NO₂ in PSR calculations at residence times of 100 ms.
- For Flame NO_x fidelity, X is the maximum mole fraction of NO and NO₂ in freely propagating flame calculations.

6.3 Methodology

For this study, MLOCK1.0 is adapted to create MLOCK1.1 as described below, towards the challenge of minimalistic NO_x modelling.

6.3.1 Virtual Reaction Network Generation

In the case of NO_x chemistry, the actual physically occurring reaction mechanism is relatively complex, and consequently, the detailed kinetic models that simulate this already comprise over fifteen species, e.g., Grimech3.0 [113] has seventeen nitrogen-containing species. Notwithstanding this, the methodology employed here recognises the industry-defined performance envelope and necessarily aims to describe this complex chemical kinetics with minimalistic detail.

Industry demands a reaction network comprising as few species additional to the fuel species as possible. For NO_x, by definition this is two (NO and NO₂). For this minimalistic NO_x modelling challenge, we know from experience that the implementation of conventional mechanism reduction, as deployed in MLOCK1.0, would not result in a virtual reaction network that is suitably minimised in size. Instead, for this application, the virtual reaction network of the overly-reduced model is constructed from combinatoric theory using a combinatorial Latin Square design, as shown in Figure 6.1. Combinatorial design is a branch of mathematics that deals with arranging elements in a set into patterns according to specified rules. In the case of a virtual reaction network, this involves combining nodes together and following strict rules to construct a scheme of virtual reactions. This approach allows for the systematic generation of the maximum number of connections for a given set of nodes (species array). Thus, the minimum-sized virtual reaction network with sufficient degrees of freedom for successful optimisation should hypothetically be created. If a

successful optimisation is not achieved, the species array may be iteratively expanded providing increased degrees of freedom to the optimisation algorithm, whilst still retaining a minimal-sized reaction network that is viable.

The combinatorial Latin Square virtual reaction network generation method allows for the nitrogen containing nodes to interact with the nodes of the associated fuel reaction network, by systematic combinatorics [197]. As we don't have an automated procedure for this like we do for conventional model reduction, the key is to be consistent, following logical steps that can be coded so that the procedure can be automated, and the results obtained be replicated in the absence of human input. Given this, and that the MLOCK optimisation algorithm allows vast degrees of freedom, it is important that safe-guarding measures are imposed to prevent adulteration of the reaction flux of the base-fuel combustion kinetics. Therefore, two selection criteria are applied to define the node array for the Latin Square:

1. Nodes must contain elements that comprise the target nodes i.e., O or N for NO or NO₂,
2. Nodes must not be a molecule (excluding combustion products and reactants i.e., CO₂, H₂O, NO, NO₂ and O₂).

This results in a nine node Latin Square given by Figure 6.1. To generate the connections the following rules are then applied to the Latin Square:

3. Reactant combinations must only be two-node.
4. All nodes in the underlying fuel sub-model are permitted to be a product node of a connection.
5. Connection products may be one-, two- and three-node.

The virtual reaction network construction is then completed by applying the below rules to the results of the combinatorial Latin Square:

6. All connections are set as reversible.
7. All duplicate connections are removed.

8. Connections that are found to cause any considerable numerical stiffness in optimisation are set as unidirectional and subsequently removed from the network if stiffness persists.

The remaining challenge is to assign to the connections a set of weights (virtual reaction rate constants), that allow the overall compact model to achieve the performance properties defined by industry to high fidelity. Note, the thermodynamic and transport properties of NO and NO₂ are taken from the NUIGMECH1.0 detailed model.

	CO ₂	H ₂ O	HO ₂	O	O ₂	OH	N ₂	NO	NO ₂	N
CO ₂							NO + CO + N	NO ₂ + CO		NO + CO
H ₂ O							NO + N + H ₂	NO ₂ + H ₂ NO ₂ + H + H	NO + H ₂ O ₂ NO + OH + OH NO + HO ₂ + H	NO + H ₂ NO + H + H
HO ₂							NO ₂ + N + H NO + N + OH	NO ₂ + OH NO ₂ + O + H	NO + H ₂ O ₂ + O NO + H ₂ O + O ₂	NO + OH NO + O + H NO ₂ + H
O							NO + N N + N + O	NO ₂ N + O ₂	NO + O ₂	NO
O ₂							NO + NO NO ₂ + N NO + N + O	NO ₂ + O		NO + O NO ₂
OH							NO + N + H	NO ₂ + H N + HO ₂	NO + HO ₂ NO + H + O ₂	NO + H
N ₂	NO + CO + N	NO + N + H ₂	NO ₂ + N + H NO + N + OH NO + NO + H NO ₂ + OH	NO + N N + N + O	NO + NO NO ₂ + N NO + N + O	NO + N + H			NO + NO + N	
NO	NO ₂ + CO	NO ₂ + H ₂ NO ₂ + H + H	NO ₂ + O + H N + O ₂ + OH	NO ₂	NO ₂ + O	NO ₂ + H		N ₂ + O ₂ N + NO ₂		N ₂ + O
NO ₂		NO + H ₂ O ₂ NO + H ₂ + O ₂ NO + OH + OH NO + HO ₂ + H	NO + H ₂ O ₂ + O NO + H ₂ O + O ₂	NO + O ₂		NO + HO ₂ NO + OH + O NO + H + O ₂	NO + NO + N		NO + NO + O ₂	NO + NO N ₂ + O ₂
N	NO + CO	NO + H ₂ NO + H + H	NO + OH NO + O + H NO ₂ + H	NO	NO + O NO ₂	NO + H		N ₂ + O	NO + NO N ₂ + O ₂	N ₂

Figure 6.1. Combinatorial Latin Square used to construct the NO_x virtual reaction network. The second combinatorial array produces 93 connections. 52 duplicates are removed (Step 7). 2 connections are set as unidirectional and a further 12 are removed due to numerical stiffness (Step 8). Rate of production analysis removes a further 18 connections from the final compact model construct. This results in 11 discrete connections in the virtual reaction network of the final compact model construct.

6.3.2 Optimisation of the Kinetics Component

Performance optimisation is performed by MLOCK1.1 which systematically generates, assigns, and evaluates sets of virtual Arrhenius parameters for each connection in the NO_x virtual reaction network. Figure 6.2 shows the MLOCK1.1 process flow to consist of two

Scans, Bound Refinement, and an Assessment stage. The Coarse Scan and Bound Refinement algorithm perform identically to those in MLOCK 1.0, the difference being the optimisation targets and the number of connections optimised. In MLOCK1.1 all connections in the NO_x virtual reaction network undergo optimisation. In the Coarse Scan, 0-D calculations are used as optimisation targets, similar to MLOCK1.0 Phase 1, however, in the Refined Scan, both 0-D and 1-D calculations are used as optimisation targets. In both Scans, the number of model candidates produced, n , is equal to 80,000. Following the selection of the Compact Model, MLOCK1.1 performs a rate of production analysis to identify and remove connections in the NO_x virtual reaction network making negligible contribution to the NO_x virtual reaction flux, which can thus be removed without affecting the compact model's calculations.

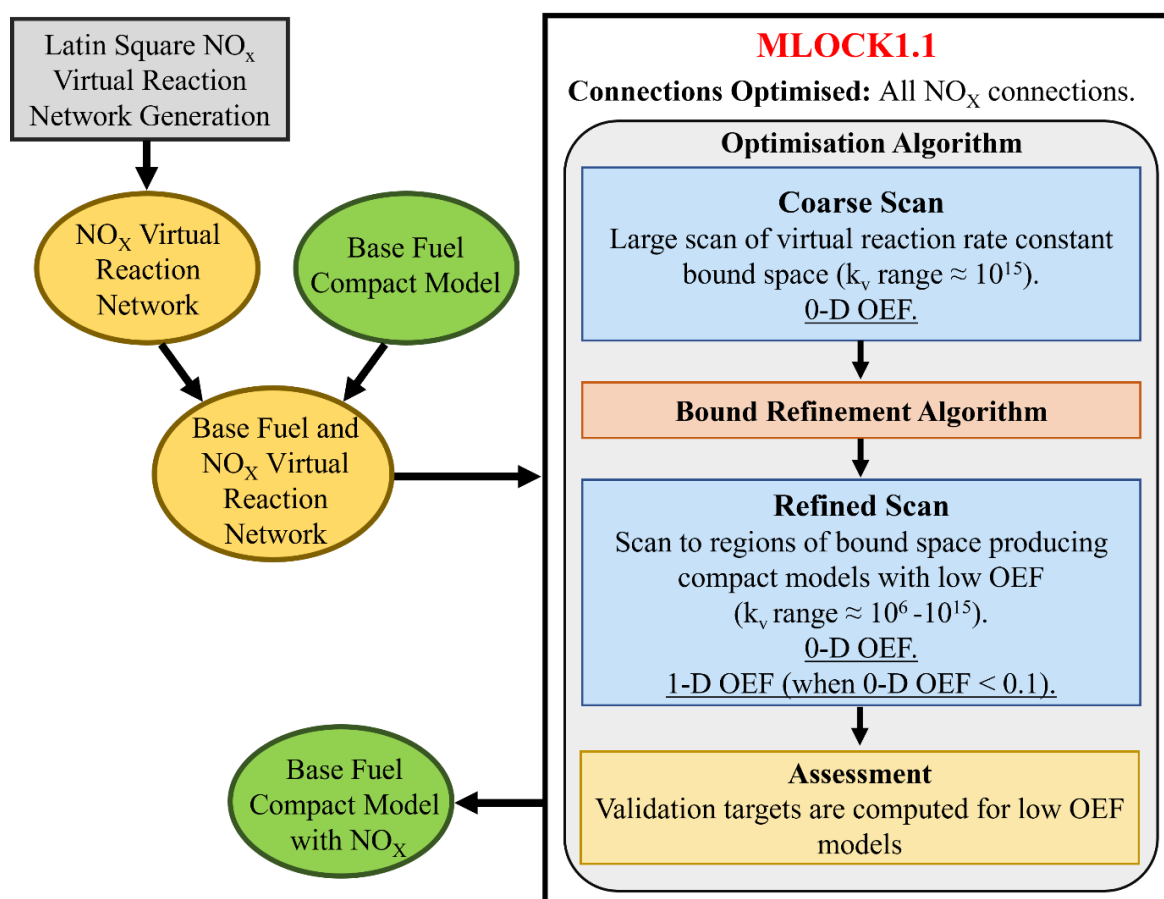


Figure 6.2. Process flow for MLOCK1.1. For the models discussed in this study, note that (i) the 0-D OEF used in both the Coarse and Refined Scans is composed of NUIGMECH1.0 perfectly stirred reactor calculations of NO and NO₂ mole fractions at the conditions in Table 6.2 (ii) the 1-D OEF used in the Refined Scan is composed of NUIGMECH1.0 premixed laminar flame calculations of NO and NO₂ mole fractions at the conditions in Table 6.2.

6.3.2.1 One-Dimensional Objective Error Function (0-D OEF)

The 0-D Objective Error Function (0-D OEF) is composed of NUIGMECH1.0 calculations of NO and NO₂ mole fractions in a perfectly stirred reactor (PSR) at residence times up to 100 ms at the conditions given in Table 6.2. PSR calculations are used as an indicator for the accurate capture of the kinetics of NO_x chemistry. The 0-D OEF is constructed such that the entire time-evolved fidelity of the model calculation is evaluated,

$$0-D\ OEF = \frac{1}{N_j N_K} \sum_k \sum_j \sum_i \left(w_j \frac{|[X_i^{red}(t_j)]_k - [X_i^{det}(t_j)]_k|}{X_{i,k}^{det}(t_j)} \right) \quad (6.9)$$

where, $[X_i^{red}(t_j)]_k$ refers to the mole fraction of the i^{th} species at time point j , at the k^{th} set of temperature, pressure, and equivalence ratio conditions given by Table 6.2, as calculated by the model candidate. t_j corresponds to the time at which NUIGMECH1.0 calculation of $[X_i]$ is equal to 100%, 70%, 50% and 30% the maximum mole fraction at that condition, i.e., $t(n[X_i^{det}]_{max})$ where n is 1.0, 0.7, 0.5 and 0.3. w_j is the j^{th} weighting factor (1.0, 0.7, 0.5, and 0.3) assigned to each of the time points to assign more importance to errors at times closer to the maximum mole fractions of NO and NO₂.

6.3.2.2 One-Dimensional Objective Error Function (1-D OEF)

In the Refined Scan, model candidates with a low 0-D OEF are tested against 1-D calculations through a 1-D OEF. The 1-D OEF quantifies the error between NO and NO₂ mole fractions in a freely propagating premixed flame as calculated by each model candidate and the NUIGMECH1.0 detailed model. The 1-D OEF is evaluated using six positions within the flame, such that the error in the reaction zone and post-flame regions are assessed,

$$1-D\ OEF = \frac{1}{N_n N_K} \sum_k \sum_x \sum_i \left(\frac{|[X_i^{red}(x_n)]_k - [X_i^{det}(x_n)]_k|}{X_{i,k}^{det}(x_n)} \right) \quad (6.10)$$

where $[X_i^{red}(x_n)]_k$ refers to the mole fraction of the i^{th} species at position n , at the k^{th} set of temperature, pressure, and equivalence ratio conditions, as calculated by the model candidate. The final objective error function in the Refined Scan is a simple summation of the 0-D OEF and 1-D OEF.

6.3.3 Assessment Stage

Similar to MLOCK1.0, the best overall compact model is selected by computing the accuracy of the calculations of each model candidates to the validation targets (of Table 6.3). The model with the highest fidelity to the validation targets is selected as the Compact Model.

6.4 Results

The application of the combinatorial Latin Square methodology generated a virtual reaction network, comprising three nodes (N, NO, NO₂) interacting through 29 connections, of which two are unidirectional. The application of rate of production analysis led to the removal of 18 connections from the NO_x virtual reaction network (black text in Figure 6.1), resulting in a Compact Model with 18 nodes and 71 connections (green text in Figure 6.1). For the purpose of this thesis, the best performing Compact Model will be referred to as *15sOp_NOx*. The NO_x performance target parameter space is vast, and so only representative calculations can be shown here. More comprehensive validation can be found in Appendix E or at [172].

An essential result is that the addition of the NO_x sub-model to the base fuel sub-model (*NUIGMECH_15sOp*) does not perturb the calculations of the underlying base fuel sub-model. Figure 6.3 demonstrates this by showing the laminar burning velocity (S_u) and ignition delay time (IDT) calculations of *15sOp_NOx* and *NUIGMECH_15sOp* at representative conditions. As a result, *15sOp_NOx* accurately reproduces IDT, S_u , and speciation data relevant to methane combustion.

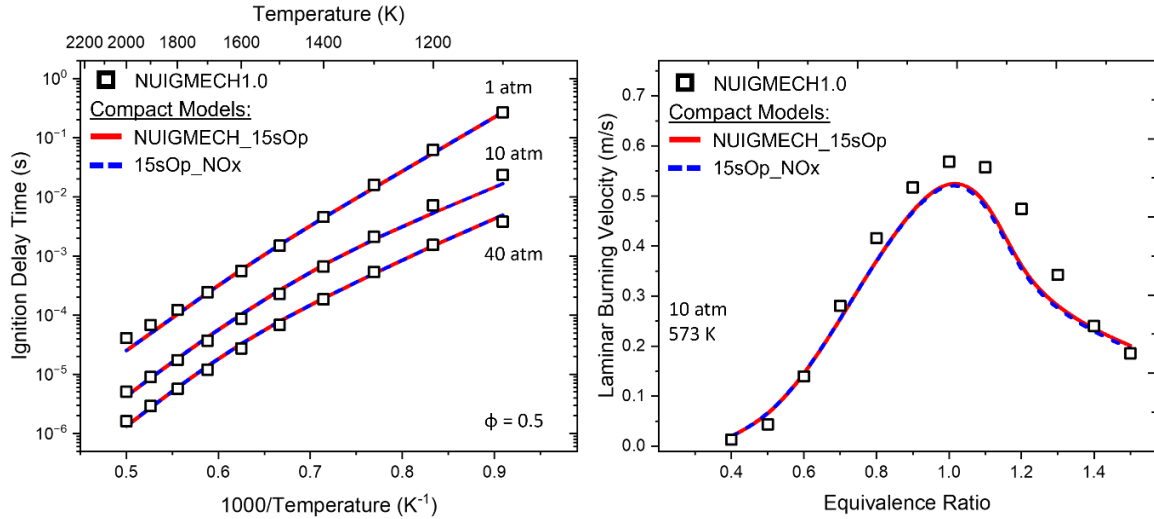


Figure 6.3. Ignition delay time as a function of temperature (left) and laminar burning velocity as a function of equivalence ratio (right) for methane/air mixtures at various pressures using the NUIGMECH1.0 detailed model, 15-node compact model for methane combustion (NUIGMECH_15sOp) and 18-node compact model for NO_x formation (15sOp_NOx) during methane combustion (15sOp_NOx).

6.4.1 Model Performance at Zero-Dimensional Simulations

A plethora of model candidates were produced with accurate replication of NUIGMECH1.0 0-D calculations of NO_x across the wide range of operating conditions in Table 6.1. Figure 6.4 shows the PSR profiles of NO and NO₂ at a range of conditions to show the typical performance of 15sOp_NOx. Generally, 15sOp_NOx accurately reproduces NUIGMECH1.0 NO_x calculations, but at some conditions, it has a slight error in time resolution derived from the ignition time error of the underlying methane compact model.

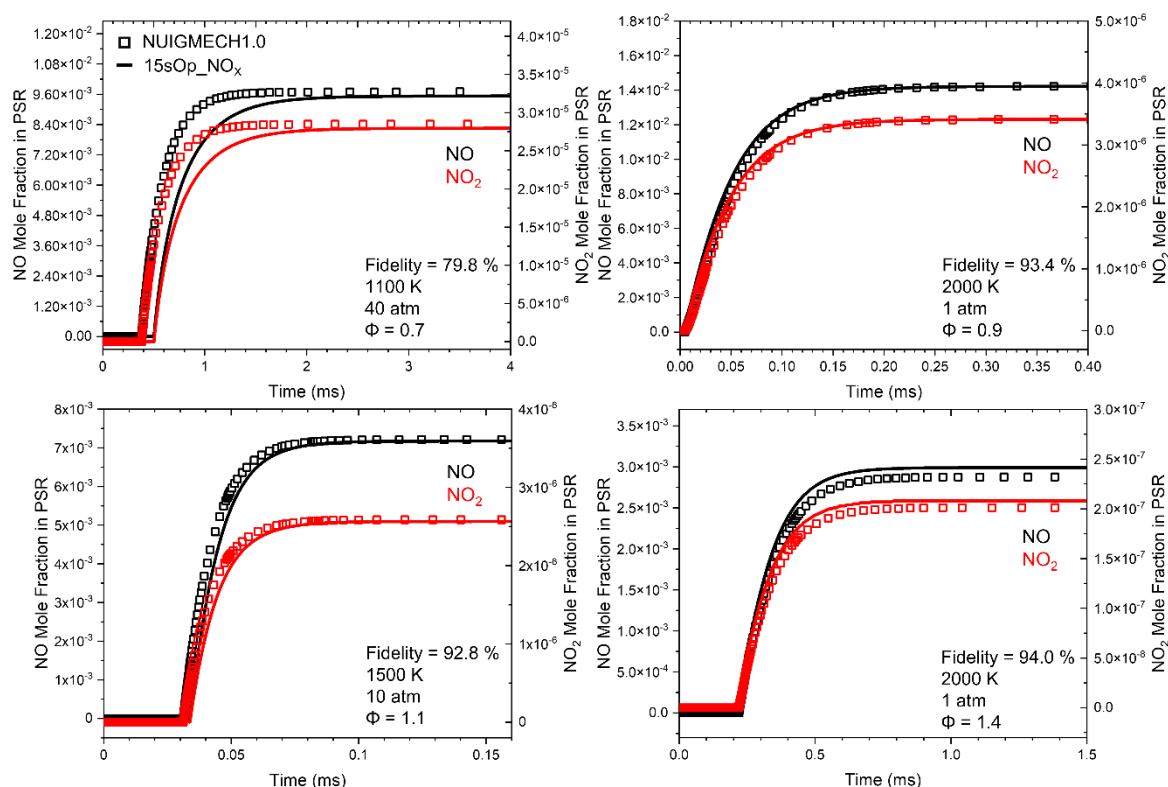


Figure 6.4. NO and NO₂ mole fractions in perfectly stirred reactor calculations using NUIGMECH1.0 (symbols) and 15sOp_NOx (lines) at a range of temperatures, pressures, and fuel/air mixture fractions to show the representative performance of the model. 15sOp_NOx accurately replicates the detailed model calculations.

Figure 6.5 shows maximum NO_x mole fractions in PSR calculations at 1500 K at 1, 10, and 40 atm using both NUIGMECH1.0 and 15sOp_NOx. 15sOp_NOx has a fidelity of 97.5% at 1500 K with the performance decreasing slightly at very lean and very rich conditions, where a more complex virtual reaction network is required to accurately describe the more complex chemistry occurring. The same is true at 1100 K (85.1% fidelity), whereas at 2000 K there is a good replication across all equivalence ratios (99.5% fidelity) owing to the much simpler chemistry occurring at high temperatures. If excellent fidelity at very lean conditions is essential, the operating conditions included in the 0-D OEF may be altered to capture and better replicate the chemistry here. However, this will likely come at the expense of a decrease in fidelity at rich conditions.

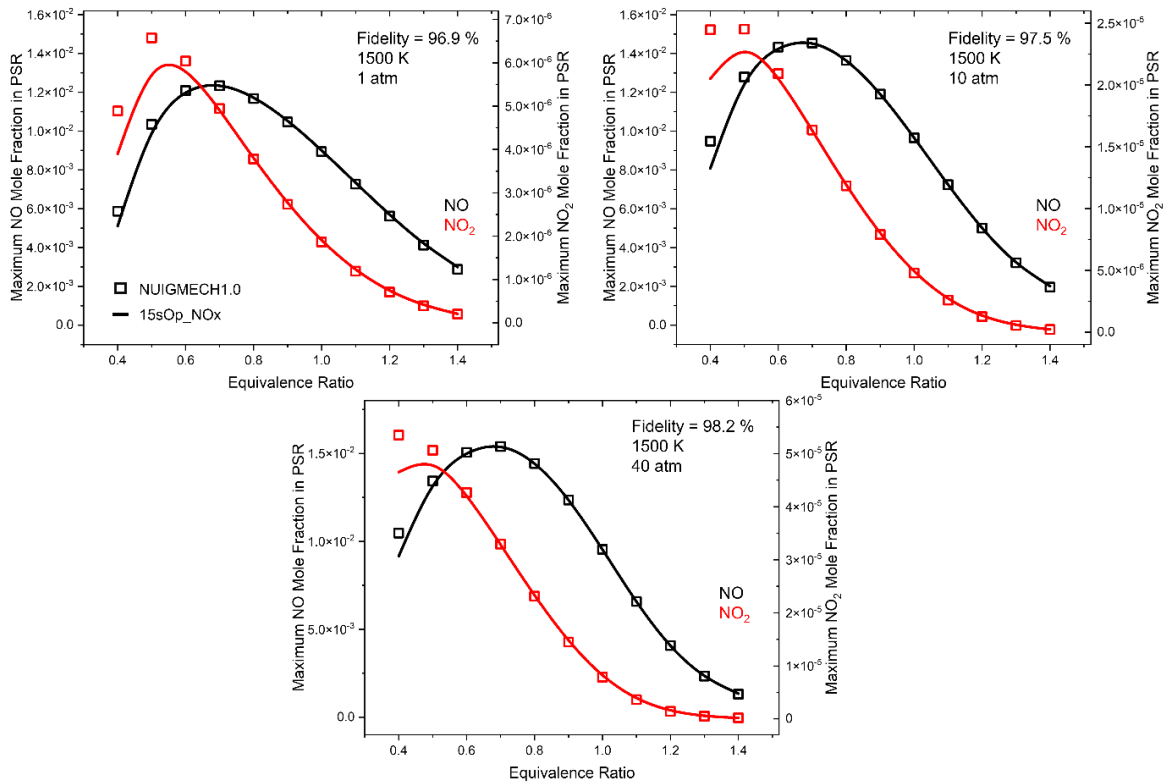


Figure 6.5. Maximum NO and NO₂ mole fraction from perfectly stirred reactor calculations using NUIGMECH1.0 (symbols) and 15sOp_NOx (lines) at 1500 K and 1, 10 and 40 atm at lean to rich fuel/air mixture fractions. 15sOp_NOx accurately replicates the detailed model calculations.

6.4.2 Model Performance at One-Dimensional Simulations

Compact models were produced with high fidelity to 1-D calculations across limited ranges of equivalence ratios, however, no model was produced with an accurate replication across the entire performance envelope, revealing the limitations of the current NO_x virtual reaction network. The 18-node compact model has a good replication of both NO and NO₂ mole fractions in premixed laminar flame calculations at lean and stoichiometric fuel/mixture fractions, however, a drop in fidelity occurs at rich conditions. Figure 6.6 shows the mole fractions of NO and NO₂ in a premixed laminar flame at 573 K, 10 atm and at equivalence ratios 0.7, 0.9, 1.1 and 1.4, where the fidelity of 15sOp_NOx calculations of NO_x mole fractions is 87.8%, 91.2%, 75.5% and 0.0% respectively.

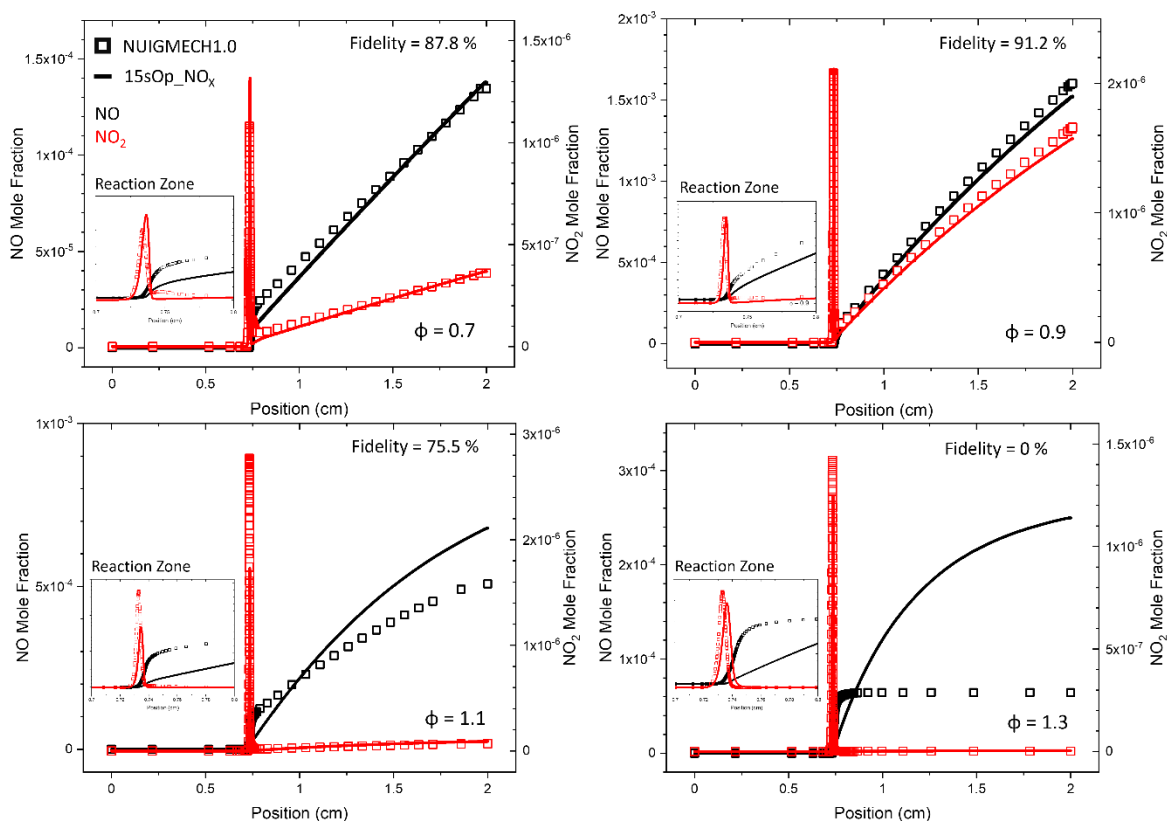


Figure 6.6. NO and NO₂ mole fractions in freely propagating flame calculations using NUIGMECH1.0 (symbol) and 15sOp_NO_x (line) at 573 K, 10 atm and fuel/air equivalence ratios 0.7 – 1.3. Inset shows expanded view of the reaction zone. 15sOp_NO_x accurately replicates the detailed model calculations at lean and stoichiometric conditions, however, fidelity deteriorates at rich conditions.

Therefore, with this minimal construct, two performance options are available; (i) produce a compact model that has excellent fidelity at a limited range of equivalence ratios, or (ii) produce a compact model with a relatively lower, but more consistent fidelity across the entire equivalence ratio range. 15sOp_NO_x represents the later with a Flame NO_x fidelity (i.e., NO_x fidelity in 1-D calculations) of 56.9%, however, 2 other models were identified with high fidelity Flame NO_x fidelity at equivalence ratios that 15sOp_NO_x was poor. The results of these three models, including the additional models termed *15sOp_NO_x_1* and *15sOp_NO_x_2*, are shown in Table 6.4 and Figure 6.7. The compact models can be found in Appendix F.

6.4.3 Benchmarking to State-of-Art Compact Models

The challenge of describing NO_x formation using a minimally-sized kinetic model has been attempted before. However, most works apply analytical techniques that are not compatible with industry standard reaction kinetic solvers such as ChemKin and/or are not presented in the standard ChemKin format (e.g., [46, 198, 199]). Thus, such descriptions may not abide by the FAIR principles of data science and are outside the parameters given to us by Industry. However, recently Sun et al. [200] reported a 22 species model for methane/air combustion with NO (but not NO₂) formation. To our knowledge, this is the only methane with NO_x compact model of the order of approximately twenty species that uses standard ChemKin reaction kinetics descriptors. Sun et al. appear to apply the Direct Relation Graph with Sensitivity Analysis (DRGSA) method to reduce the GRIMech3.0 detailed model. An important difference to the MLOCK1.1 methodology of this work, is that the Sun et al. method considers interactions of the base fuel reaction kinetics with the NO_x reaction kinetics. That is, the prompt NO_x pathways are retained in the compact model. This is at the cost of four additional species, relative to the MLOCK1.1 minimalistic combinatoric method of this work. Note that the Sun et al. model also comprises just three nitrogen containing species (N, NNH, NO).

The fidelity of the compact models of this work, and that of Sun et al. relative to their respective detailed models is compared in Figure 6.7 with respect to NO_x mole fractions in a premixed laminar flame at 1-20 atm, which is the pressure range the Sun et al. model was developed for. Note, the model produced in the work of Sun et al. does not include NO₂, but this is a small fraction of the total NO_x formed at all conditions.

From Figure 6.7, the Sun et al. model shares the inability of the compact models of this work to show high fidelity at all conditions, also suggesting an apparent limitation to a three-node NO_x virtual reaction network. A more detailed summary of the performance of both models is provided in Table 6.4. The compact model of this work, 15sOp_NO_x, shows high fidelity under purely kinetic PSR conditions, but loses fidelity at flame conditions, due to poor performance at the extreme lean and rich equivalence ratios. The Sun et al. model shows similar behaviour but is of significantly lower fidelity at PSR conditions. The computational cost of these models in performing a series of 1-D laminar burning velocity calculations relative to the time taken using DRM22 is shown. DRM22 is again used as it is a reduced model familiar with the combustion community, despite not containing any NO_x formation

chemistry. It is interesting to note the lower computational cost of the Sun et al. model compared to the compact models of this work. The main reason for this, as discussed in the previous Chapter, is mainly due to inherited stiffness from the NUIGMECH1.0 detailed model. Additionally, removing NO₂ from the compact models of this work results in a decrease in computational cost to approximately 80% of DRM22.

Table 6.4. Compact model performance summary and comparison to State-of-Art. The fidelity of all model calculations is evaluated at 1, 10 and 20 atm. Ignition Delay Time (IDT) and PSR calculations are performed at 1100 – 2000 K. The fidelity of each model is evaluated at the range of fuel/air equivalence ratios specified. Time to compute a 1-D laminar premixed flame using each model is benchmarked to the DRM22 [181] model. Note: The Sun et al. model does not contain NO₂, hence, NO_x fidelity for this model is approximated as NO fidelity only.

Model	No. of Nodes	Equivalence Ratios Evaluated	IDT Fidelity (%)	PSR NO _x Fidelity (%)	S _u Fidelity (%)	Flame NO _x Fidelity (%)	Time Taken (% of DRM22)
<i>Compact Models for Performance Option (i)</i>							
15sOp_NOx for ϕ 0.5 - 1.0	18	0.5, 0.6, ..., 1.0	87.3	91.2	90.6	84.3	101.9
15sOp_NOx_1 for ϕ 0.4, 1.4	18	0.4, 1.4	86.3	86.4	76.8	76.5	100.8
15sOp_NOx_2 for ϕ 1.1 - 1.3	18	1.1, 1.2, 1.3	86.6	85.0	90.7	78.6	98.7
<i>Compact Models for Performance Option (ii)</i>							
Sun et al. [24]	22	0.4, 0.5, ..., 1.4	62.7	77.1	83.2	61.9	69.8
15sOp_NOx for ϕ 0.4-1.4	18	0.4, 0.5, ..., 1.4	86.7	89.5	88.6	56.9	101.9

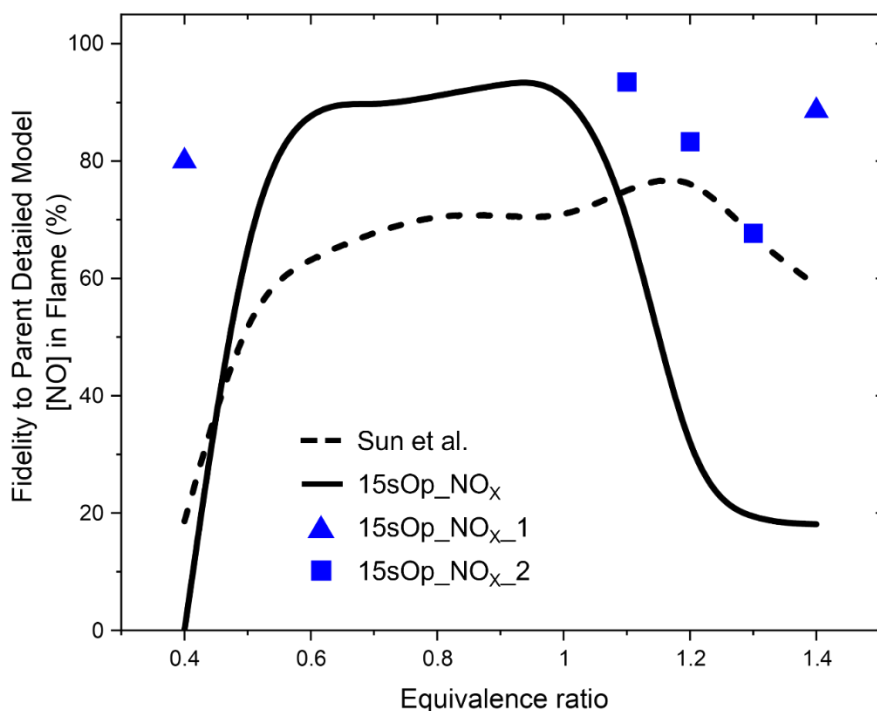


Figure 6.7. Fidelity of models produced in this work and in the work of Sun et al. to that of respective parent detailed model calculations of NO mole fractions in laminar premixed flames at 1 – 20 atm. Note that both studies show relative consistency in an apparent limit of NO_x virtual reaction networks that are three-node. Other combinations of weights can yield compact models of improved fidelity (symbols).

6.5 Discussion

In the following, the performance limit of this three-node construct is further discussed by assessing the behaviour of the MLOCK1.1 algorithm.

6.5.1 Analysis of 0-D Objective Error Function

Figure 6.8 shows the Coarse – Bound Refinement – Refined Scan procedure (of Figure 6.2) for the example of the connection $NO + N \rightleftharpoons N_2 + O$. In the Coarse Scan (black symbols), 80,000 models are produced across a large range of the virtual reaction rate constant (k_v) bound space. This is followed by the automated Bound Refinement algorithm which scores each region of the bound space based on the proportion of low OEF models produced in the region (blue line). The more negative the Z-score, the higher the density of low OEF models. 80,000 models are then produced in the Refined Scan to increase the resolution of these regions of the bound space that produce suitably large proportions of models with low OEF

(red symbols). A strong coupling exists between the virtual reaction rate constant k_v and the value of the 0-D OEF, implying this connection has a significant importance on the system. This importance is also evident through examination of Figure 6.9, which shows the Coarse Scan and subsequent Z-score significance ratings for each connection in the final compact model. From cursory examination, it is apparent that only one connection, $NO + N \rightleftharpoons N_2 + O$ (that of Figure 6.8) has a strong coupling between k_v and 0-D OEF. The binary nature of this system is further highlighted through analysing the maximum Z-scores of each connection, which in effect quantify the strength of the k_v to 0-D OEF coupling. The maximum Z-score is -120.32, from $NO + N \rightleftharpoons N_2 + O$, with that of the next largest connection being -9.01, from $NO + N \rightleftharpoons N_2 + O$, indicating a probability that the other connections exhibit a much weaker influence on the system. As MLOCK perturbs the magnitude of k_v of all the connections simultaneously, this means that combinations of k_v of all the other connections cannot be found to show a magnitude of influence similar to singular perturbation of this term. This shows the limited complexity available to a NO_x virtual reaction network that is three-node.

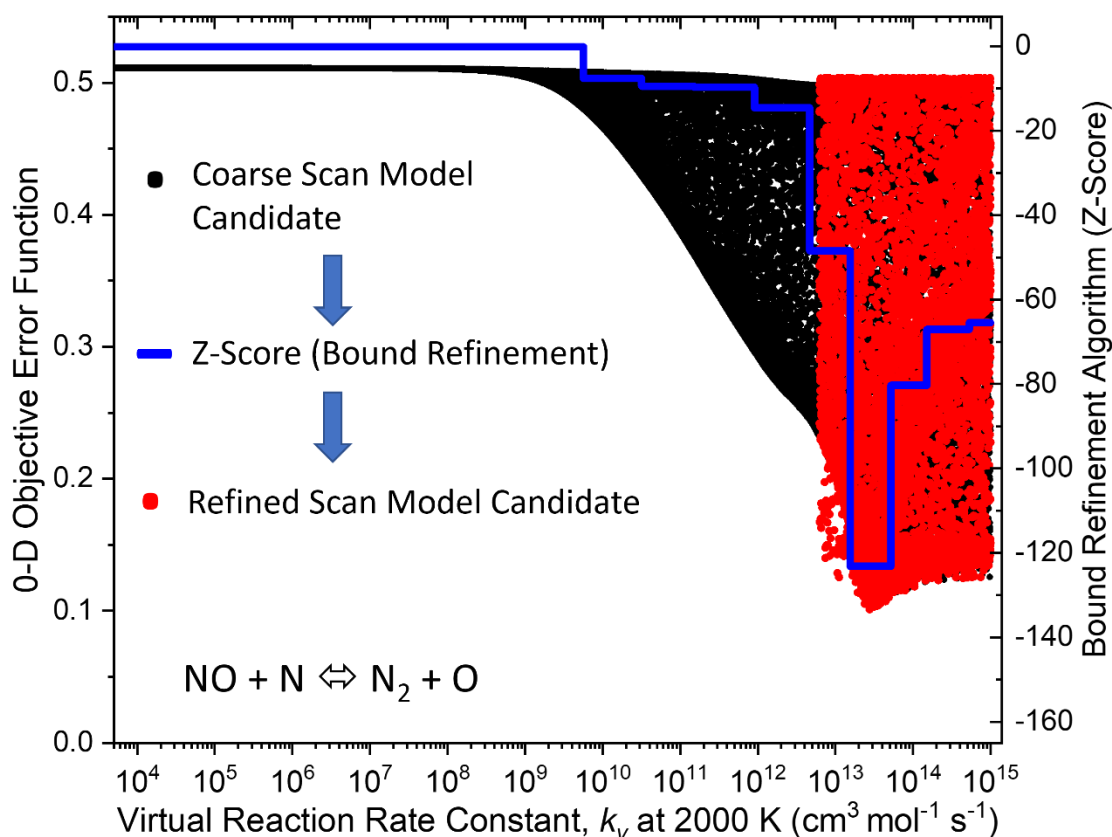


Figure 6.8. 0-D Objective Error Function of model candidates produced in the Coarse and Refined Scans as a function of the virtual reaction rate constant of the connection $NO + N \rightleftharpoons N_2 + O$.

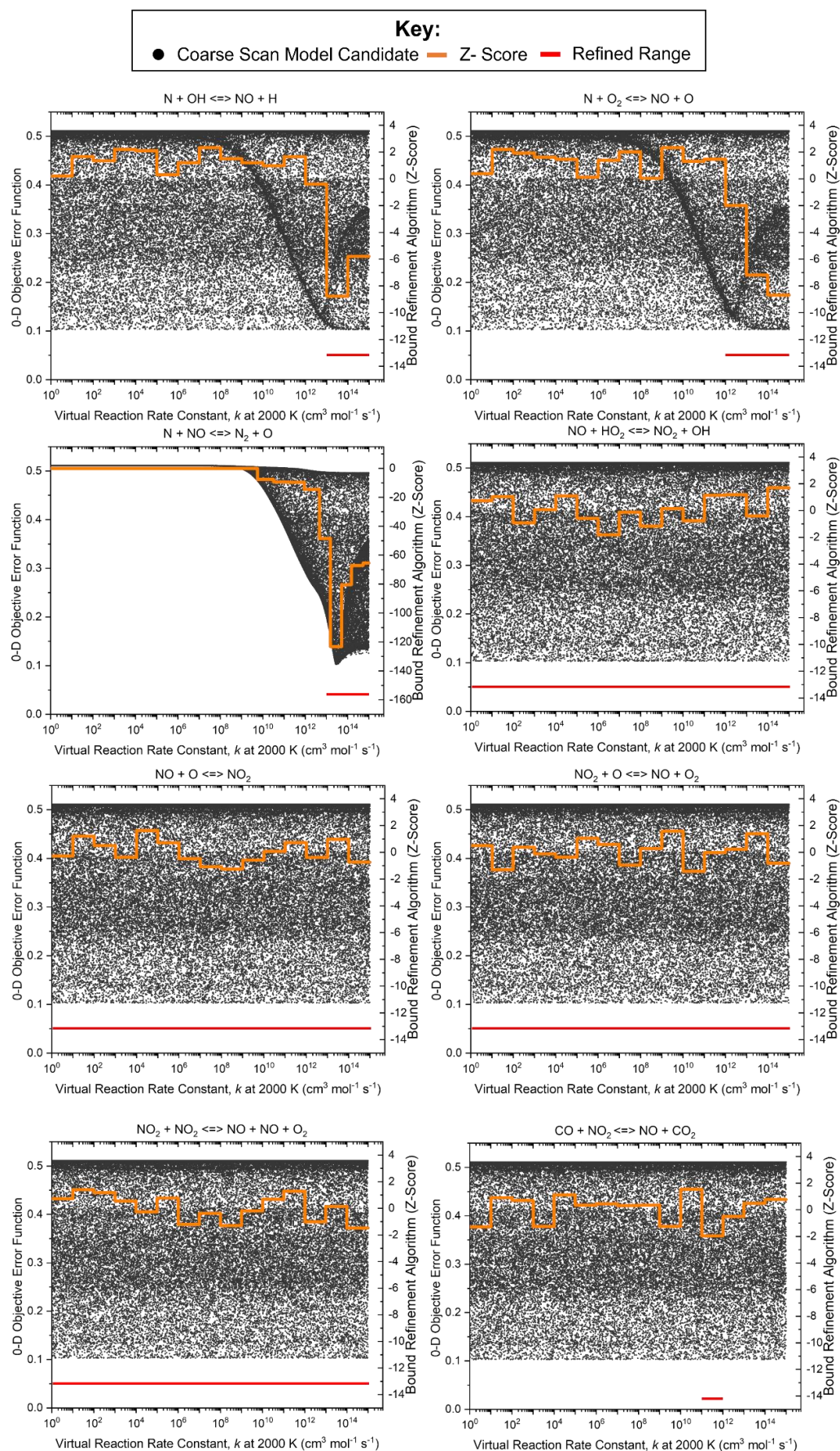


Figure 6.9. (a) 0-D Objective Error Function (OEF) of model candidates produced in the Coarse Scan as a function of the virtual reaction rate constant of final connections in the compact model.

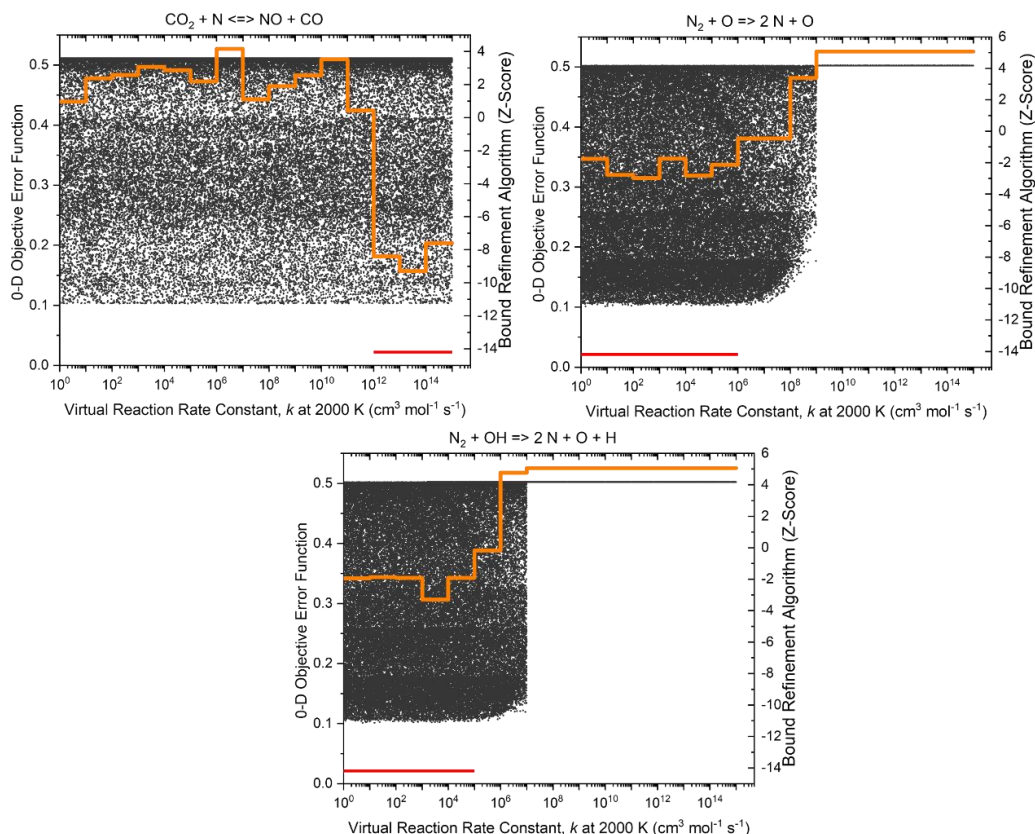


Figure 6.9. (b) 0-D Objective Error Function (OEF) of model candidates produced in the Coarse Scan as a function of the virtual reaction rate constant of final connections in the compact model.

The last two connections in Figure 6.9 (b) were found to cause considerable stiffness and as such were set to unidirectional. It is noteworthy that even though no distinct minima can be identified for these two connections, there exists a critical threshold value of k_v which a model must not exceed to have a probabilistic chance of performing well. It is seen that if the value of k_v for $N_2 + O_2 \Rightarrow N + O$ is greater than $\sim 10^9 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, no good models are produced. Similarly, the k_v for $N_2 + OH \Rightarrow 2N + O + H$ must be less than $\sim 10^8 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ to produce a good model.

Another interesting result is the existence of a high density of models following a trend in the first two connections of Figure 6.9 (a). This would indicate a coupling between the connection and the performance of the model, although not one that is particularly strong, as there is significant variability in the model performance at each k_v value. This is also reflected in the Z-scores of these connections.

6.5.2 Analysis of 1-D Objective Error Function

Despite the dominant influence of $NO + N \rightleftharpoons N_2 + O$ on the behaviour of the system, compact models are produced with high-fidelity across the complete 0-D performance envelope. However, this is not the case in 1-D calculations. This can be readily seen in Figure 6.10, which shows the 1-D OEF at lean (0.8) and rich (1.2) equivalence ratios of model candidates produced in the Refined Scan as a function of k_v for the connection $NO + N \rightleftharpoons N_2 + O$. To produce a model that performs well at lean conditions (blue symbols), the value of k_v for this connection must be approximately $3.5 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. However, this value for k_v results in a poor replication of NO_x (large OEFs) at rich conditions (red symbols). Consequently, a compact model that has fidelity greater than 57% at the comprehensive range of equivalence ratios cannot be produced using the minimal three-node NO_x virtual reaction network. Note that from Figure 6.10, there are some model candidates with values of k_v greater than $10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ where it may appear that a model candidate has been produced that performs well at both lean and rich conditions for the same value of k_v . However, upon further inspection, it is found that these models either do not actually perform well (i.e., an inaccuracy in the OEF) or that the model performs well at these specific equivalence ratios but poorly elsewhere.

Hence, this performance limit is due to the limited complexity in the virtual reaction network meaning not enough degrees of freedom exist to divert the reaction flux through the system such that the complex NO_x behaviour of the detailed model in 1-D calculations can be replicated across the complete equivalence ratio range. A possible solution is to expand the node array of the combinatorial Latin Square to increase the degrees of freedom available to the optimisation algorithm. It is likely that this option will result in models of higher fidelity over broader ranges of the performance space but will also result in a larger computational cost of both the algorithm and the resulting compact model.

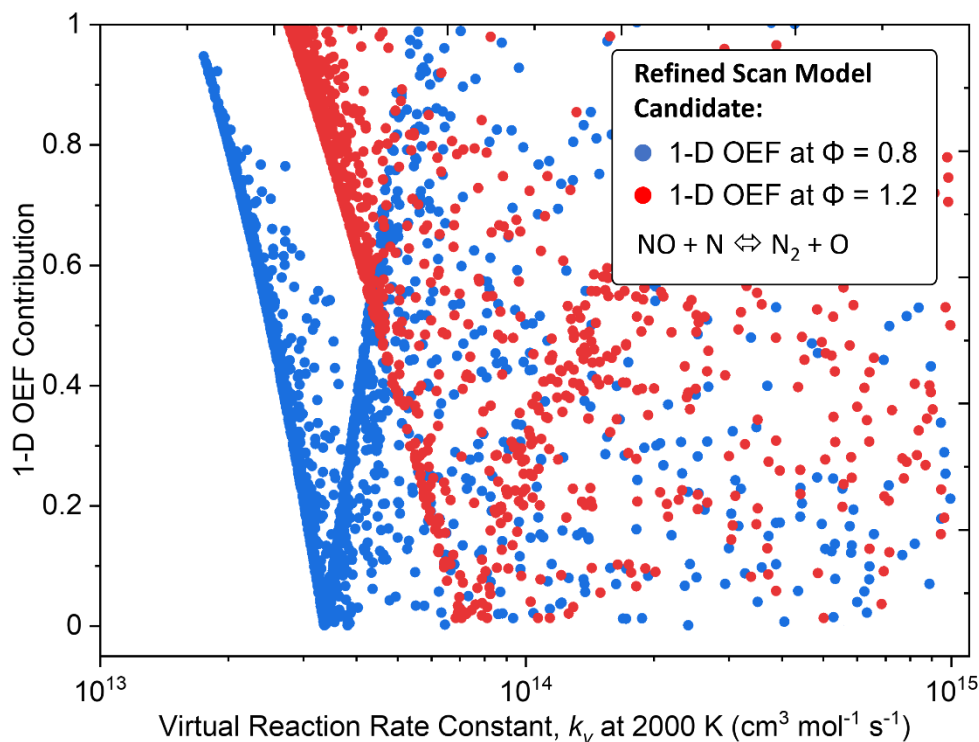


Figure 6.10. 1-D OEF (Objective Error Function) at lean (blue) and rich (red) fuel/air mixture fractions of model candidates produced in the Refined Scan as a function of the virtual reaction rate constant of the connection $\text{NO} + \text{N} \rightleftharpoons \text{N}_2 + \text{O}$.

6.5.3 Discussion on Error Functions

In the case of methane (Chapter 5), MLOCK used explicit time steps to evolve 0-D simulations. Cantera's "*advance(t)*" function was used to increase the simulation time by time t , with separate time steps for each condition. To determine the time step for each condition, detailed model calculations were loaded, which contained three-thousand time steps of equal spacing and also used the "*advance(t)*" function. This ensured that the detailed model and the model candidate had solutions of the composition and thermodynamic properties of the mixture at the same time, making it easy to compute the 0-D OEF.

The drawback of this approach is that detailed model simulations must be performed twice: once to find the time for ignition at the condition, and then again using the suitable time step t with three-thousand steps.

To avoid the need for prior knowledge of a suitable time step in time-dependent chemical simulations, the "*.step()*" function is used in Cantera. This function automatically advances the solution until the user-defined end time, with the size of the time step adapting

dynamically based on the user-defined tolerances. As a result, the time stepping produces a high density of points around the time of ignition when the state variables increase rapidly, similar to the 1-D grid-refinement method around the flame front. This function is used in this Chapter. However, the time steps used in the detailed model and model candidate may not be the same, requiring a time interpolation approach to interpolate the model candidate solution at a specific time point if an OEF like the 0-D OEF used in Chapter 5 is to be employed. This can result in unexpected problems.

For example, using this approach, the OEF is evaluated at the time points of the detailed model, resulting in a concentration of evaluations in the ignition region. While this provides valuable information about the accuracy of the ignition time prediction, it may not be an effective measure of similarity between the detailed model and the model candidate throughout the entire simulation.

Figure 6.11 illustrates this issue. It shows a model candidate that accurately reproduces the maximum mole fractions of NO, but with a 15% error in the time for ignition, derived mostly from an error in the underlying methane compact model. Therefore, computing the relative error at each point of the detailed model results in a poor OEF value of 0.552. This example highlights the problem that a model with a good replication of the time for ignition, which is a mostly a manifestation of the underlying base fuel model, but with considerable overprediction of NO mole fractions, (i.e., a poor set of NO_x virtual reaction rate constants) could have a better OEF value.

Therefore, a revised OEF was introduced which evaluates the relative errors in mole fractions at four specific time points. These correspond to the time at which the detailed model reached 100%, 70%, 50%, and 30% of the maximum mole fraction at that condition. By using these time points, a “slicing” of the mole fraction time profile of the model was obtained, providing a better representation of the similarity in the profiles. A weighting term, w_j in Equation 6.9, was introduced to place greater emphasis on errors occurring during periods of maximum mole fractions. To further complicate matters, the NO_x profiles exhibit a wide range of “shapes” across the optimisation conditions, making it challenging to develop a suitable OEF. An OEF that is effective for one condition may not accurately indicate the similarity between curves for another condition. Although not perfect, this OEF method is considerably more effective for this purpose than measuring the error at each detailed model time point, like that used in Chapter 5.

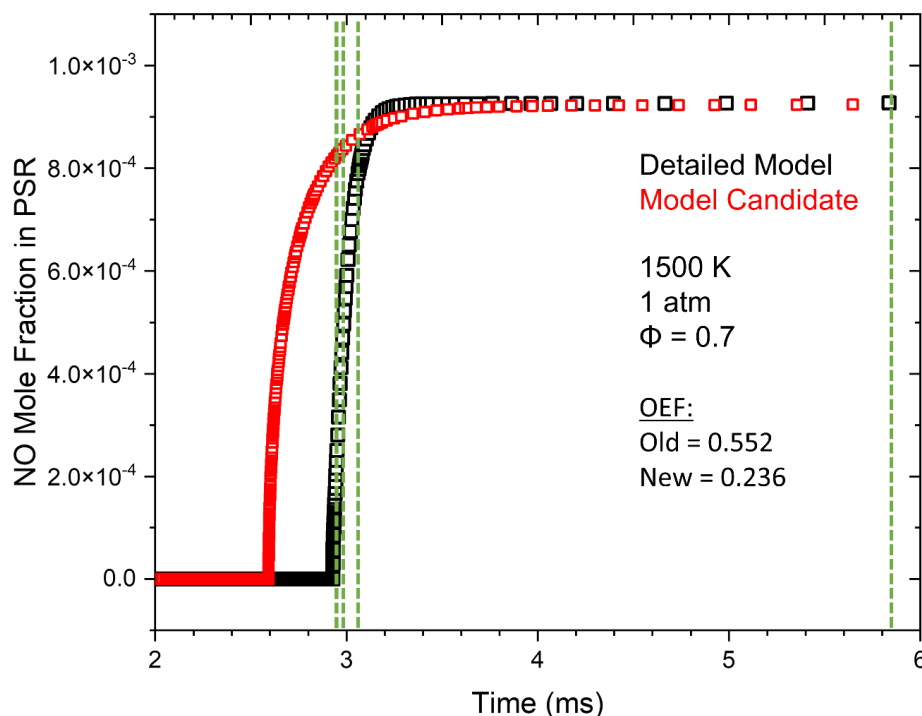


Figure 6.11. NO mole fractions in perfectly stirred reactor calculations using NUIGMECH1.0 (black) and a model candidate (red) at 1500 K, 1 atm and equivalence ratio 0.7. The green dash lines represent the time points at which the relative error between black and red symbols are computed for the 0-D OEF. This gives a better quantification of the overall model fidelity compared to evaluating the error at each detailed model time point (black symbol) as is done by the old OEF.

6.6 Conclusions

A novel data-orientated compute intensification methodology to the construction of compact kinetic models for NO_x formation is designed and demonstrated. A detail-fidelity cost-benefit performance envelope for modelling of NO_x formation in methane combustion is defined for gas-turbine industry interests. The MLOCK coded algorithm for compact model generation is adapted to NO_x modelling with the addition of a combinatorial method to allow creation of a virtual reaction network of minimal complexity with just three nitrogen containing nodes (N, NO and NO₂). This network is appended to a state-of-art 15-node Compact Model for methane/air combustion. With this construct, MLOCK1.1 automatically generates and tests 160,000 model candidates to identify the optimal sets of virtual Arrhenius parameters for the connections of the NO_x network.

Of these, for kinetically driven PSR behaviours it is shown that numerous models show fidelities in excess of 80% across the entire range of performance conditions. However, for

flame conditions, it is not possible to find one model with a fidelity greater than 57% across the entire industry-defined performance envelope. It is shown that the loss of fidelity is due to the distinctive NO_x kinetic behaviours at extreme lean, and extreme rich equivalence ratios, which cannot be simultaneously captured by such a simple three-node virtual reaction network.

However, using the same minimal three-node virtual reaction network, it is shown that three distinct compact models, each valid at a limited range of equivalence ratios do collectively meet the industry defined performance envelope. Though further development is required, the results of this work do appear to support the concept that high-fidelity compact models can be automatically produced using data-intensive methodologies, with the output conforming to FAIR industry standard (i.e., ChemKin) model formats.

Chapter 7

Compact Models for Liquid Fuel Combustion

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7.1 Introduction

Liquid transportation fuels, commonly *liquid fuels*, are complex mixtures composed of thousands of discrete hydrocarbon molecules with varying chemical properties. These hydrocarbons can be categorised based on the differences in the bonding between carbon atoms in their structure.

- **Alkanes** are a family of saturated hydrocarbons that have a general chemical formula of C_nH_{2n+2} . The carbon atoms are bonded together with single covalent bonds between each adjacent pair of atoms. The physical properties of alkanes are dependent on their molecular structure and size, with larger alkanes typically exhibiting higher boiling points and densities compared to smaller alkanes. Within alkanes, there are two subclasses, *normal alkanes* and *iso-alkanes*.

Normal alkanes, denoted by the suffix *n*-, have a straight-chain hydrocarbon structure, with each carbon atom bonded to its neighbours in a linear arrangement. They display a distinctive distribution of electron density, with each carbon-hydrogen bond contributing to the overall molecular shape and stability. Figure 7.1 shows typical normal alkanes found in liquid fuels.

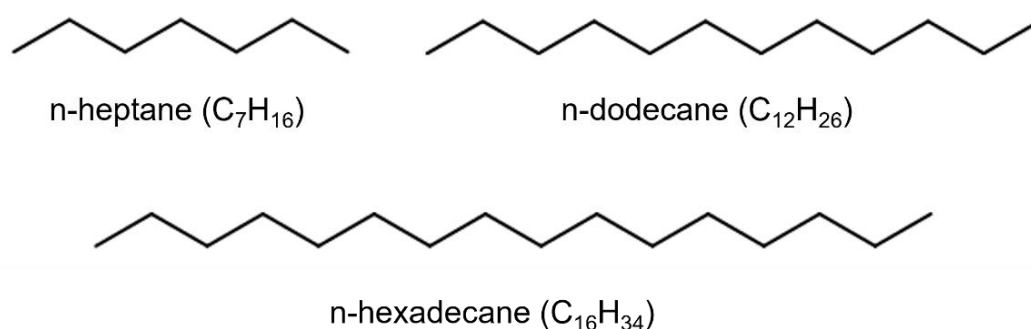


Figure 7.1. Common n-alkanes in liquid fuels.

Iso-alkanes, often denoted by the suffix *i*-, have a branched molecular structure, with some carbons bonded to more than two other carbons. This degree of molecular asymmetry results in a different distribution of electron density compared to normal alkanes manifesting in differences in reactivity and physical properties. Due to this branching, iso-alkanes are more reactive at high temperatures, due to greater proportion of tertiary carbons, and less reactive at lower temperatures, due to the branching acting as a steric hindrance to RO_2 , compared to n-alkanes. Figure 7.2 shows typical iso-alkanes found in liquid fuels.

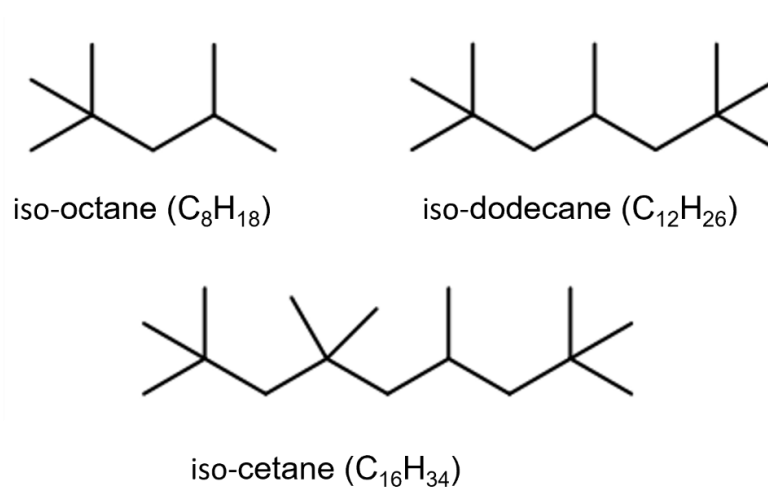


Figure 7.2. Common iso-alkanes in liquid fuels.

- **Cyclo-alkanes** are a family of hydrocarbons that have a cyclic molecular structure, where the carbon atoms are arranged in a ring formation. Due to the cyclic arrangement of their carbon atoms, cycloalkanes display a unique distribution of electron density, which gives rise to differences in reactivity and physical properties compared to n- or iso-alkanes of similar size. Figure 7.3 shows typical cycloalkanes found in liquid fuels.

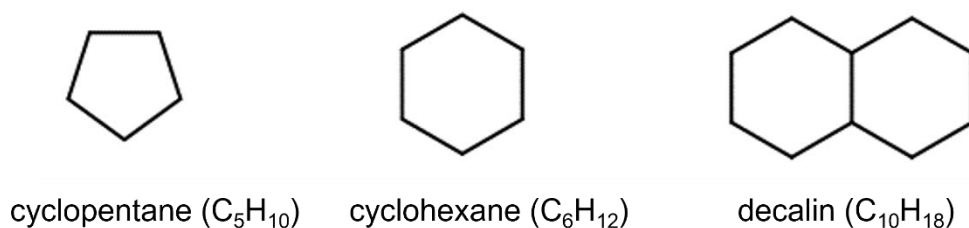


Figure 7.3. Common cyclo-alkanes in liquid fuels.

- **Aromatics** are a family of hydrocarbons that have an aromatic ring. The aromatic ring is composed of six carbon atoms in a cyclic arrangement of alternating double and single bonds. The delocalised pi electron cloud contributes to the stability of these species resulting in a lower degree of reactivity compared to alkanes. Figure 7.4 shows typical aromatics found in liquid fuels.

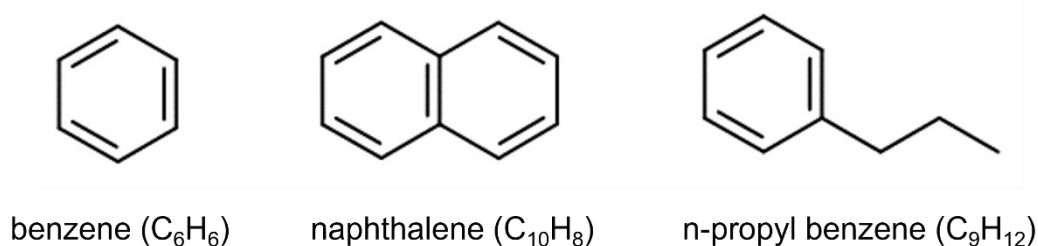


Figure 7.4. Common aromatics in liquid fuels.

In order to develop a kinetic model for a fuel, it is necessary to have information about its composition or approximate composition. While in previous Chapters, a single compound fuel molecule (methane) was used, liquid fuel combustion involves a much more complicated process due to the large number and variety of discrete molecules that comprise the fuel. For instance, diesel is composed of thousands of alkanes and aromatics, the majority comprised of between ten and twenty carbon atoms [201]. Therefore, it is impractical to represent the precise composition of such fuels in terms of individual species. Furthermore, even if the composition of a liquid fuel could be completely described in terms of discrete species, the essential kinetic data required to generate a kinetic model (e.g., rate constants, thermodynamic properties) is generally unknown for the majority of large hydrocarbon molecules. As a result, surrogate modelling is commonly utilised to address these challenges.

7.2 Compositional Modelling

Compositional modelling is a technique that is used to model complex fuels with chemical compositions that are unknown or too complicated to replicate. This approach utilises a simplified representation of the chemical composition of a fuel, using a limited number of chemical species, called a surrogate. The surrogate composition is such that it captures the essential physical and chemical properties of the fuel, thereby providing a good approximation of the gas phase combustion characteristics of the liquid fuel, as illustrated in Figure 7.5.

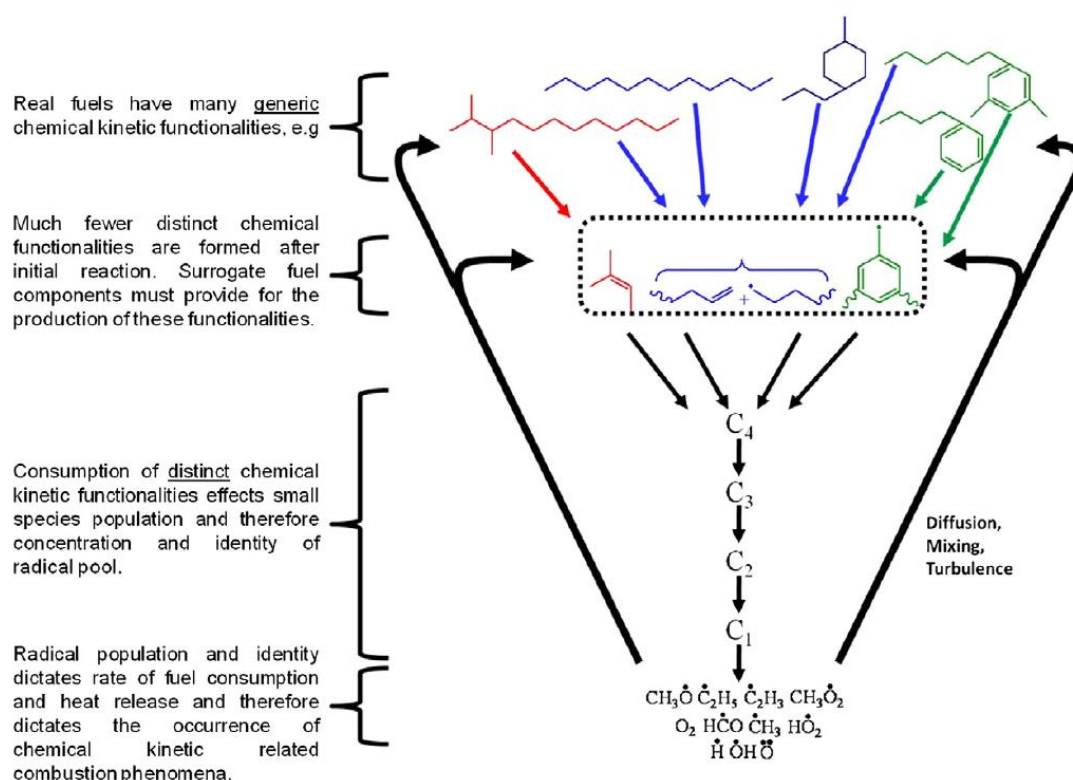


Figure 7.5. Schematic diagram of real fuel oxidation and concept of distinct chemical functionality as it applies to high temperature combustion kinetic phenomena. From Dooley et al. [106].

The first step in surrogate modelling is to define these essential physical and chemical properties, called the combustion property targets. Relevant properties used in literature include density, viscosity, molecular weight, distillation curve, hydrogen-to-carbon ratio (H/C), atom type composition, derived cetane number (DCN), and sooting propensity, among others.

Next, chemical species are selected to comprise the surrogate “palette”, which is a list of potential species that will be included in the surrogate. This selection process is crucial and should prioritise species with appropriate chemical and physical properties from a diverse range of hydrocarbon classes, to enable a mixture composition that matches the targeted properties. As liquid fuels contain molecules with large molecular weights, it is necessary to include alkanes with chain lengths greater than ten. However, if the ultimate aim of the study is to produce an accompanying kinetic model, it is important to only select species that have relevant information available on the reaction mechanisms and kinetics.

Following this, a selection process is used to choose the relevant concentration of species in the palette to best reproduce the target properties. The final step involves constructing a detailed kinetic model by integrating the detailed models for each of the components (species) in the surrogate.

The use of surrogate modelling has been applied extensively to a variety of liquid fuels, resulting in an extensive body of literature. As such, a comprehensive review of the literature is not provided here. However, several excellent review papers on this topic have been published, including: Leclerc [103] for the case of gasoline and diesel; Dagaut and Cathonnet [202] for kerosene; Pitz and Mueller [203] for diesel; Lai et al. [204] for biodiesel; Ranzi et al. [205] for kerosene, gasoline, diesel and bio-derived liquid fuels; and Sarathy et al. [206] and Zhen et al. [207] for gasoline.

In the previous three decades, the use of standard surrogates as simplified representations of liquid fuels has become commonplace. Primary reference fuels (PRFs), consisting of n-heptane and iso-octane, are routinely used as a surrogate for liquid fuels such as gasoline. These are used due to the magnitude of reliable kinetic data available, stemming from the work of Curran et al. on the modelling of n-heptane [105] and iso-octane [104] oxidation. However, the n-heptane and iso-octane mechanisms can not accurately describe the cycloalkane and aromatic oxidation processes, leading to inaccuracies, particularly at low temperatures where aromatics are considerably less reactive than alkanes [208]. Additionally, the absence of aromatics in the surrogate leads to an inaccurate replication of pollutant emissions [209]. To overcome some of these limitations, toluene reference fuels (TRFs), composed of toluene, n-heptane, and iso-octane, have been extensively used. Toluene, as the most representative aromatic compound, leads to a more accurate representation of aromatic oxidation and the effect of aromatics on the reactivity of the fuel,

particularly at low temperatures. However, many authors (e.g., [106, 107, 207, 210-214]) have recognised the need for more sophisticated surrogate formulations to better represent the range of aromatics, alkenes, and linear, branched and cyclic alkanes present in liquid fuels to fully replicate the combustion behaviour and physical properties of liquid fuels. As a result, a common practice in the field has been to employ multi-component surrogate definitions. However, this can lead to surrogate kinetic models containing large numbers of species.

7.2.1 Surrogate Model Complexity and Reduced Models

The number of species in the resulting surrogate kinetic model depends on a number of factors:

1. The number of components comprising the surrogate definition. As more surrogate components are included, more elementary reactions, and hence species, are needed to describe the consumption of the fuel.
2. The complexity and comprehensiveness of the combustion property targets. The more complex the target properties and the larger the number of properties included as targets, the more surrogate components are needed.
3. The level of accuracy in the description of the reaction mechanism. A more fundamentally accurate description of the reaction mechanism of each surrogate component requires more species and reactions.
4. The size and complexity of the liquid fuel. Larger molecular weight liquid fuels require alkanes of longer chain lengths to be included in the surrogate definition to match the target properties. The larger the molecular weight of the alkane, the more species participating in the reaction mechanism.

Detailed models for large alkanes routinely comprise over one thousand species. For instance, the *NUIGMECH1.1* [215] detailed model for hydrocarbon oxidation up to n-heptane (C_7H_{16}) comprises 2,747 species and the recently released *C3MechV3.3* detailed model [216], which details n-alkane oxidation up to n-dodecane ($C_{12}H_{26}$), comprises 3,761

species. Hence, the number of species needed to construct a detailed model for a multi-component liquid fuel surrogate is in the thousands. For example, the gasoline surrogate model [217] which contains oxidation up to C_8 , and the diesel surrogate model [218] which contains oxidation up to C_{12} developed in Lawrence Livermore National Lab (LLNL) comprise 1,874 and 2,885 species respectively.

Models of this size are of limited utility, with the need for supercomputers to compute even zero-dimensional (0-D) calculations using industry-standard solvers. Hence, reduced models must be constructed. A common approach is to construct a reduced model by assembling reduced submodels of the surrogate components. This typically requires optimisation of several reactions to ensure harmony between the different submodels. For instance, Ra and Reitz [219] developed a kinetic model for a diesel surrogate with eight components. It was constructed by combining reduced sub models for PRF, toluene, cyclohexane, dimethyl ether, ethanol, and methyl butanoate to produce a model with 113 species. Important reactions linking surrogate fuel components to important intermediates were then optimised to better replicate ignition delay time.

However, in such an approach, the retention of the multi-component surrogate definition means that a large number of species must be retained to ensure an accurate description of the oxidation of each surrogate component, thus, preventing the production of kinetic models with suitably low numbers of species for use in high-repetition multi-dimensional simulations, such as those routinely used by the gas turbine industry.

A notable exception to this general statement is the decoupling methodology [73, 74]. This method allows for the creation of high-fidelity kinetic models for liquid fuels with less than 100 species, using a multi-component surrogate definition. The chemistries of small molecular weight species ($H_2/O_2/C_1$) are described in detail using a detailed model, preserving an accurate depiction of their reaction mechanisms. In contrast, the C_2 - C_3 chemistry is described with a reduced model, while the C_{4+} chemistry is represented using a limited number of species and pathways. This approach leverages the knowledge that the combustion characteristics of liquid fuels are mainly determined by the behaviour of small molecules and radical species, while the high-carbon chemistry mainly serves to provide pathways to these reactive species, as discussed in Chapter 3.

This method has been applied to a range of fuels in recent years. Chang et al. [212] developed a four-component (n-decane/iso-octane/methyl cyclohexane/toluene) surrogate model for

diesel with 70 species. Yu et al. [220] applied this method to construct a five-component (n-decane/iso-octane/iso-cetane/decalin/toluene) diesel surrogate with 74 species. Bai et al. [221] developed a kinetic model for diesel comprising 83 species using a three-component (n-hexadecane/iso-cetane/ α -methyl naphthalene) surrogate definition. It is also worth noting that this approach has also recently been applied to produce surrogates for biodiesel [222-224] and Fischer–Tropsch diesel [225].

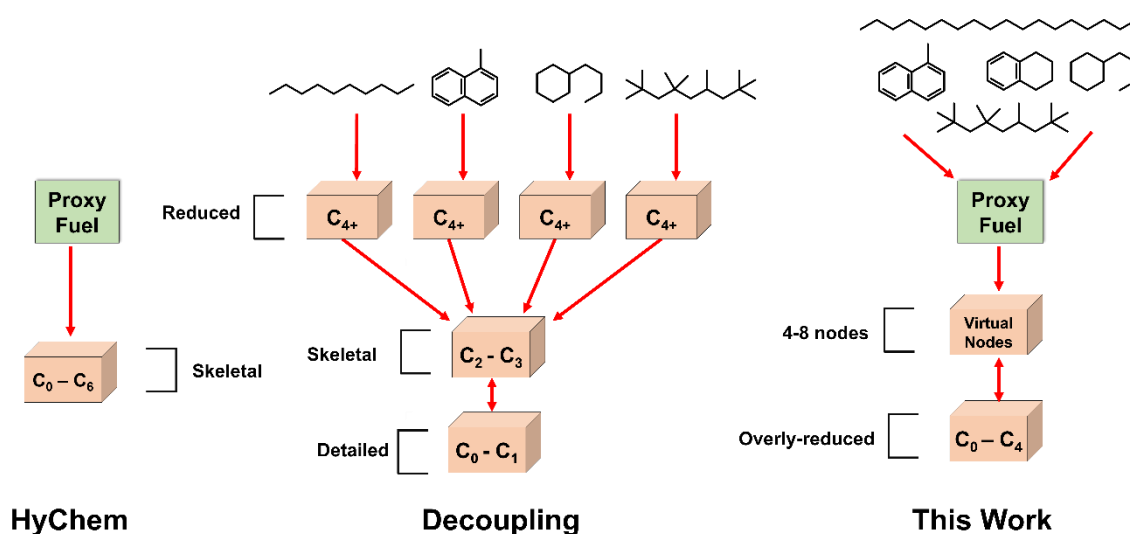


Figure 7.6. Schematic comparing the state-of-art methods to produce minimally-sized kinetic models with the approach used in this work. Table 7.1 shows the number of species in models produced by HyChem and Decoupling methods for kerosene and diesel.

An alternative approach to multi-component surrogate modelling is to lump the surrogate components into one virtual (or proxy) fuel species, whose thermochemical and physical properties are an average of the surrogate composition. This reduces the number of species needed to describe the initial breakdown of the fuel. This is the approach taken in the HyChem [69] methodology, as described in Chapter 3.

This has enabled the production of kinetic models for a range of kerosene fuels with 41 species for high temperatures through the use of model reduction techniques on a detailed HyChem model. Additionally, models for Jet A [70], JP-5 [70] and gasoline [68] with 48, 50 and 57 species respectively, have been produced that include low temperature chemistry. Figure 7.6 provides an illustration highlighting the difference in these approaches.

Our industry partner, Siemens Energy, has mandated the development of a kinetic model for Arabian Extra Light (AXL), a low-density crude oil with low sulphur content, comprising less than 40 species. By analysis of Table 7.1, which shows the current state-of-art in terms of minimally-sized kinetic models for middle and heavy distillate liquid fuels, this is a daunting challenge. It is clear that a new methodology is needed to produce a model on this scale. Note, no meaningful kinetic model exists in the literature for a crude oil.

Table 7.1. State-of-art minimally-sized kinetic models for middle and heavy distillate fuels. Note, gasoline is not included due to the considerably smaller molecular weight.

Author	Liquid Fuel	No. Species	Methodology
Wang et al. [70]	Kerosene (High Temperature)	41	HyChem
Wang et al. [70]	Kerosene	48	HyChem
Chang et al. [212]	Diesel	70	Decoupling
Chen et al.[225]	Diesel	73	Decoupling
Yu et al. [220, 221]	Diesel	74	Decoupling

In this work the concept of Compact Models is extended to liquid fuels. The methodology developed in this work to produce a compact model for a liquid fuel is described next. The method is then demonstrated on AXL and the performance of the Compact Model evaluated.

7.3 Methodology

The aim of this work is to develop a generalised methodology to allow for the creation of compact kinetic models for liquid fuels, enabling the production of Compact Models for a range of large hydrocarbon fuels. The process flow of the methodology proposed in this work, as shown in Figure 7.7, is as follows:

- 1) The liquid fuel combustion property targets are identified.

- 2) The surrogate palette is defined, with the constraint that reliable kinetic information must be available in the literature for each component (species).
- 3) A multi-component surrogate composition is defined by application of an in-house coded optimisation algorithm. This algorithm systematically evaluates the suitability of permutations of the surrogate pallet components to find the composition with the minimal error to the combustion property targets.
- 4) A detailed model containing the surrogate components is identified or constructed. A library of detailed model calculations is populated with the performance, validation, and optimisation conditions.
- 5) A proxy fuel species is defined with properties representative of the average of the surrogate components.
- 6) Virtualisation is performed to simplify initial fuel decomposition to small molecules, with retention of the detailed model description of C₀-C₄ chemistry.
- 7) MLOCK1.0 Phase 1 is used to find optimised virtual Arrhenius parameters for the new connections that link the virtual species to the C₀-C₄ chemistry. The resulting model is called the *Virtualised Detailed Model*.
- 8) The *Virtualised Detailed Model* is then reduced using path flux analysis (PFA) to produce an Overly-Reduced model.
- 9) Finally, MLOCK1.2 is applied to optimise the Overly-Reduced Model to produce a compact model for high temperatures.

A more detailed description of the method follows.

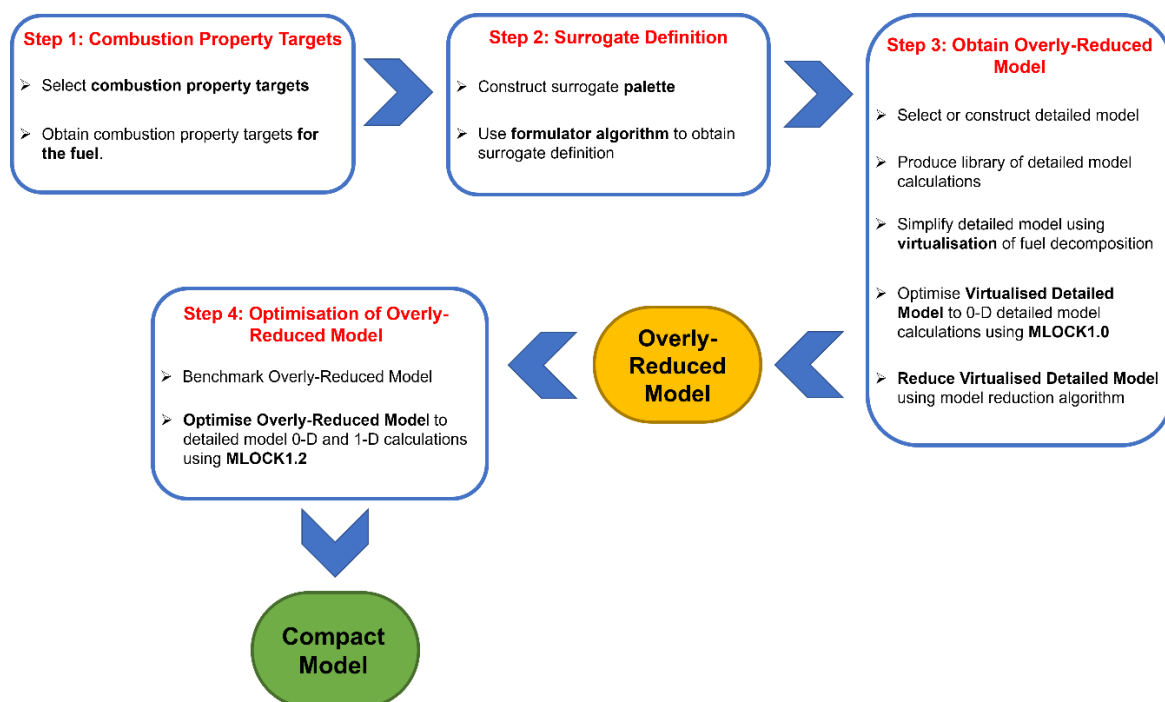


Figure 7.7. Process flow of the methodology proposed in this work to produce a compact model for a liquid fuel surrogate.

7.3.1 Step 1: Selection of Combustion Property Targets

As combustion kinetic phenomena (e.g., ignition delay time) are a result of the molecular structure, the purpose of a combustion property target in surrogate modelling is to serve as an indicator for the correctness of specific molecular functionalities to ensure an accurate replication of the liquid fuel combustion behaviour. Therefore, the selection of the combustion properties is an important step in the surrogate modelling process. The subsequent sections provide an overview of the combustion property targets utilised in this methodology.

7.3.1.1 Hydrogen-to-Carbon Ratio (H/C)

The H/C quantifies the number of hydrogen atoms relative to carbon atoms in the fuel mixture. In turn, this defines the ratio of carbon dioxide to water formed from combustion, which is a major variable in the enthalpy of the fuel. Hence, this provides an indicator for a range of relevant combustion kinetic phenomena which are sensitive to the enthalpy of the fuel, such as adiabatic flame temperature and laminar burning velocity. The H/C also impacts

the rate of formation of the radical pool which is an indicator for reactivity [226]. Typical H/C for liquid fuels are in the range of 1.7 to 2.3 [227].

7.3.1.2 Average Molecular Weight

The average molecular weight of a mixture is the weighted average of the molecular weights of the individual species that comprise it. As the Lewis-Jones collisional diameter and well depth of a molecule scales with the molecular weight [228], this influences mixture properties such as density, heating value, and volatility. Therefore, to replicate the diffusive properties of the liquid fuel, the molecular weight must be reasonably matched. Inaccuracies will manifest in errors in flame phenomena such as extinction limits and to a lesser extent, burning velocity [109]. The average molecular weight of liquid fuels increases with the boiling point of the distillation cut and varies considerably depending on the origin, especially in the case of crude oil [229-231].

7.3.1.3 Derived Cetane Number

The derived cetane number (DCN) characterises the ignition quality of liquid fuels. It is a measure of the ignition delay of a fuel, using an Ignition Quality Tester (IQT) [232-236], in accordance with ASTM D6890 [237]. The fuel is injected into an IQT, which is a heated constant-volume chamber. This fuel injection results in a decrease in pressure, however, the pressure inside the IQT chamber increases as combustion begins. The ignition delay is defined as the time between injection and the chamber reaching the pre-injection pressure. The longer the ignition delay, the less reactive the fuel and the lower the DCN. Diesel and kerosene typically have DCNs in the range of 40 to 60 [231, 237-240]. The DCN is selected to quantify the ignition quality to serve as an indicator for the correctness in kinetic potential of the surrogate composition.

7.3.1.4 Threshold Sooting Index

To quantify the sooting propensity of a mixture, the smoke point measurement is routinely used. This measurement, performed by following the standard test method ASTM D1322 [241], defines the maximum smoke-free laminar diffusion flame. In general, the qualitative

ordering of the smoke point of mixtures is well reproduced across studies, however, the actual smoke point reveals considerable variability due to the subjective nature of the measuring process. In essence, due to the measurement procedure there is a significant degree of systematic bias taken by individuals, resulting in a non-reproducibility of measurements between studies. To address this, Calcote and Manos [242] defined the threshold sooting index TSI as,

$$TSI = a \left(\frac{\text{Molecular Weight}}{\text{Smoke Point}} \right) + b \quad (7.1)$$

where smoke point is in mm and molecular weight is in g mol^{-1} . The constants a (mm mole g^{-1}) and b (dimensionless) place the TSI on a uniform scale from 0 to 100 and are unique to each experimental set up. The constants therefore calibrate and normalise the measurements to allow comparison across studies.

The sooting propensity of a fuel is strongly dependent on the molecular structure of the fuel. The sooting tendency of hydrocarbons follows the order of aromatics > cycloalkanes > iso-alkanes > n-alkanes. Therefore, the Total Sooting Index (TSI) of a fuel can be used as an effective indicator of the relative proportion of different hydrocarbon classes present in the fuel.

However, it is often the case that the smoke point of the fuel is not within the measurable range of the device (10 - 45mm). This is especially true for bio-derived fuels, such as alternative aviation fuels [243] and biodiesels [244], which have very large smoke points owing to the reduced sulphur and aromatic content. Therefore, the virtual smoke point methodology [245] was developed to allow the determination of the smoke point of such fuels. This method exploits the linear-by-mole mixing relationship of the TSI to determine the TSI of a fuel. A pure component with a known molecular weight is added to the fuel to form a series of mixtures with smoke points within the measurable range of the apparatus. By plotting the TSI of each mixture as a function of the mole fraction of the added component, the TSI of the fuel can be estimated by extrapolating to zero mole fraction.

7.3.1.5 Atom Types

Proton nuclear magnetic resonance (^1H NMR) spectroscopy provides chemical structural information on a liquid mixture. A number of studies have developed methods to predict

physical and chemical properties of a liquid fuel based on the results from ^1H NMR [246-249].

NMR exploits the fact that hydrogen nuclei resonate at a characteristic frequency depending on the local bonding environment of the atom. Therefore, nuclei in similar bonding environments will resonate at similar frequencies. This enables the assignment and quantification of the population of various atom types in a fuel sample. An atom type is an atom in a specific electronic environment [250]. For instance, n-alkanes comprise two hydrogen atom types, depending on the hydrogen-carbon bonding. A hydrogen atom attached to a mid-chain carbon is referred to as a *paraffinic* CH_2 atom type, while one attached to an end-chain carbon is known as a *paraffinic* CH_3 atom type. Similarly, in iso-alkanes there exist three hydrogen atom types, *paraffinic* CH_3 , CH_2 and CH . However, in the case of benzene, there exists only one hydrogen atom type (*aromatic* CH). Figure 7.8 provides an illustration of this concept with the carbon and hydrogen atom types found in a hydrocarbon sample identified.

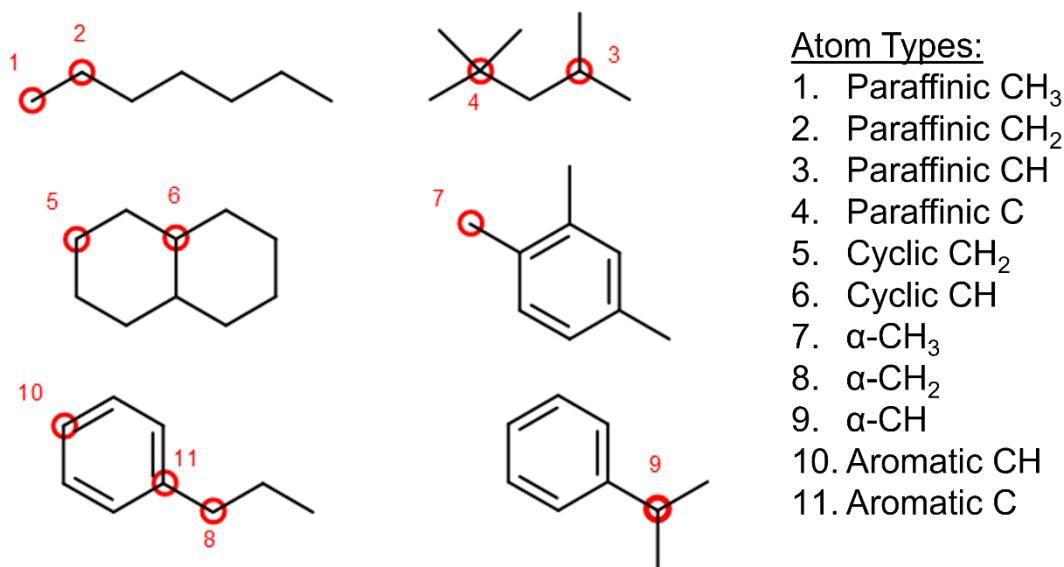


Figure 7.8. Nuclear magnetic resonance (NMR) atom types in hydrocarbons.

A brief explanation of the assignment and quantification of atom types from ^1H NMR spectra is provided here. A detailed description of the technique is provided by Ure et al. [250].

The peaks in the NMR spectra are assigned to each atom type and the integral of the area under each peak, I , is calculated. This integral is directly proportional to the number of H atoms associated with the specific atom type. Hence, the hydrogen mole fraction for a given atom type, x , can be calculated by,

$$XH_x(^1H) = \frac{I_x}{\sum_{i=x} I_i} \quad (7.2)$$

To account for atom types that have no associated hydrogen atom, i.e., paraffinic and aromatic quaternary carbon (number 4 in Fig 7.6), a conversion from hydrogen integral, I_x to carbon integral, I_x^* , must be performed for each atom type.

As each hydrogen atom is bonded to a carbon in a liquid fuel, this conversion is rather straightforward. The carbon integral for an atom type is obtained by dividing the hydrogen integral for that atom type by the number of hydrogen atoms in the atom type (e.g., $I_{CH_3}^* = I_{CH_3}/3$). The carbon integral for aromatic quaternary carbon is calculated using the assumption that the α -CH₃, α -CH₂ and α -CH atom types each has one quaternary carbon.

Once this has been performed, the H/C according to this conversion process, H/C_{NMR} , can be calculated by,

$$H/C_{NMR} = \frac{\sum_x I_x}{\sum_x I_x^*} \quad (7.3)$$

In most cases, the value for this will be greater than the actual H/C for the fuel, as paraffinic quaternary carbons are unaccounted for. Thus, by assuming that the discrepancy in H/C is the result of the unaccounted paraffinic quaternary carbons, the carbon integral for this atom type can be calculated. Hence, the use of relative atom type compositions from ¹H NMR as combustion property targets allows the matching of chemical functionalities of the liquid fuel.

7.3.2 Step 2: Surrogate Definition

The definition of a surrogate for a fuel consists of two steps: selection of surrogate palette components, and the formulation of the optimal combination of palette components.

7.3.2.1 Surrogate Palette Selection

To attain the highest possible accuracy in surrogate modelling, it is imperative to establish a palette of species that encompasses a broad spectrum of chemical and physical properties. This allows for greater versatility in finding a combination of species that closely matches the combustion property targets. For instance, relying solely on one aromatic species to fulfil the requirement of aromatic atom types may result in limitations in accurately replicating other targets, due to its inherent chemical characteristics. For example, if this species has a low molecular weight, it may not be possible to accurately reflect the desired molecular weight target. Consequently, to grant the desired degree of flexibility, multiple components are selected that possess characteristics of relevance.

As the objective of this study is the creation of a kinetic model, a crucial aspect of the methodology is to ensure that accurate kinetic information is available for the components comprising the surrogate palette. Palette components are selected to cover the main hydrocarbon classes and NMR atom types while maximising the possibility of matching the molecular weight of the liquid fuel.

7.3.2.2 Surrogate Formulation

Once the surrogate palette has been established, an in-house algorithm is employed to determine the optimal surrogate formulation that results in the minimal deviation from the target combustion properties. A version of this algorithm was initially created by former group member, Dr. Andrew Ure. However, I have improved and generalised it for this work. This algorithm employs a systematic approach to evaluate the suitability of every possible combination of the palette components.

A matrix is constructed containing the minimum and maximum mole fraction of each component. A comprehensive library is generated, comprising all the possible combinations of the designated palette components. To reduce the computational cost of the algorithm, a filtering process is applied to the library to eliminate any entry (combination of components) that would not be able to meet the desired property targets, thus streamlining the optimisation process. For instance, a restriction is implemented ensuring that every combination in the library must contain at least one n-alkane, iso-alkane, and aromatic component.

The algorithm then selects an entry from this library and the Sci-Py “*optimize*” function [251] finds the optimum molar composition of the components, within the bounds prescribed in the matrix. The optimum composition is found by minimisation of the Surrogate objective error function (OEF), which is a mathematical measure of the error between the calculated combustion property targets of the surrogate and that of the liquid fuel,

$$Surrogate\ OEF = \frac{1}{N_p} \sum_i w_i \left(\frac{P_i^{surr} - P_i^{real}}{P_i^{real}} \right) \quad (7.4)$$

where P_i is the value of the i^{th} combustion property target, superscript *surr* and *real* denote the surrogate calculation and the liquid fuel value, respectively, of the combustion property target. N_p is the number of combustion properties included in the error function and w_i is a weighting function assigned to the i^{th} property target. Linear-by-mole mixing rules are used to compute the combustion property target of each potential surrogate, except for H/C which is computed by calculating the number of carbons and hydrogens contributed from each component.

The Nelder-Mead algorithm [252, 253], which is a direct search, non-gradient method, is used as the optimisation function to minimise the error function. A simplex (a geometrical figure in n -dimensional space that has $n + 1$ vertices) is constructed, where n is the number of variables being optimised (i.e., the number of surrogate components). The simplex is iteratively modified until a minimum in the objective error function is found. Once every entry in the library has been evaluated, the surrogate with the lowest objective error function is selected as the liquid fuel surrogate. A comparison study between the effectiveness of the Nelder-Mead algorithm and other optimisation algorithms available in the Sci-Py package is available in Appendix G.

7.3.3 Step 3: Overly-Reduced Model Construction

Once the composition of the liquid fuel surrogate has been determined, the next step is to identify a detailed model that accounts for the oxidation of its components. Ideally, this model should already be available, as constructing one through the combination of existing submodels can be a complex and time-consuming task. A library of detailed model

calculations is then created, using the surrogate definition as the fuel. These will act as validation, performance, and optimisation targets in the compaction process.

To mitigate the complexity of modelling the reaction mechanism of multiple components in a fuel surrogate, a virtual fuel species is defined with a molecular formula that represents an average of the surrogate components. This helps to simplify the description of the fuel oxidation process.

Expanding upon the knowledge that the overall kinetic combustion behaviour of a fuel can be replicated by replicating the formation and consumption rate of its radical pool, as introduced in Chapter 3.6.3, Dooley et al. [106, 107] introduced the concept of distinct chemical functionalities. Consider the oxidation of a liquid fuel at high temperatures. Following the initial oxidation steps of the fuel molecules, there exists a number of n-alkyl, i-alkyl, cyclo-alkyl, and benzyl radicals. The product array resulting from the decomposition of these radicals is dependent upon the thermochemical molecular environment at the radical site. Radicals with similar environments will undergo similar molecular processes to form a similar array of products.

Hence, a theory is proposed that the decomposition of these intermediate species product arrays is what most significantly affects the radical pool and therefore, the combustion kinetic behaviour of the liquid fuel. It was this, and similar thinking, that lead to the HyChem and decoupling methods described previous.

7.3.3.1 Virtualisation of the Detailed Model

In this work, this concept is leveraged to simplify the detailed model by removing all chemistry above C₄ and replacing it with a *virtual scheme* that describes initial fuel oxidation by linking the fuel molecule to C₀-C₄ chemistry using a limited number of virtual species and virtual reactions. This scheme, illustrated in Figure 7.9, is comprised of eight virtual species, called “*virtual bins*”. For each of the four main hydrocarbon classes in liquid fuels (n-alkane, iso-alkane, cyclo-alkane, and aromatic), there exists two virtual bins: one that represents the product of unimolecular fuel decomposition, and one that represents the product of fuel hydrogen abstraction.

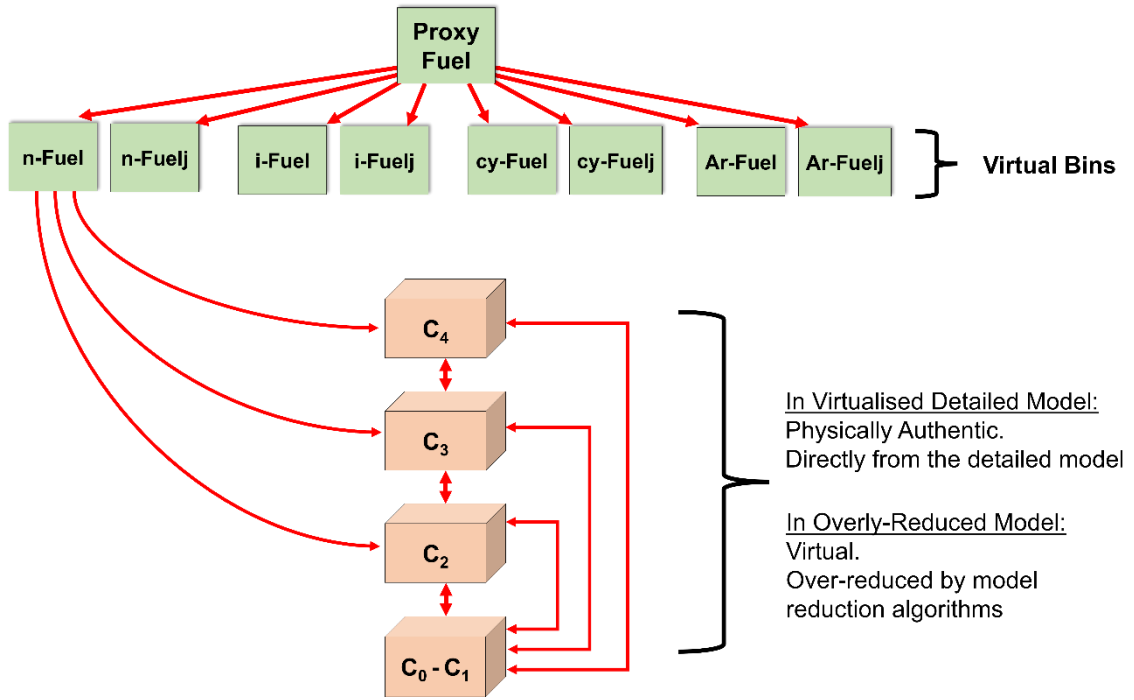


Figure 7.9. Schematic of the virtualised scheme proposed in this work. Note, all virtual bins are linked to the C_2 - C_4 chemistry, however, to simplify the illustration and ensure clarity only those of n -Fuel are depicted. In the Virtualised Detailed Model, the C_0 - C_4 chemistry is that of the parent detailed model. This chemistry is then reduced to produce the Overly-Reduced Model.

The purpose of this scheme is to emulate the reaction flux of the more intricate detailed model by replicating the effect of distinct chemical functionalities. This is accomplished by creating pathways that link the fuel molecule to important intermediates. The proxy fuel node is linked to each of the four fuel unimolecular decomposition virtual bins by one connection of the form,



where x is n , i , cy and Ar . These virtual bins are then linked to C_2 - C_4 chemistry through a series of connections which are generated following the rules,

1. $x-Fuel \Rightarrow Y C_m H_{2m} + Z C_m H_n$
2. $x-Fuel \Rightarrow Y C_m H_{2m} + Z C_{m-1} H_n$
3. $x-Fuel + H \Rightarrow Y C_m H_{2m} + Z C_m H_n + H_2$
4. $x-Fuel + H \Rightarrow Y C_m H_{2m} + Z C_{m-1} H_n + H_2$

where the first product is a molecule and the second is a radical, m represents the carbon number (2 to 4), and Y and Z are constants to ensure elemental balance.

The proxy fuel node is linked to the hydrogen abstraction virtual species by five connections of the form,



where X is O , H , OH , HO_2 and O_2 .

The connections linking the hydrogen abstraction virtual bins to the C_2 - C_4 chemistry are generated following rules 1 and 2 above. These virtual bins do not undergo hydrogen abstraction (rules 3 and 4) as they are considered quasi-radicals.

The virtual Arrhenius parameters prescribed to each of the connections linking the fuel to the virtual bins are obtained through analogy to similar reactions in the reaction mechanism of the surrogate component(s) of the same hydrocarbon class. For instance, consider the connection $Fuel + O \Rightarrow 2\ n-Fuel + OH$. The virtual Arrhenius parameters are obtained by identifying similar pathways in the reaction mechanism of the n-alkane(s) in the surrogate, summing the rate constant of these reactions across a temperature range and fitting the results to obtain a set of virtual Arrhenius parameters that embodies these pathways.

The virtual Arrhenius parameters for the connections linking the virtual bins to the underlying C_2 - C_4 chemistry are obtained through optimisation, as described next. The thermodynamic and transport properties for these species are obtained through analogy to species in the detailed model with similar chemical formula and hydrocarbon class.

7.3.3.2 Optimisation of Virtualised Detailed Model

As there are no directly analogous pathways for the bin decomposition connections, the virtual Arrhenius parameters are obtained through optimisation. MLOCK1.0 Phase 1, as described in Chapter 4, is employed to obtain parameters for these connections that result in an accurate replication of the detailed model 0-D calculations. The 0-D objective error function (OEF) used in this MLOCK application is different to that of Chapter 4, due to the use of the `.advance()` method for time integration, as discussed in Chapter 6. The revised 0-D OEF is a combination of two error functions, one that measures the relative error in the

maximum mole fraction of the species between the model candidate and detailed model perfectly stirred reactor (PSR) calculations at each condition, and one that measures the relative error in the maximum derivative mole fraction with respect to time between the model candidate and detailed model calculations at each condition, as,

$$O-D\ OEF = \frac{1}{2N_K} \sum_k \sum_i \left(\frac{[X_i]_{max,k}^{red} - [X_i]_{max,k}^{det}}{[X_i]_{max,k}^{det}} + \frac{(Y_i^{red})_k - (Y_i^{det})_k}{(Y_i^{det})_k} \right) \quad (7.7)$$

where superscript *red* and *det* refer to model candidate and detailed model calculations, $[X_i]_{max,k}$ denotes the maximum mole fraction of species *i* at the k^{th} set of operating conditions, $(Y_i)_k$ refers to the maximum derivative mole fraction with respect to time of species *i* at the k^{th} set of operating conditions and N_K refers to the number of operating conditions evaluated.

7.3.3.3 Reduction of Virtualised Detailed Model

Path flux analysis (PFA) is performed on the optimised Virtualised Detailed Model to produce the Overly-Reduced Model, as shown in Figure 7.10. Similar to the case of methane, the exact model reduction technique that is used is not of primary concern. In this operation, all virtual bins, all C₂-C₄ species that are linked to the virtual bins, and the H₂/O₂ sub model are locked-off from reduction.

7.3.4 Step 4: Optimisation of Overly-Reduced Model

The Overly-Reduced Model is then optimised using MLOCK1.2. PSR and S_u sensitivity analysis is performed on the Overly-Reduced Model and all connections that have a normalised sensitivity coefficient greater than ±0.05 are selected for optimisation. MLOCK1.2 uses the 0-D OEF (of Equation 7.7) in the Coarse – Bound Refinement – Refined Scan – Genetic Seed Scan process, similar to MLOCK1.0. However, the 1-D OEF is evaluated in the Refined and Genetic Seed Scans for model candidates with suitably low 0-D OEFs, similar to MLOCK1.1. The 1-D OEF is that of Equation 4.2, however it is shown again here for convenience,

$$1-D\ OEF = \frac{1}{N_k} \sum_k \left(\frac{|S_{u,k}^{red} - S_{u,k}^{det}|}{S_{u,k}^{det}} \right) \quad (7.8)$$

where $S_{u,k}$ is the laminar burning velocity at the k^{th} set of temperature, pressure, and equivalence ratio conditions and N_k is the number of conditions. The final OEF is then the average of the 0-D and 1-D OEF.

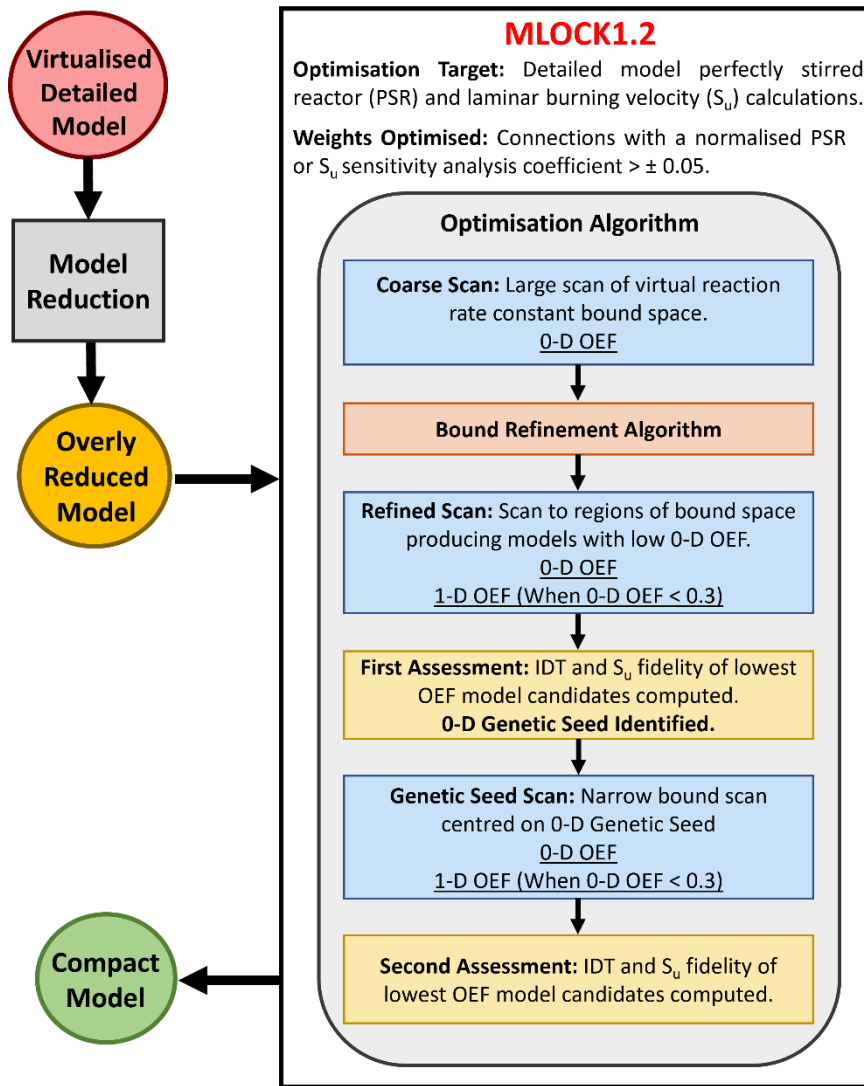


Figure 7.10. Process flow for MLOCK1.2. This MLOCK version is used to optimise the Overly-Reduced Model to 0-D and 1-D calculations of the detailed model. Note, the optimisation and validation conditions used in this study are presented in Table 7.7 and Table 7.8 respectively.

7.4 Application to Arabian Extra Light (AXL)

This methodology is demonstrated through its application to produce a compact model for Arabian Extra Light (AXL) crude oil combustion at high temperatures comprising less than forty species. For this study, the diesel surrogate model developed by Wang et al. [254] at Lawrence Livermore National Laboratory (LLNL) was utilised as the detailed model. This model, comprising 6,476 species, details hydrocarbon oxidation with the inclusion of n-alkanes up to C₂₀, thereby enabling the selection of large molecular weight surrogate pallet components. This model is referred to as *LLNL_6476s* henceforth. Table 7.2 shows the set of calculations that Siemens Energy provided as pertinent to their gas turbine design and fuel research efforts in respect to AXL/air combustion. Hence, this set of calculations will serve as the performance conditions to which the compact model must be highly accurate. Note, as *LLNL_6476s* contains nearly 6,500 species, it is not possible to perform one-dimensional (1-D) calculations using this model without the use of a modified solver. Therefore, a conservatively-reduced skeletal model is produced, as discussed later, and used for the 1-D performance, optimisation, and validation conditions.

Table 7.2. Performance targets for AXL/air combustion defined by gas-turbine Industry sponsor. These targets are defined by Industry as being required for their gas turbine design and fuel research efforts and as such their accurate replication is required from the compact model. Compact model performance will be benchmarked to replication of these targets.

Reactor Physics	Property	Pressure (atm)	Equivalence Ratio	Temperature (K)
Perfectly Stirred Reactor	[OH], [CO], [CO ₂], [H ₂ O]	1, 10, 20, 30, 40	0.4, 0.5,..., 1.5	1200, 1300, ..., 2000
Constant Volume Constant Internal Energy	IDT	1, 10, 20, 30, 40	0.5, 1.0, 1.5	1200, 1300, ..., 2000
Freely Propagating Flame	S _u	1, 10, 20, 30, 40	0.4, 0.5,..., 1.5	500, 700, 900

To quantify the accuracy of the compact models to the performance and validation conditions, fidelity indexes are used,

$$Fidelity (\%) = \frac{100}{N} \sum_k \left(1 - \frac{|X_k^{compact} - X_k^{detailed}|}{X_k^{detailed}} \right) \quad (7.9)$$

where X_k is the calculation (e.g., laminar burning velocity) at the k^{th} set of pressure, temperature, and equivalence ratio conditions and N is the number of conditions included. A value of 100% indicates a model with perfect replication of the detailed model calculations.

- For IDT fidelity, X represents the time at which derivative temperature by derivative time is at a maximum.
- For S_u fidelity, X is the laminar burning velocity.
- For PSR fidelity, X is the maximum mole fraction of CO, OH, H₂O and CO₂, the time at which this maximum occurs, and the steady-state concentration of CO, OH, H₂O and CO₂ at residence times of 100 ms.

7.4.1 Selected Combustion Property Targets

The combustion property targets used in this work are shown in Table 7.3. The H/C of AXL, determined through CHN elemental analysis at the UCD School of Chemistry by Rónán Crowley is 1.84. This is in good agreement with the values provided by Siemens Energy engineers (1.88). The average molecular weight of AXL, as determined by two-dimensional gas chromatography (GC x GC), provided to us by Siemens Energy is 224.46 g mol⁻¹. This is in-line with expectations of a light crude oil and is similar to the molecular weight of n-hexadecane (C₁₆H₃₄) at 226.41 g mol⁻¹. The DCN of AXL, as determined by CFR Engines Inc, is 53.53 which is what one would expect from a diesel or kerosene fuel. Proton Nuclear Magnetic Resonance (¹H NMR) was performed on AXL by Dr. Andrew Ure. Based on the results, AXL contains 18.2% (mole percent carbon) of paraffinic CH₃ atom types, 45.2% of paraffinic CH₂ atom types, and 11.5% of total aromatic atom types. These atom types were selected as the combustion property targets, as the competition between n-alkanes and aromatics, as well as the ratio of paraffinic CH₃ to CH₂ atom types, play a major role in the reactivity and the propensity to soot of the fuel.

The TSI of AXL was determined using the virtual smoke point method as the smoke point of AXL was very low and difficult to measure due to flame instability. Seven mixtures of AXL and methylcyclohexane were produced, and the smoke point measured. Figure 7.11

shows the results of these measurements, resulting in a virtual smoke point of 13.8 ± 1.1 mm. This is similar to diesel which has a smoke point of approximately 13 – 19 mm [244, 255]. From this the TSI was calculated to be 62.6 ± 4.59 using a and b parameters of $4.01 \text{ mm mol g}^{-1}$ and -2.62 , respectively. This is similar to single-ring aromatics [242].

Table 7.3. Combustion property targets of AXL. Note, no uncertainty was provided by Siemens Energy on the average molecular weight, so an estimate of 10% uncertainty is assumed.

Combustion Property Target	Value	Measurement Technique	Performed at
Average Molecular Weight (g mol^{-1})	224.5 ± 22.5	GC x GC	Siemens Energy
Threshold Sooting Index	62.6 ± 4.6	Virtual Smoke Point	Trinity College Dublin
Hydrogen/Carbon	1.84 ± 0.04	Elemental Analysis	University College Dublin
Derived Cetane Number	53.5 ± 1.3	ASTM D6890	CFR Engines Canada ULC
Paraffinic CH_3 (mole % carbon)	18.2 ± 10.0	Proton Nuclear Magnetic Resonance	Trinity College Dublin
Paraffinic CH_2 (mole % carbon)	45.2 ± 10.0	Proton Nuclear Magnetic Resonance	Trinity College Dublin
Total Aromatic (mole % carbon)	11.5 ± 4.0	Proton Nuclear Magnetic Resonance	Trinity College Dublin

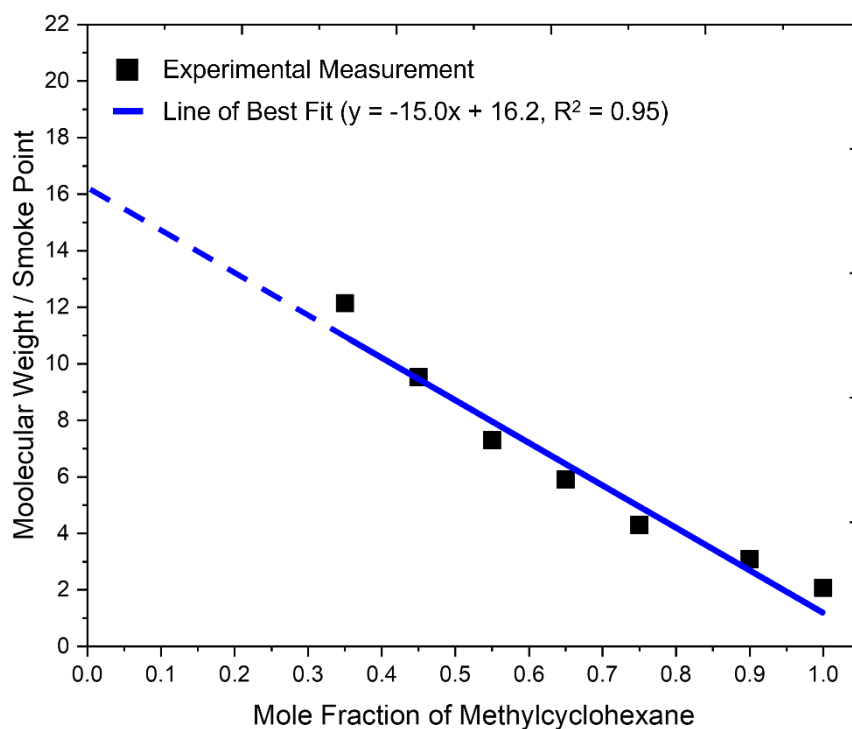


Figure 7.11. Molecular weight divided by smoke point of a series of methylcyclohexane/AXL mixtures. Extrapolation to the y intercept allows for the calculation of the virtual smoke point of AXL to be 13.8 mm.

7.4.2 Arabian Extra Light (AXL) Surrogate

The surrogate pallet considered in this work, shown in Figure 7.12, contains species covering the major hydrocarbon classes and NMR atom types.

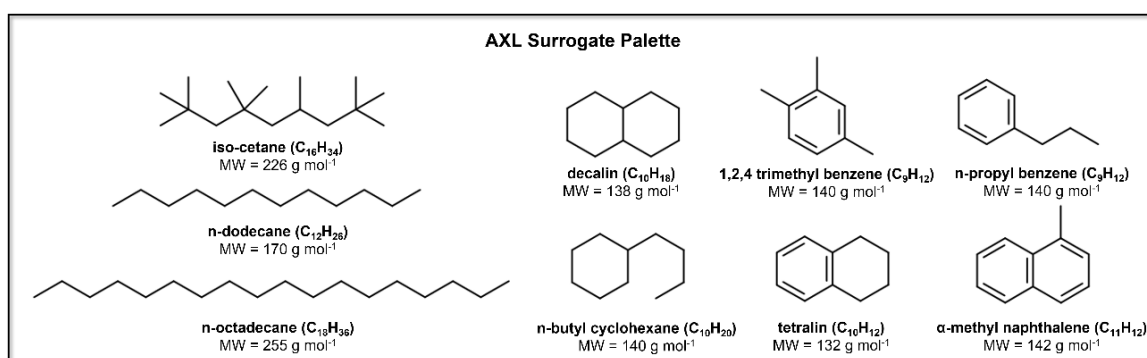


Figure 7.12. Surrogate palette for AXL used in this work. This palette includes large molecular weight species from the major hydrocarbon classes, and covers important NMR atom types.

The in-house surrogate formulator algorithm was implemented to find the combination of surrogate palette components that resulted in the smallest error to the combustion property targets, as expressed by the Surrogate OEF in Equation 7.4. The value of w in the OEF was set to 0.5 for DCN and unity for all other targets. The surrogate definition with the lowest OEF, and thus selected as the AXL surrogate was n-octadecane/iso-cetane/n-butyl cyclohexane/tetralin/ α -methyl naphthalene at a mole fraction mixture composition of 0.346/0.178/0.247/0.114/0.115 as shown in Figure 7.13. The combustion property targets of this five-component surrogate for AXL are shown in Table 7.4.

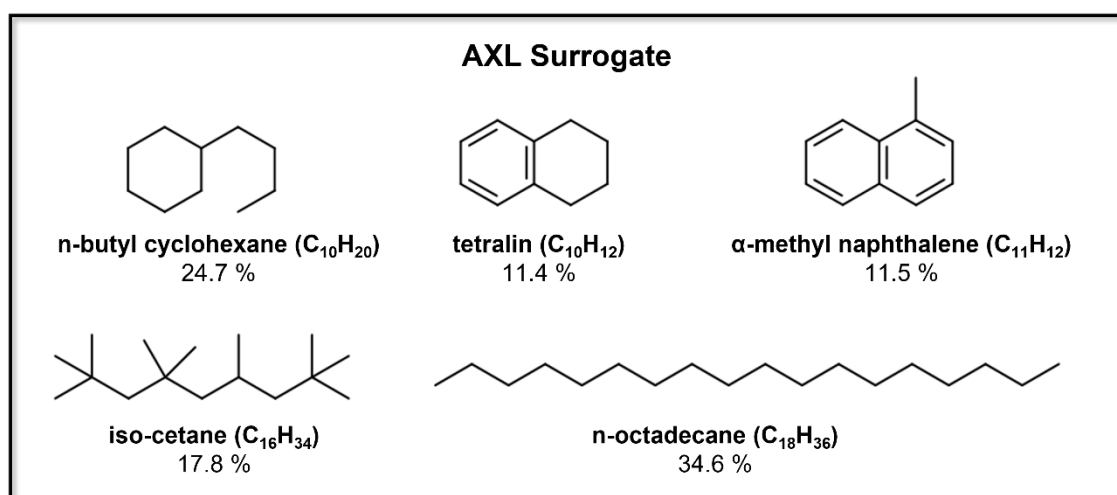


Figure 7.13. Five-component surrogate for Arabian Extra Light (AXL) crude oil as defined in this study (in mole percent).

Table 7.4. Combustion property targets of AXL (experimental) and AXL Surrogate (computed).

Combustion Property Target	AXL	AXL Surrogate	Relative Error
Average Molecular Weight (g mol^{-1})	224.5 ± 24.5	194.4	13.4 %
Threshold Sooting Index	62.6 ± 4.6	28.0	55.3 %
Hydrogen/Carbon	1.84 ± 0.04	1.90	3.2 %
Derived Cetane Number	53.5 ± 1.3	52.1	2.7 %
Paraffinic CH_3 (mole % carbon)	18.2 ± 10.0	18.2	0.0 %
Paraffinic CH_2 (mole % carbon)	45.2 ± 10.0	48.8	8.0 %
Total Aromatic (mole % carbon)	11.5 ± 4.0	11.5	0.0 %

To validate the AXL surrogate and kinetic model, ignition delay time (IDT) calculations were performed using LLNL_6476s using the five-component AXL surrogate, and the results compared to experimental data. Experimental measurements on diesel were used due to the absence of experimental data on AXL. The results, as shown in Figure 7.14, show that the IDT calculations of the AXL surrogate are similar to experimental results from diesel, which is what one would expect. A library of detailed model calculations was constructed for the performance, optimisation, and validation targets of Tables 7.2, 7.5, 7.6, 7.7, and 7.8.

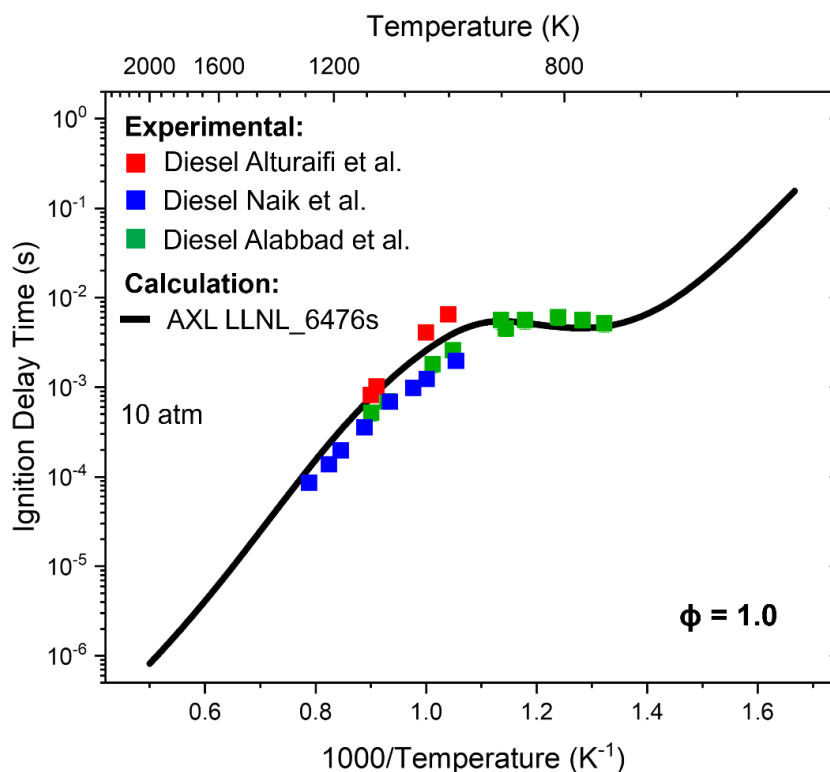


Figure 7.14. Ignition delay time measurements at 10 atm and at stoichiometric fuel/air mixture. The LLNL_6474s detailed model is used to model IDT of AXL mixtures (line). Experimental data on the IDT of diesel obtained from the works of Alturaifi et al. [256], Naik et al. [257], and Alabbad et al. [258]. This highlights the similarity of the AXL surrogate calculations to experimental data from similar fuels.

7.4.3 Virtualisation of LLNL_6474s Detailed Model

The five-component surrogate was lumped to create a single proxy fuel species called *vAXL* with a chemical formula $C_{14}H_{26}$. This results in a H/C of 1.86 and a molecular weight of 194 g mol⁻¹. The thermodynamic and transport parameters of n-tetradecane ($C_{14}H_{30}$) were used for *vAXL*.

LLNL_6476s was then virtualised by the method outlined in Section 7.3.3.1 to produce a *Virtualised Detailed Model* comprising 429 nodes and 2,365 connections. This led to the creation of eight virtual bins, *n-AXL*, *n-AXLj*, *i-AXL*, *i-AXLj*, *cy-AXL*, *cy-AXLj*, *Ar-AXL* and *ArAXLj*. The chemical formula of the fuel unimolecular decomposition bins (*n-AXL*, *i-AXL*, *cy-AXL*, *Ar-AXL*) was set to C_7H_{13} with the hydrogen abstraction bins (*n-AXLj*, *i-AXLj*, *cy-AXLj*, *Ar-AXLj*) set to C_7H_{12} . The thermodynamic and transport parameters of heptane (C_7H_{16}) were used for *n-AXL*, 1-heptyl (C_7H_{15}) was used for *n-AXLj*, iso-octane (C_8H_{18}) was used for *i-AXL*, an iso-octane radical (C_8H_{17}) was used for *i-AXLj*, methyl cyclohexane

(C_7H_{14}) was used for both *cy-AXL* and *cy-AXLj*, and toluene (C_7H_8) was used for both *Ar-AXL* and *Ar-AXLj*.

Next, the virtual Arrhenius parameters for the connections linking *vAXL* to the virtual bins were obtained. Figure 7.15 shows an example of how this was performed for the connection $vAXL \Rightarrow 2\ n\text{-}AXL$. The reaction rate constant of all n-octadecane decomposition reactions in LLNL_6476s at temperatures ranging from 500 – 2000 K are calculated and summed. These values are then plotted and fitted using a modified Arrhenius dependence to get a set of virtual Arrhenius parameters that represent the summed reaction rates. The new virtual Arrhenius parameters ($A = 1.08E34\ s^{-1}$, $n = -4.79$, $E_A = 89513\ cal\ mol^{-1}$) are used for the connection $vAXL \Rightarrow 2\ n\text{-}AXL$.

By following the connection generation rules, each unimolecular decomposition virtual bin is linked to the C_2 - C_4 chemistry by ten connections (five unimolecular decomposition, five hydrogen abstraction) and each hydrogen abstraction bin is linked to the C_2 - C_4 chemistry by five unimolecular decomposition connections.

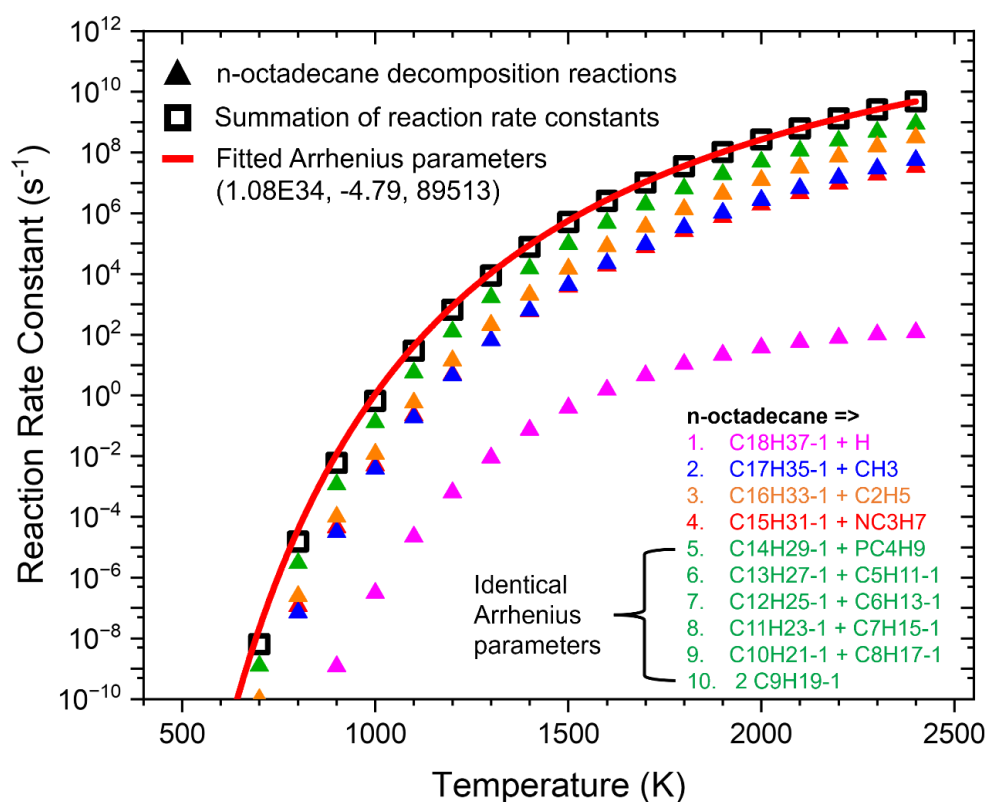


Figure 7.15. Reaction rate constants of every n-octadecane unimolecular decomposition reaction in LLNL_6476 (triangles) as a function of temperature. The rates at each temperature point are summed (squares) and fitted (line) to obtain a set of Arrhenius parameters to represent the combined rate of these reactions. This will be used to represent the reaction $vAXL \Rightarrow 2\ n\text{-}AXL$.

7.4.4 Optimisation of Virtualised Detailed Model

MLOCK1.0 was used to obtain the Arrhenius parameters of the sixty connections linking the virtual bins to the C₂-C₄ chemistry by Phase 1 optimisation. The optimisation targets used by MLOCK1.0 are shown in Table 7.5. The validation targets used in the Assessment stages of MLOCK1.0 are shown in Table 7.6. Note, that no 1-D calculations are performed. As PFA only evaluates 0-D simulations, an accurate replication of 1-D calculations is not strictly necessary.

As there are no starting initial guesses for the n' and E_A' parameters, the n' parameter was set to 0 and the bounds for E_A' set as 0 to 100,000 cal mol⁻¹ to grant sufficient freedom to the algorithm. The number of model candidates produced in each scan, n , was 20,000, due to the considerable computational cost associated with the calculations of a model of this size.

This optimisation resulted in a 429-node model with an excellent replication of the 6476-species *LLNL_6476s* PSR calculations (PSR fidelity of 98.1% to conditions of Table 7.2). Figure 7.16 shows the PSR calculations of important species using the Virtualised Detailed model and *LLNL_6476s* at representative conditions, with more detailed validation available in Appendix H.

Table 7.5. Optimisation targets that comprise the OEFs evaluated in the Scans of MLOCK1.0 for the optimisation of the Virtualised Detailed Model. An optimisation target provides an indicator of model performance in 0-D and 1-D calculations at Industry relevant operating conditions. MLOCK1.0 uses these targets to optimise the model candidates.

Purpose	Reactor Physics	Property	Pressure (atm)	Equivalence Ratio	Temperature (K)
Phase 1 Optimisation Targets	Perfectly Stirred Reactor	[C ₂ H ₄], [CO], [OH], [H]	1, 10, 40	0.7, 1.0, 1.4	1200, 1600, 2000

Table 7.6. Validation targets that are evaluated in the Assessment of MLOCK1.0 for the optimisation of the Virtualised Detailed Model. A validation target is a calculation that acts as an important indicator of overall model performance. MLOCK1.0 uses these targets to calculate model fidelity.

Purpose	Reactor Physics	Property	Pressure (atm)	Equivalence Ratio	Temperature (K)
Phase 1 Validation	Constant Volume Constant Internal Energy	IDT	1, 10, 40	0.5, 1.0, 1.5	1200, 1300, ..., 2000

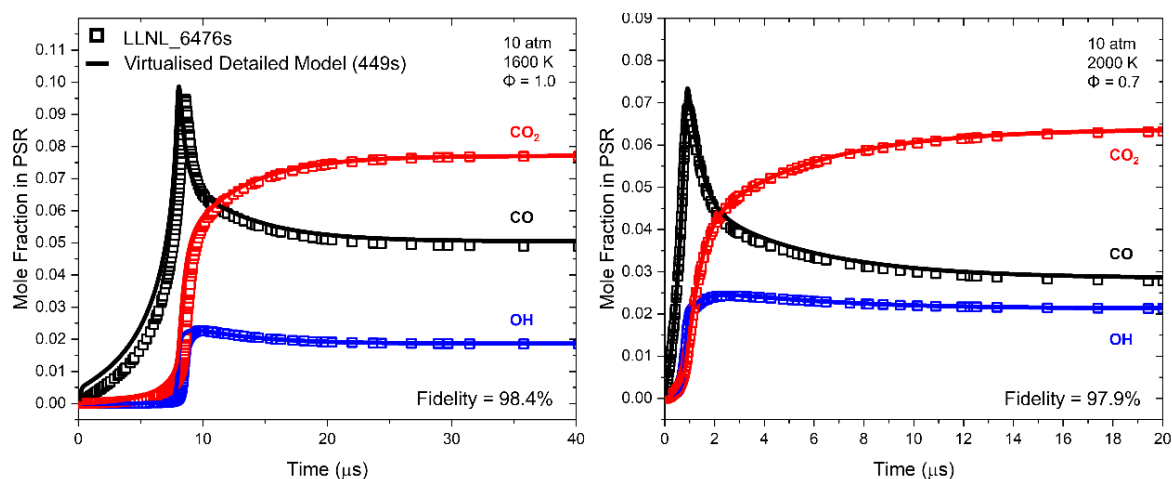


Figure 7.16. Perfectly stirred reactor (PSR) profiles of important species for AXL/air mixtures using LLNL_6476s (symbols) and 429-node Virtualised Detailed Model (lines) at representative conditions. More comprehensive accounting can be found in Appendix H.

7.4.5 Reduction of Virtualised Detailed Model

The Virtualised Detailed Model was then reduced using PFA to produce an Overly-Reduced Model with 35 nodes and 189 connections. PFA was performed by producing a numerical database of time dependent chemical species concentration profiles in a homogenous constant volume reactor up until the point of ignition using AXL/air mixtures at 1, 10, 20, 30, and 40 atmospheres (atm), 1200 – 2000 K and at equivalence ratios 0.5, 1.0 and 1.5. A series of models of varying size were produced using PFA and the IDT fidelity of the models calculated. The error threshold was increased until the point where further increase resulted in species of interest being removed.

This was also performed using direct relation graph with error propagation (DRGEP) and the results compared, as shown in Figure 7.17. This highlights that the type of model reduction algorithm used is not of primary concern for the purpose of over-reduction as the results converge, similar to methane combustion (Figure 3.5).

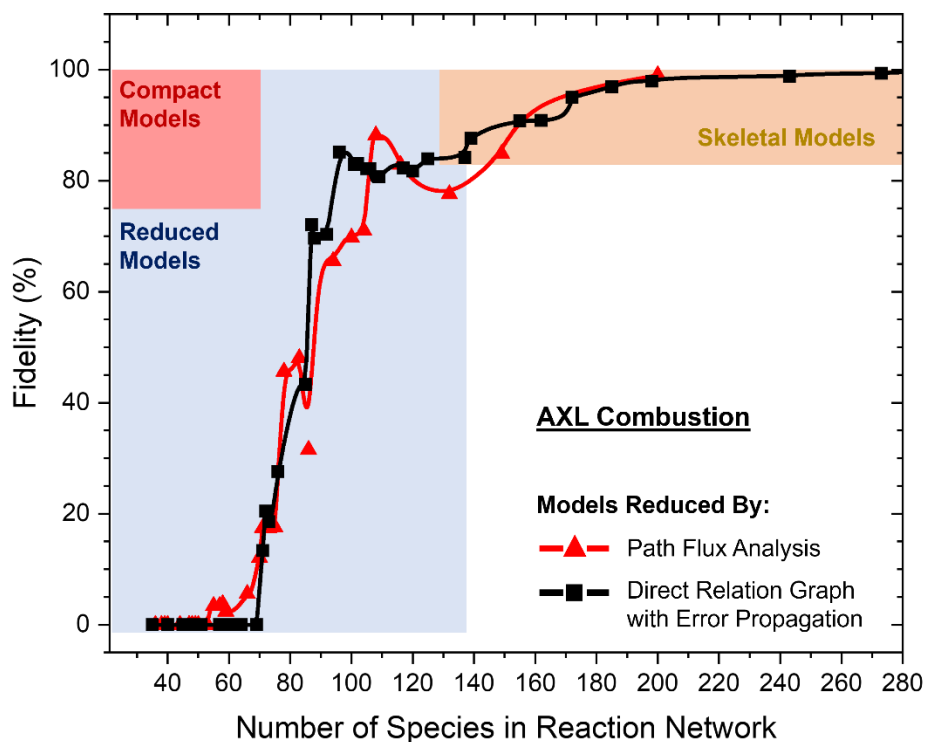


Figure 7.17. Dependence of fidelity of model calculation for AXL/air combustion on complexity of reaction network, as indicated by number of species. Fidelity is the inverse maximum error in reduction procedure. The reduction was performed at: 1-40 atm, 1200-2000 K, AXL/air equivalence ratios 0.5 – 1.5.

7.4.6 Optimisation of Overly-Reduced Model

The Overly-Reduced Model resulting from PFA had a PSR, IDT and S_u fidelity at the conditions of Table 7.2 of 75.1%, 66.3% and 79.2% respectively. MLOCK1.2 was applied to this construct using the optimisation targets of Table 7.7. The 1-D OEF is calculated for model candidates in the Refined Scan with a 0-D OEF less than 0.3. The overall OEF is equal to the average of the 0-D OEF and 1-D OEF. The validation conditions used in the Assessment steps are shown in Table 7.8. In this work, the number of model candidates produced in each scan, n , is 200,000.

Table 7.7. Optimisation targets that comprise the OEFs evaluated in the Scans of MLOCK1.2. An optimisation target provides an indicator of model performance in 0-D calculations at Industry relevant operating conditions. MLOCK1.2 uses these targets to optimise the model candidates.

Purpose	Reactor Physics	Property	Pressure (atm)	Equivalence Ratio	Temperature (K)
Phase 1 Optimisation Targets	Perfectly Stirred Reactor	[C ₂ H ₄], [CO], [OH], [H]	1, 10, 40	0.7, 1.0, 1.4	1200, 1600, 2000
	Freely Propagating Flame	S _u	10	0.8, 1.05, 1.3	500

Table 7.8. Validation targets that are evaluated in the Assessment in each Phase of MLOCK1.2. A validation target is a calculation that acts as an important indicator of overall model performance. MLOCK1.2 uses these targets to calculate model fidelity.

Purpose	Reactor Physics	Property	Pressure (atm)	Equivalence Ratio	Temperature (K)
Phase 1 Validation	Constant Volume Constant Internal Energy	IDT	1, 10, 40	0.5, 1.0, 1.5	1200, 1300, ..., 2000
	Freely Propagating Flame	S _u	1, 10, 40	0.4, 0.5, ..., 1.5	500

For the purpose of this thesis, the 35-node compact model produced in this work will henceforth be referred to as *TCD_35sOp_HT*. *TCD_35sOp_HT* has a PSR fidelity of 86.0%, an IDT fidelity of 79.6% and a S_u fidelity of 89.1% at the set of performance conditions of Table 7.2. The performance target parameter space is vast, and so only representative calculations are shown here. More comprehensive validation can be found in Appendix I.

Figure 7.18 shows the S_u and IDT calculations of the detailed model, Overly-Reduced Model and *TCD_35sOp_HT* at representative conditions to illustrate the effect of MLOCK1.2 on the performance of the model. *TCD_35sOp_HT* accurately replicates IDT and S_u calculations of the detailed model across the performance envelope. Additionally, the compact model has a good replication of LLNL_6476s calculations of important PSR speciation data across the performance envelope of Table 7.2. Figure 7.19 shows the PSR profiles of key species at two representative conditions to illustrate the typical performance of the compact model. The compact model can be found in Appendix J.

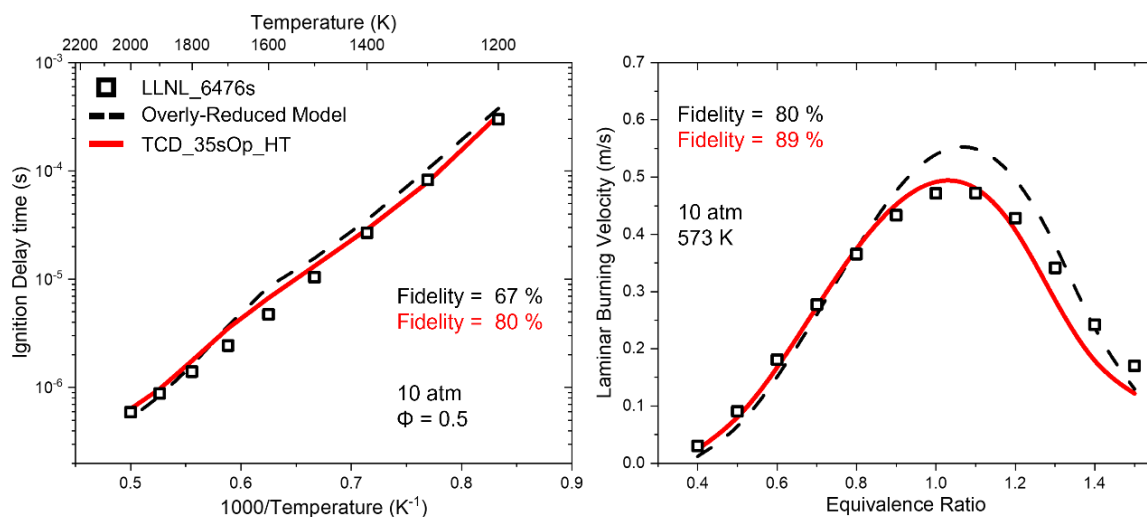


Figure 7.18. Ignition delay time as a function of temperature (left) and laminar burning velocity as a function of equivalence ratio (right) for AXL/air mixtures at 10 atm using the detailed model (symbols) and 35-node compact model (lines). Note, a conservatively reduced skeletal model derived from LLNL_6476s is used as the detailed model for 1-D calculations, as discussed later.

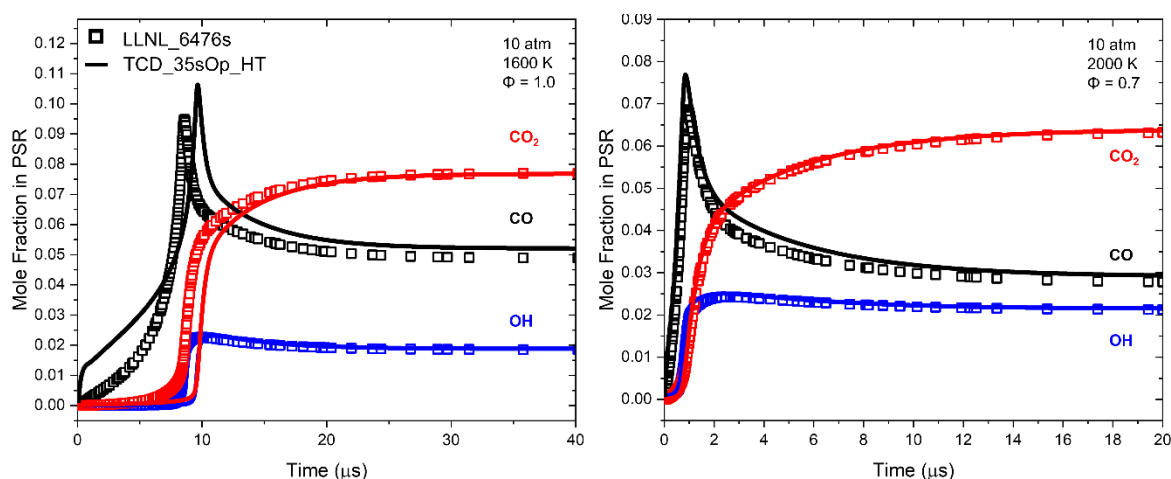


Figure 7.19. Perfectly stirred reactor profiles of important species for AXL/air mixtures at 10 atm using the detailed model (symbols) and 35-node compact model (lines) at representative conditions. More comprehensive accounting can be found in Appendix I.

7.5 Discussion

7.5.1 0-D Objective Error Function Analysis

Figure 7.20 shows MLOCK1.2 data from the Coarse Scan and Bound Refinement from the optimisation of the 35-node Overly-Reduced Model. Fifteen connections of the Overly-Reduced Model had either a PSR or S_u normalised sensitivity coefficient greater than ± 0.05

and hence were selected for optimisation. Analysis of Figure 7.20 shows that there is rich behaviour occurring across the connections, however, only the connection $HCO + M \rightleftharpoons CO + H + M$ has a well-defined minimum. Additionally, no good models are produced if the value of this connection is below $10^8 \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$. Although not as defined, a minimum is observed in the range $10^7 - 10^8 \text{ s}^{-1}$ for the connection $i\text{-AXL} \Rightarrow C_2H_3 + 2.5 C_2H_4$. This indicates that if a model is produced in this region there is a high probability that it will have a low OEF but a model outside of this range can still have a low OEF. Furthermore, if the virtual rate constant is above 10^{12} for connections $C_2H_3 + O_2 \rightleftharpoons CH_2O + HCO$ and $C_2H_3 + C_2H_3 \rightleftharpoons C_4H_6$ there is a high probability that the model will perform poorly.

The 0-D OEF used in this study acts as a suitable indicator for model performance at other 0-D calculations. Figure 7.21 shows the IDT fidelity of model candidates produced in the Refined Scan as a function of their 0-D OEF. Although the relationship isn't perfect, a clear coupling exists between these variables, with an R^2 of 0.69, therefore confirming the suitability of the OEF formulation.

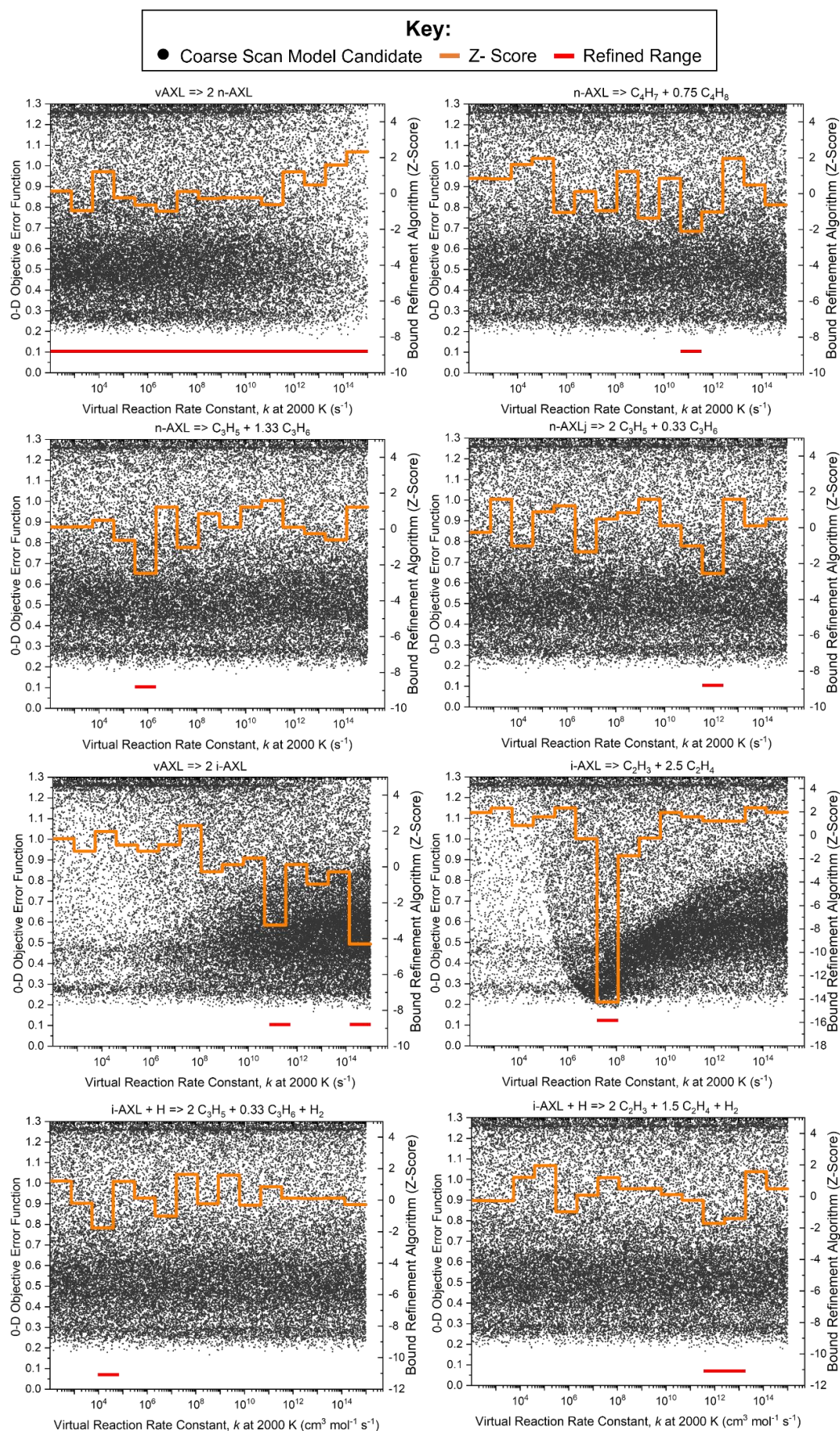


Figure 7.20 (a). 0-D Objective Error Function (OEF) of model candidates produced in the Coarse Scan as a function of the virtual reaction rate constant of connections in the 35-node AXL model.

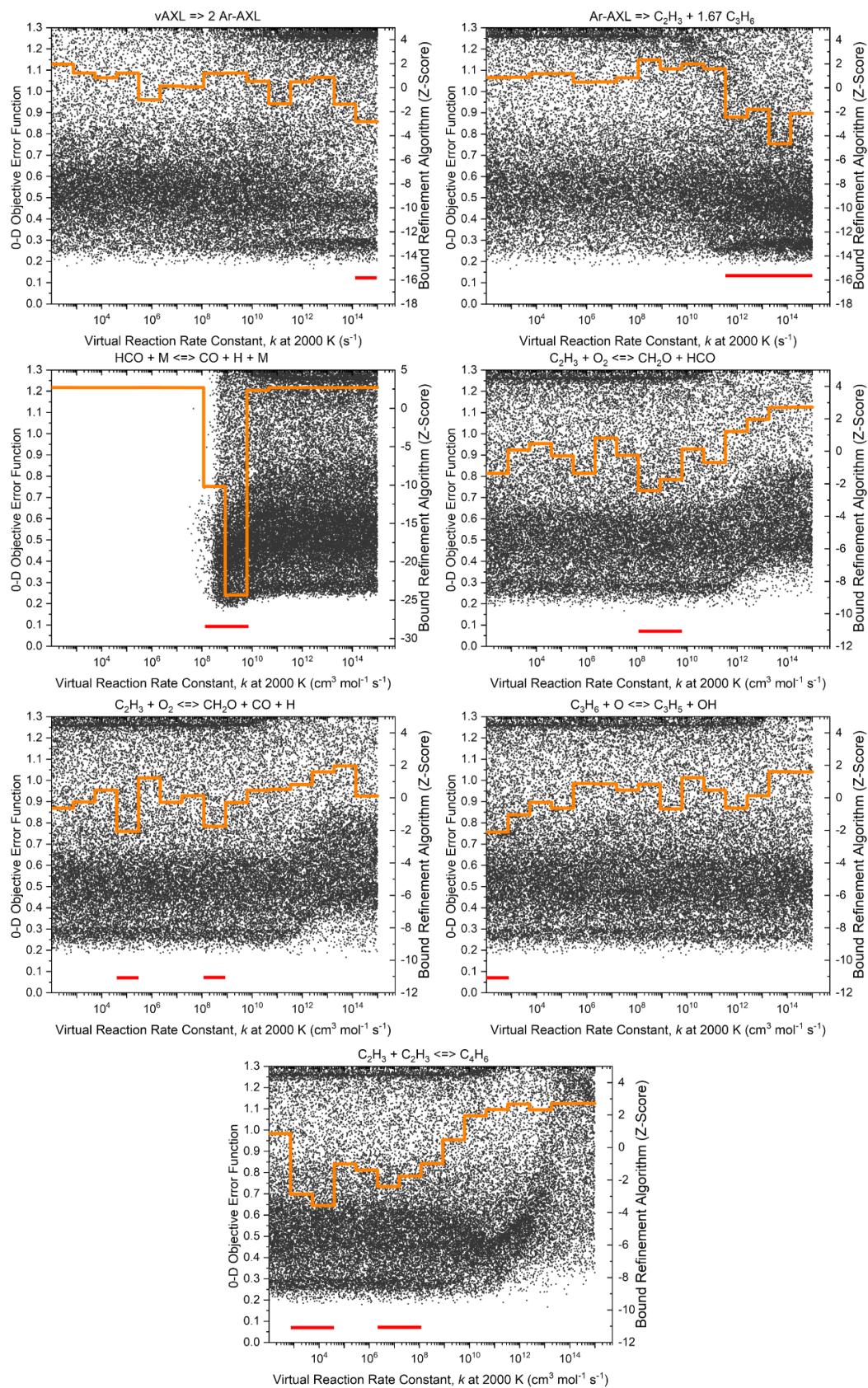


Figure 7.20 (b). 0-D Objective Error Function (OEF) of model candidates produced in the Coarse Scan as a function of the virtual reaction rate constant of connections in the 35-node AXL model.

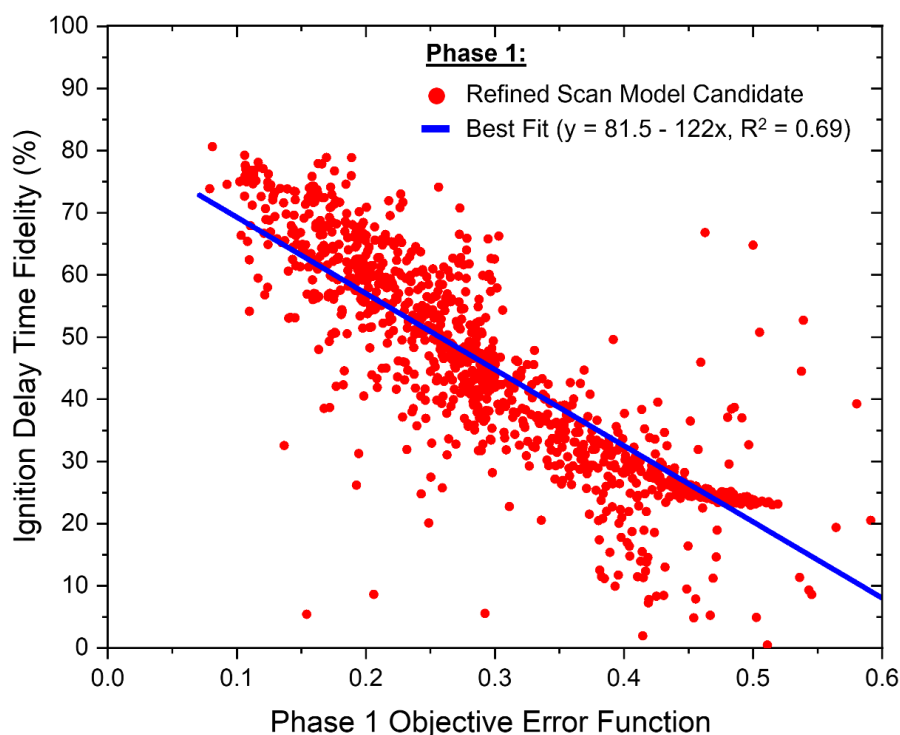


Figure 7.21. Ignition delay time fidelity of model candidates produced in the Refined Scan as a function of the 0-D Objective Error Function (OEF). IDT fidelity assessment is performed at 10 atm, 1200 – 2000 K, and equivalence ratios 0.5 – 1.5. This shows a strong coupling between 0-D OEF and IDT fidelity, confirming the suitability of the OEF formulation used in MLOCK1.2 to optimise the 35-node Overly-Reduced Model (Fig 7.8).

7.5.2 Effect of Surrogate Palette Complexity on Surrogate Formulation

The requirement of accurate kinetic data for the surrogate palette components imposed a significant constraint on this study, resulting in compromises on the accuracy of replication of certain combustion properties. Additionally, producing a surrogate for AXL is considerably more challenging compared to liquid fuels such as diesel and kerosene for a number of reasons.

Firstly, matching the molecular weight of AXL, which is larger than commercial diesel or kerosene, requires the presence of significant proportions of large n-alkanes and iso-alkanes. Since there is no kinetic data available for aromatic or cycloalkane molecules with molecular weights close to that of AXL, the surrogate palette is limited as it contains only aromatic and cyclo-alkanes with molecular weights in the range of 120 – 143 g mol⁻¹. However, matching the paraffinic CH₃ and CH₂ atom types imposes a limit on the amount of n- and iso-alkanes that can be included in the surrogate composition, hence a considerable

portion of the surrogate must be comprised of these relatively low-molecular weight components, lowering the average molecular weight.

Secondly, and along the same lines as above, a certain percentage of aromatics must be present in the surrogate composition to accurately represent the percentage of aromatic atom types in AXL. However, the molecular weight of these components is relatively low, which, in turn, lowers the overall molecular weight of the surrogate composition.

Thirdly, AXL has a much higher TSI compared to other liquid fuels such as diesel which is typically in the range 20-30 [244]. Cyclo-, n-, and iso-alkanes typically have a TSI less than 20. Therefore, to match the TSI of AXL, a significant proportion of aromatics must be included in the surrogate composition. However, this leads to an under-prediction of the DCN and H/C ratio, and an over-estimation of the aromatic atom types. As a result, it was not possible to develop a surrogate for AXL using this palette with both an accurate replication of DCN, H/C and aromatic atom types, and a TSI greater than approximately 30. Hence, an accurate replication of the TSI was sacrificed in order to match a larger number of property targets, and to produce an accurate encapsulation of real fuel kinetic behaviour in non-sooting phenomena. To achieve a TSI that matches that of AXL, it is necessary to include non-aromatic components with a high sooting tendency and a DCN of approximately 40 or above, or aromatic components with a significant number of paraffinic CH_3 and CH_2 atom types. Unfortunately, none of the molecules in the LLNL_6476s detailed model, which is state-of-art in terms of large molecular weight hydrocarbon oxidation, meet these criteria.

7.5.3 1-D Detailed Model Calculations

Using the assumption that in flame calculations, low temperature chemistry does not have a major contribution, a skeletal model was used for the 1-D optimisation, validation, and performance targets. This model was obtained by applying a conservative model reduction procedure to LLNL_6476s and validating the skeletal model to high temperature 0-D calculations. A series of skeletal models of incrementally smaller number of species were produced and the PSR and IDT calculations compared to LLNL_6476s. Figure 7.22 shows the IDT results of these skeletal models. The results show that the 652 species skeletal model replicates the high temperature 0-D calculations of LLNL_6476s to a high fidelity, and

hence, the resulting S_u calculations should provide a good approximation of the detailed model.

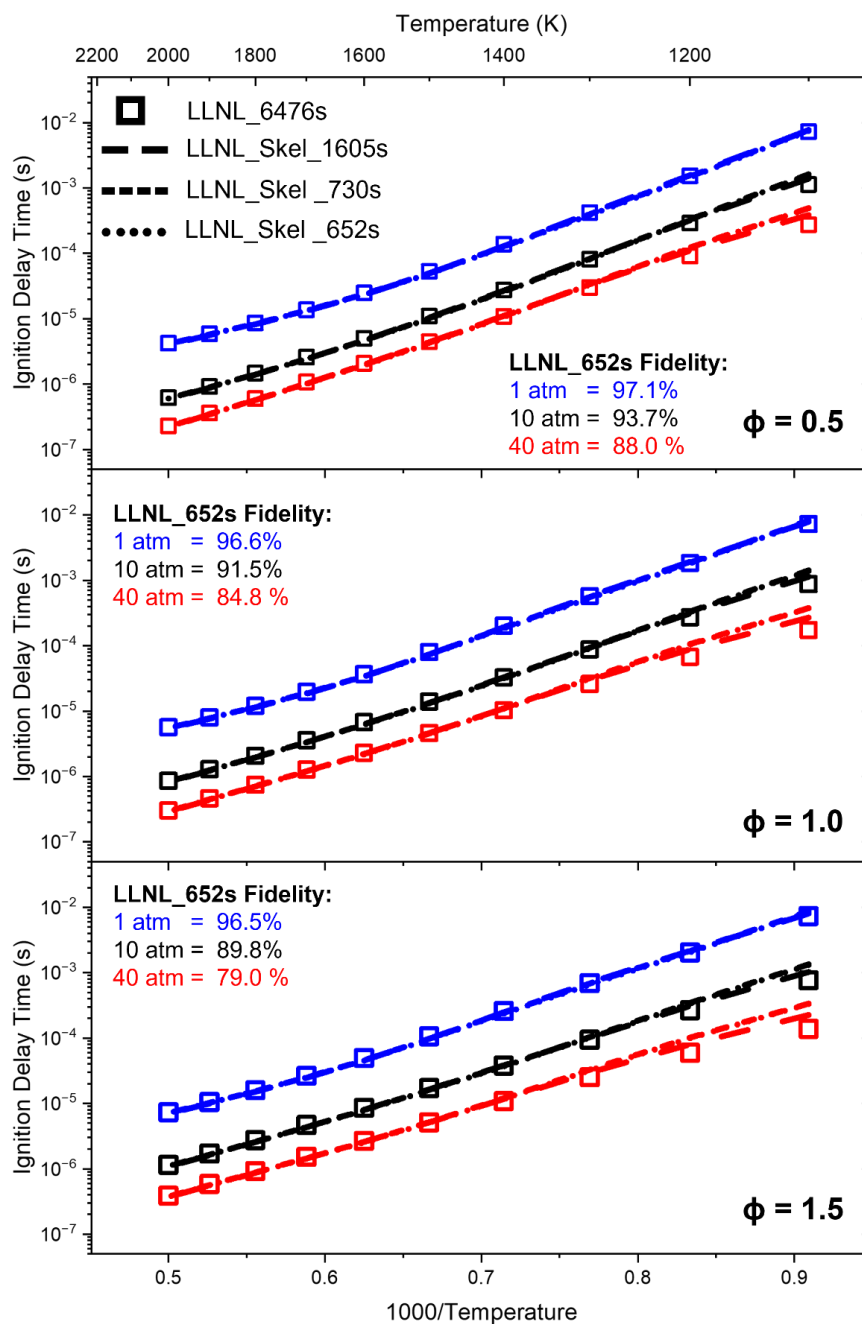


Figure 7.22. Ignition delay time as a function of temperature for lean, stoichiometric, and rich AXL/air mixtures at 1, 10 and 40 atm using the LLNL_6476s detailed model and a series of skeletal models. The 652 species skeletal model has a high fidelity to the 6476 species detailed model at high temperatures.

To validate the S_u calculations of the LLNL_652s surrogate for AXL in the absence of experimental data, S_u calculations were performed on the pure components of the surrogate, and the results were compared to experimental data. The validation results are shown in Figure 7.23. It was observed that the calculated S_u values showed an underprediction of the experimental data for iso-cetane by approximately 10%. More concerning however is that the computed S_u of NBCH did not show agreement with experimental data (b).

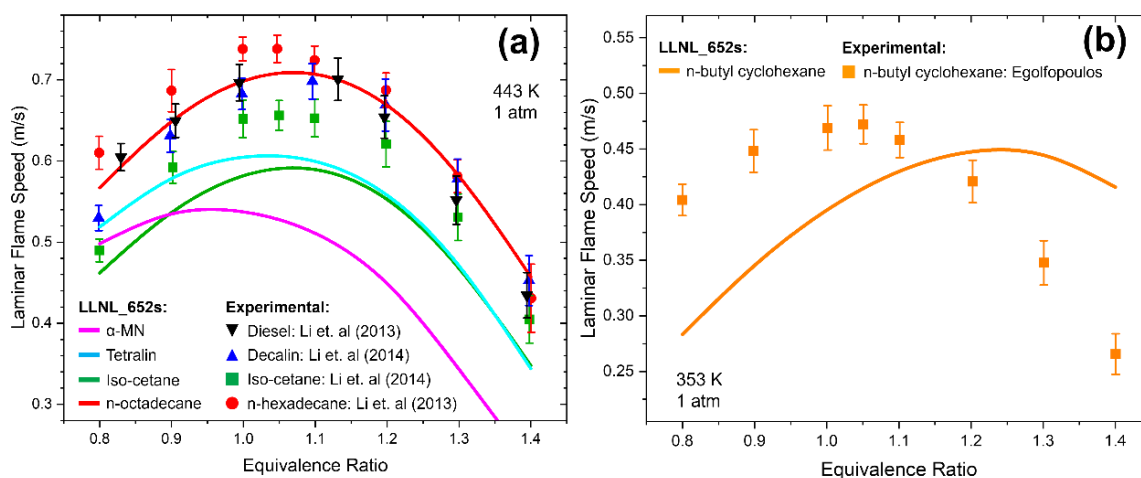


Figure 7.23. Laminar burning velocity as a function of fuel mixture equivalence ratio of pure components in AXL surrogate using LLNL_652s (lines) and experimental data (symbols). Experimental data from: diesel [259], n-hexadecane [259], iso-cetane [260], decalin [260] and n-butyl cyclohexane [261]. Decalin is used for comparison purposes.

To explore whether the aforementioned discrepancy is a consequence of our reduction process, we reached out to LLNL to request S_u calculations on the pure components at the conditions depicted in Figure 7.23 using the LLNL_6476s model. LLNL has developed a sophisticated solver that can converge up to an order of magnitude fast than conventional solvers such as those used in ChemKin and Cantera [262], enabling 1-D calculations to be performed using a model such as LLNL_6476s.

Dr. Russell Whitesides, a staff engineer in LLNL, kindly performed these calculations using said solvers. The results, shown in Figure 7.24 (a), demonstrate that the S_u calculations performed with the LLNL_6476s (by LLNL) and LLNL_652s (by TCD) models are in good agreement, with a maximum variation of less than 10%. Hence, our reduction process was

valid and the reason for the discrepancy between computed S_u and experimental data for NBCH is derived from the LLNL_6476s detailed model.

To understand the source of this error, a rate of production analysis was performed. This analysis identified the presence of several radicals in high concentrations in the burned gas. Further investigation revealed that these radicals were produced unidirectionally, with no corresponding consumption reactions. To address this issue, the LLNL_652s model was modified. The unidirectional reactions involving these radicals were set to bidirectional, producing a channel for their consumption. This minor modification resulted in a closer agreement between LLNL_652s calculations and the experimental data compared to the previous calculations, as shown in Figure 7.24 (b).

Therefore, this new edited model was selected to provide the 1-D optimisation, validation, and performance calculations for this study. It should be noted that this was a temporary solution. A more comprehensive and theoretical fix is currently being developed by LLNL to address the underlying issues.

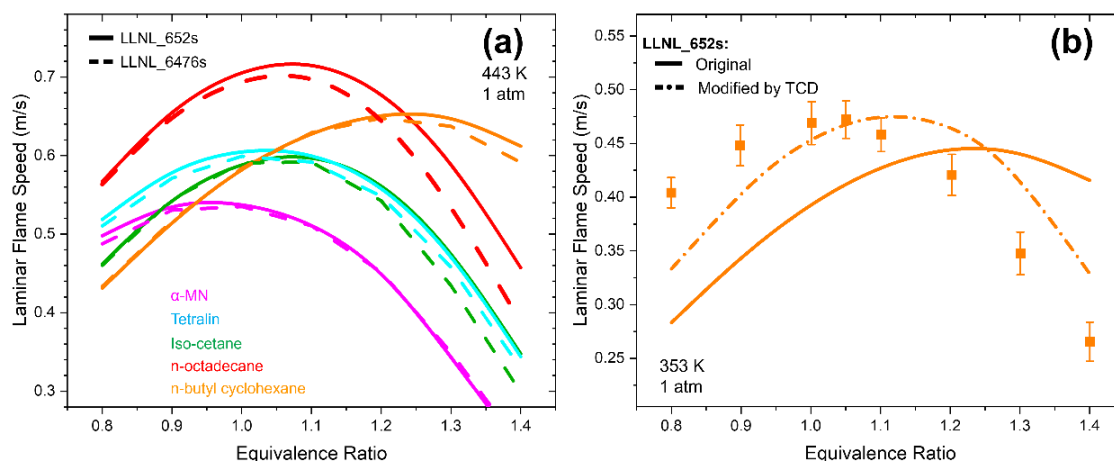


Figure 7.24. Laminar burning velocity as a function of fuel mixture equivalence ratio of pure components in AXL surrogate using LLNL_652s (lines). (a) Shows that LLNL_6476s detailed model (dashed) calculations, as performed by Dr. Russell Whitesides of LLNL, are similar to the LLNL_652s skeletal model of this work. (b) Shows the calculations of the updated LLNL_652s model (dash and dot) after the modifications to several reactions.

7.6 Compact Model for AXL at Low Temperatures

The compact model approach of this work was extended to the task of low temperature chemistry, with the aim of producing a model capable of accurately replicating pertinent low temperature calculations. Three different approaches were undertaken to produce a compact model with high fidelity to the set of performance conditions of Table 7.9. The only difference between Table 7.9 and Table 7.2 is the extension of the performance envelope for 0-D calculations from 1200 K to 600 K. To do this a virtual reaction network was constructed to create pathways that will allow for the replication of low temperature chemistry using a minimum number of additional nodes.

Table 7.9. Performance targets for AXL/air combustion at low, intermediate, and high temperatures. Compact Model performance will be benchmarked to replication of these targets.

Reactor Physics	Property	Pressure (atm)	Equivalence Ratio	Temperature (K)
Perfectly Stirred Reactor	[OH], [CO], [CO ₂], [H ₂ O]	1, 10, 20, 30, 40	0.4, 0.5,..., 1.5	600, 700, ..., 2000
Constant Volume Constant Internal Energy	IDT	1, 10, 20, 30, 40	0.5, 1.0, 1.5	600, 700, ..., 2000
Freely Propagating Flame	S _u	1, 10, 20, 30, 40	0.4, 0.5,..., 1.5	500, 700, 900

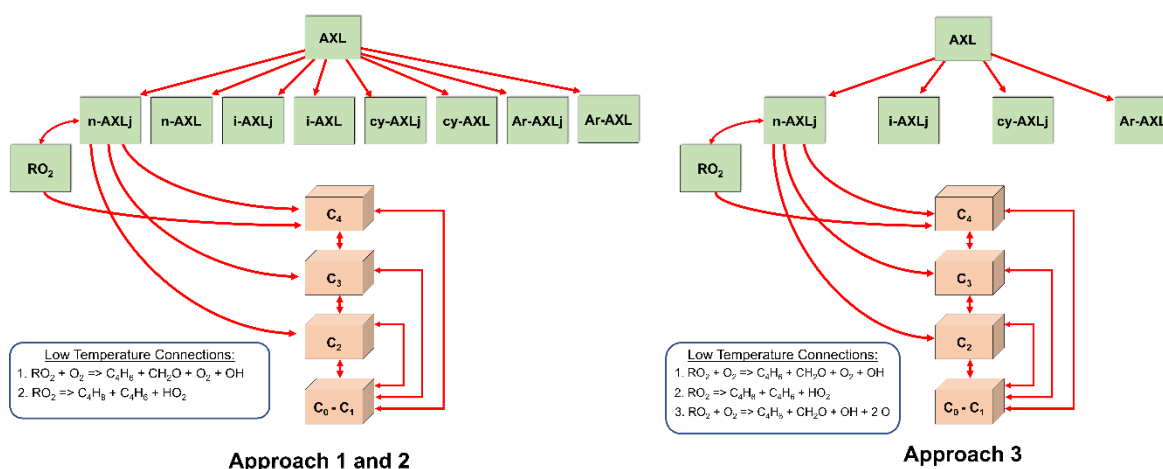


Figure 7.25. Schematic of the virtualised scheme of the three Approaches tested in this study. The difference between Approach 1 and 2 is the selection of optimisation targets, shown in Table 7.10. Note, all virtual bins are linked to the C₂-C₄ chemistry, however, to simplify the illustration and ensure clarity only those of n-AXLj are depicted.

Building on the knowledge that reactivity in liquid fuels at low temperatures and in the negative temperature coefficient (NTC) region is dominated by n-alkane chemistry [263-267], a virtual node called RO_2 was produced. Figure 7.25 shows a schematic of the virtual reaction networks tested in this work. The RO_2 node is connected to the $n\text{-AXLj}$ node in a bidirectional connection and represents oxygen addition to the fuel radical. From this, two reaction pathways of differing degrees of chain branching were constructed to grant sufficient flexibility in the system to replicate the low temperature reaction flux at a range of temperatures. The connection $RO_2 + O_2 \Rightarrow C_4H_6 + CH_2O + OH + 2 O$ was introduced to act as a reactivity promoting channel, with the production of five radicals, whereas the connection $RO_2 \Rightarrow C_4H_8 + C_4H_6 + HO_2$ was introduced to act as a path for decreased reactivity.

The thermodynamic and transport properties of $C_7H_{15}O_2$ were used for RO_2 . MLOCK1.2 was then employed to find the optimal combination of virtual Arrhenius parameters of these new connections and other sensitive connections necessary to divert the reaction flux such that the complex low temperature behaviour of the detailed model is embodied through this simplified scheme.

The optimisation and validation targets used in the three approaches are shown in Tables 7.10 and 7.11 respectively. Note, the same validation conditions are used in all three approaches. The bounds for the connections of the low temperature virtual reaction network were set as $-1 < n < 1$ and $-50000 < E_A < 20000 \text{ cal mol}^{-1}$.

Table 7.10. Optimisation targets that comprise the OEFs evaluated in the Scans of MLOCK1.2 in each of the low temperature Compact Model approaches. An optimisation target provides an indicator of model performance in 0-D calculations at Industry relevant operating conditions. MLOCK1.2 uses these targets to optimise the model candidates.

Purpose	Reactor Physics	Property	Pressure (atm)	Equivalence Ratio	Temperature (K)
Approach 1 Optimisation Targets	Perfectly Stirred Reactor	[C ₂ H ₄], [CO], [OH], [H], [CH ₂ O]	1, 10, 40	0.7, 1.0, 1.4	600, 800, 1000
	Freely Propagating Flame	S _u	10	0.8, 1.05, 1.3	500
Approach 2 Optimisation Targets	Perfectly Stirred Reactor	[C ₂ H ₄], [CO], [OH], [H]	1, 10, 40	0.7, 1.0, 1.4	600, 800, 1000, 1200, 1600, 2000
	Freely Propagating Flame	S _u	10	0.8, 1.05, 1.3	500
Approach 3 Optimisation Targets	Perfectly Stirred Reactor	[C ₂ H ₄], [CO], [OH], [H]	1, 10, 40	0.7, 1.0, 1.4	600, 800, 1000, 1200, 1600, 2000
	Freely Propagating Flame	S _u	10	0.8, 1.05, 1.3	500

Table 7.11. Validation targets that are evaluated in the Assessment stages of MLOCK1.2 in each of the low temperature Compact Model approaches. A validation target is a calculation that acts as an important indicator of overall model performance. MLOCK1.2 uses these targets to calculate model fidelity.

Purpose	Reactor Physics	Property	Pressure (atm)	Equivalence Ratio	Temperature (K)
Phase 1 Validation	Constant Volume Constant Internal Energy	IDT	1, 10, 40	0.5, 1.0, 1.5	600, 700, ..., 2000
	Freely Propagating Flame	S _u	1, 10, 40	0.4, 0.5, ..., 1.5	500

7.6.1 Approach 1: Append to TCD_35sOp_HT and Optimise to Low Temperatures

The first approach is to append the low temperature virtual reaction network to TCD_35sOp_HT and optimise this new model to low temperatures using MLOCK1.2, whilst locking off all connections that are sensitive to 0-D calculations at high temperatures. PSR and S_u sensitivity analysis was performed and any connection with a normalised sensitivity coefficient greater than ± 0.05 at 600, 800 or 1000 K was selected. However, any connection with a PSR normalised sensitivity coefficient greater than ± 0.05 at 1200, 1600 or 2000 K was excluded from optimisation, to prevent a significant perturbation of calculations at which TCD_35sOp_HT was optimised. This led to the selection of ten connections for optimisation.

7.6.1.1 Results

The best model resulting from this approach has a good replication of LLNL_6476s low temperature 0-D calculations at lean conditions, however the performance of the model decreases considerably at stoichiometric and rich conditions. Figure 7.26 shows the ignition delay time of this model (blue line) at 10 atm. This model retains a high fidelity to 0-D calculations at high temperatures (IDT fidelity at 10 atm of 79.7% at 1200 – 2000K).

A possible explanation for the difficulty in replicating low temperature calculations could be that certain connections, which are important at low temperatures, have been excluded from the optimisation process, because they are sensitive at high temperatures. This is highlighted in Figure 7.27, which shows the results of PSR sensitivity analysis at 600, 800 and 1000 K. The connections in red have a normalised sensitivity coefficient greater than ± 0.05 at high temperatures. Hence, it is clear to see that the exclusion of these connections places a considerable constraint on the degrees of freedom available to MLOCK, hampering the likelihood of obtaining a high-fidelity model at low temperatures.

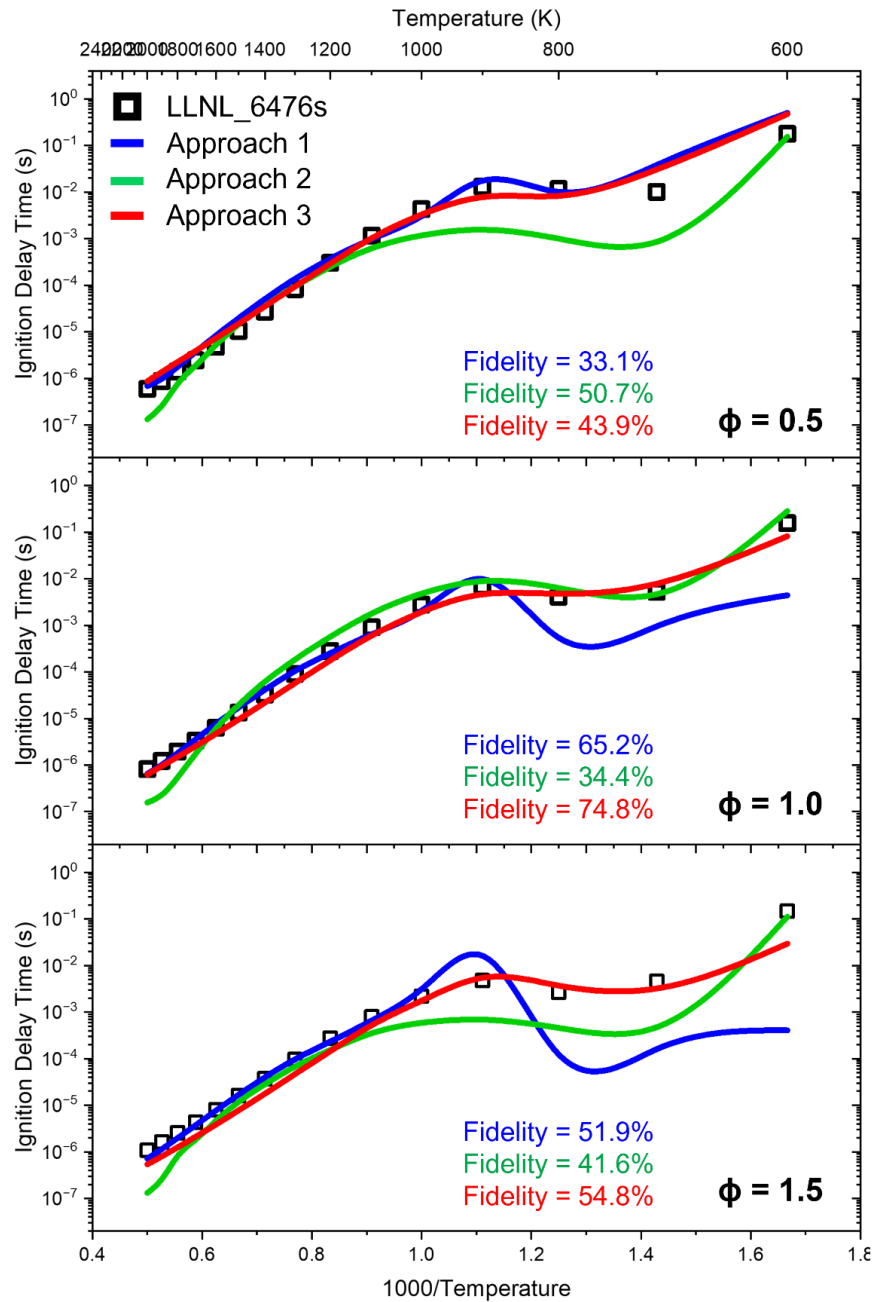


Figure 7.26. Ignition delay time as a function of temperature for lean, stoichiometric, and rich AXL/air mixtures at 10 atm using the LLNL_6476s detailed model (symbols) and the best models from Approach 1 (blue), Approach 2 (green) and Approach 3 (red).

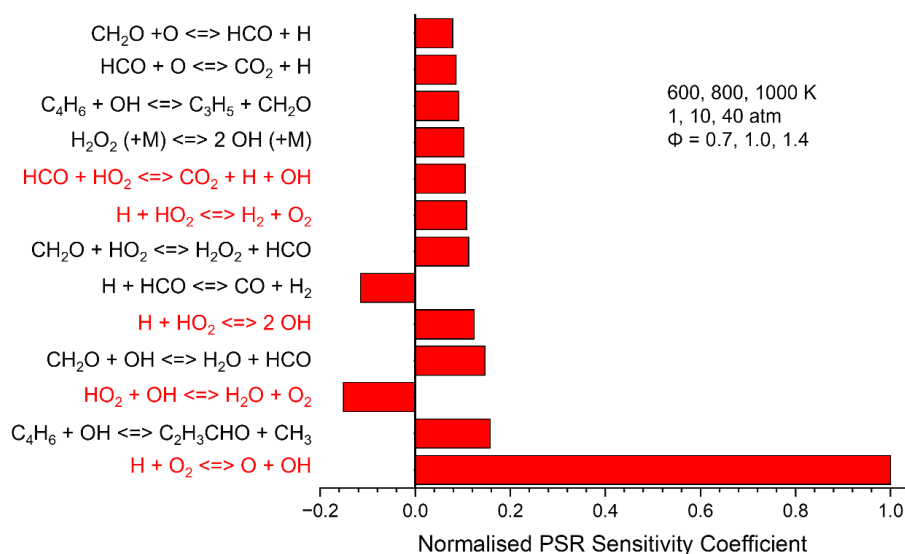


Figure 7.27. Results from perfectly stirred reactor (PSR) sensitivity analysis on TCD_35sOp_HT at the set of optimisation conditions of Approach 1. Red text indicates connection that are sensitive at high temperatures and hence are excluded from optimisation. This illustrates the constraint of this restriction.

7.6.2 Approach 2: Append to TCD_35sOp_HT and Optimise to All Temperatures

In this approach, the same low temperature virtual reaction network is appended to TCD_35sOp_HT. However, based on the findings of Approach 1, all connections with a PSR or S_u normalised sensitivity coefficient greater than ± 0.05 at any temperature were selected and optimised to both low and high temperatures, as outlined in Table 7.10. This resulted in thirty-two connections undergoing optimisation.

7.6.2.1 Results

The best model resulting from this approach has a reasonably good replication of LLNL_6476s 0-D calculations across the performance conditions, with the best performance at lean conditions, as shown in Figure 7.26 (green line). The model fidelity decreases at temperatures in excess of 1700 K and at very rich conditions. However, the model calculations depict the NTC region across the equivalence ratio range.

Reaction path analysis of 0-D PSR calculations, however, reveal that no RO_2 is produced at low or intermediate temperatures, and the accuracy of the calculations at these temperatures is due to the altering of virtual reaction rate constants of connections outside

of the low temperature virtual reaction network. The reason for this is that the unimolecular fuel decomposition pathway to n -AXL dominates over hydrogen abstraction pathways to n -AXLj. Hence, insufficient n -AXLj is created to allow for the production of RO_2 .

In other words, as low temperature calculations were not “seen” in the optimisation of the Overly-Reduced Model to produce TCD_35sOp_HT, the virtual reaction rate constants of some connections were moved to a space that means that an accurate replication of low temperature chemistry is not possible. Therefore, two approaches can be made to address this. The first is to include all virtual bin connections in the optimisation to low and high temperatures and implement safeguarding measures such that suitable n -AXLj is produced. The second approach is to simplify the virtual bin scheme to remove the competition between unimolecular fuel decomposition and fuel hydrogen abstraction bins. The later approach was taken in this work, as discussed next.

7.6.3 Approach 3: Simplified Virtual Bin Scheme

To address the issue of insufficient n -AXLj production, the virtual bin scheme was simplified. All fuel unimolecular decomposition virtual bins were removed (n -AXL, i -AXL, cy -AXL, Ar -AXL) and v AXL unimolecular decomposition was rewritten to go to n -AXLj, i -AXLj, cy -AXLj, Ar -AXLj bins, as shown in Figure 7.25. Additionally, an extra connection was added to the low temperature virtual reaction network to grant additional flexibility to MLOCK to replicate the complex low temperature behaviour of the detailed model. The new connection, $RO_2 + O_2 \Rightarrow C_4H_6 + CH_2O + OH + O_2$, grants an additional mode of reactivity for the virtual reaction flux at low temperatures.

As the virtual bin scheme has been modified, the calculations of TCD_35sOp_HT are no longer accurate to the detailed model. Hence, the Overly-Reduced Model is used as the starting point, as opposed to TCD_35sOp_HT. This simplification results in a 32-node virtual reaction network comprised of 153 connections.

PSR and S_u sensitivity analysis was performed on this model and any connection that had a normalised sensitivity coefficient greater than ± 0.05 at any temperature in the optimisation conditions was selected for optimisation. This resulted in sixty-one connections undergoing optimisation.

7.6.3.1 Results

The best model from this approach has a good replication of 0-D calculations across the performance conditions of Table 7.9. The ignition delay time calculations of this model at 10 atm are shown in Figure 7.26 (red line). Using reaction path analysis, it was found that RO_2 is produced at low and intermediate temperatures with most of the reaction flux proceeding through the $RO_2 + O_2 \Rightarrow C_4H_6 + CH_2O + OH + O_2$ channel. Additionally, no RO_2 is produced at high temperatures, where n -AXLj to C_2 - C_4 pathways are favoured. Hence, this model seems to embody the authentic reaction flux sufficiently well.

This model has an excellent replication of the detailed model S_u calculations at lean conditions, however, the model performance deteriorates at stoichiometric conditions and fails to converge at rich conditions, as shown in Figure 7.28. Furthermore, no model candidates were produced in this instance of MLOCK1.2 with both acceptable fidelity to IDT and an acceptable S_u fidelity at rich conditions. To achieve a better replication to the complete set of 0-D and 1-D performance conditions of Table 7.9, a more complex low temperature virtual reaction network is required.

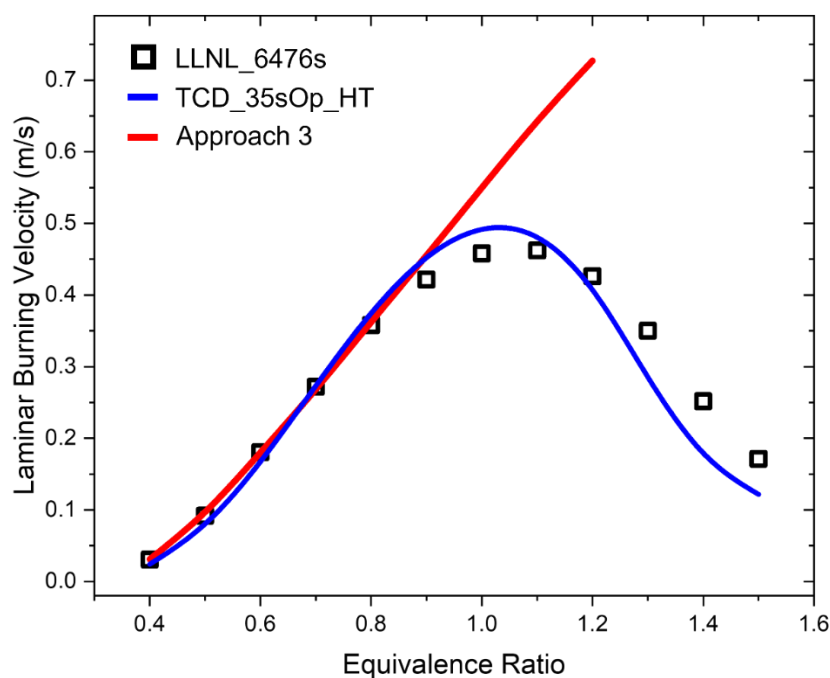


Figure 7.28. Laminar burning velocity as a function of fuel mixture equivalence ratio for AXL/air combustion using LLNL_652s (symbols), TCD_35sOp_HT (blue) and the best model from Approach 3 (red).

7.7 Conclusions

This work presents a detailed step-by-step generalised approach to generate a high fidelity compact model for a complex hydrocarbon fuel. Due to the intricate nature of liquid fuels, a surrogate modelling strategy is employed. The first step entails identifying desired combustion property targets, as well as a set of potential surrogate components with their corresponding combustion property targets collected. An in-house formulator algorithm is then utilised to determine the optimal combination of surrogate components that can precisely reproduce the combustion property targets with minimal error. Following this, a detailed model which includes a description of the reaction mechanisms of the surrogate components is sourced. This detailed model is subsequently simplified using virtualisation, in which a virtual scheme is employed to represent fuel decomposition through a minimal number of virtual species referred to as virtual bins. The resultant Virtualised Detailed Model is optimised to the fully detailed model 0-D calculations using MLOCK1.0, ensuring a highly accurate replication of 0-D calculations. Model reduction is then applied to the Virtualised Detailed Model to produce an Overly-Reduced Model. Finally, this model is optimised to detailed model 0-D and 1-D calculations using MLOCK1.2.

This approach is demonstrated for the example of Arabian Extra Light (AXL) crude oil. A five-component surrogate for AXL is defined consisting of n-octadecane/iso-cetane/n-butyl cyclohexane/tetralin/ α -methyl naphthalene at a mole fraction mixture composition of 0.346/0.178/0.247/0.114/0.115. The diesel surrogate model developed by Lawrence Livermore National Lab is selected as the detailed model for this work. The high-carbon chemistry is removed from this model and the products of the initial fuel decomposition stages are represented using eight discrete virtual bins. A set of rules is employed to generate connections linking the fuel molecule to these virtual bins and then linking these bins to C₂-C₄ chemistry.

Next, MLOCK1.0 is employed to find the optimal Arrhenius parameters of these new connections, resulting in a 429-node model with a PSR fidelity of 98.1% to the 6,476 species detailed model across a wide range of conditions. PFA is used to reduce this construct to a 35-node model, which is then optimised using MLOCK1.2 to detailed model 0-D and 1-D high temperature calculations. The resulting compact model exhibits a PSR, IDT and S_u fidelity of 86.0%, 79.6% and 89.1% respectively at the set of Industry-defined performance conditions.

This concept was extended to low temperatures to produce a compact model that emulates the detailed low temperature behaviour using a minimal number of nodes. Three approaches were tested, and approach three was found to be the most promising. In this approach a virtual reaction network for low temperatures was constructed. A virtual RO_2 node, which represents oxygen addition to the fuel radical, was connected to the $n\text{-AXL}_j$ node based on the knowledge that reactivity at low temperatures is dominated by n -alkane chemistry. Three reaction pathways linking this node to the underlying core chemistry were then constructed. These pathways are of varying degrees of chain branching, creating several modes of reactivity, increasing the degrees of freedom available to MLOCK1.2. The number of virtual bins was reduced to four by removing the fuel decomposition bin and rewriting $v\text{AXL}$ decomposition into the $x\text{-AXL}_j$ bins. This was to ensure production of sufficient levels of $n\text{-AXL}_j$.

The resulting model was optimised using MLOCK1.2 to 0-D and 1-D calculations at both low and high temperatures. The 32-node compact model exhibits a good replication of the 6,476 species detailed model 0-D calculations across the complete performance envelope and has a high fidelity to 1-D calculations at lean conditions. However, the limitations of this approach are revealed at rich conditions in 1-D calculations, where the model fails to converge. However, this approach results in a promising model that can replicate key combustion properties of interest to fuel research with high fidelity. The promising results of the approach indicate significant potential for future development. Additionally, the methodology's generalisability allows for its application to other liquid fuels, including sustainable aviation fuels (SAF).

Chapter 8

Conclusions and Perspectives

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8.1 Conclusions

The main goal of this thesis was to explore the possibility of creating high-fidelity kinetic models that are compact in size, using an automated algorithm. This was to respond to an Industry brief that required minimally-sized kinetic models that can be easily integrated with computational fluid dynamics (CFD) simulations, whilst retaining a high predictive fidelity to sets of calculations that are pertinent to the gas turbine design process. To allow for easy implementation of these codes in Industry-standard solvers, these models were required to retain the ChemKin kinetic model format.

To achieve this, this thesis introduces the concept of Compact Models, which provide a virtual description of the reaction mechanism whilst adhering to the ChemKin format. A Compact Model is produced by constructing a virtual reaction network using a minimum number of model descriptors (species/nodes), and optimising the model parameters to a target set of combustion kinetic data. As the description of the reaction mechanism is now virtual, reactants and products can be linked without the requirement of the existence of an intrinsic reaction coordinate, granting extra degrees of freedom to the system to allow for the manipulation of the reaction flux such that pertinent combustion kinetic phenomena can be reproduced. This departure from physical authenticity in the reaction mechanism description allows for the creation of high-fidelity models that are compact in size and easily implementable in industry-standard software.

Optimisation is performed using a novel compute-intensification coded algorithm termed Machine Learned Optimisation of Chemical Kinetics (MLOCK). The MLOCK algorithm is intentionally designed to require minimal starting information, removing the need for expert knowledge in the compaction (production of a compact model) process. Instead, MLOCK leverages the availability and capabilities of high-performance computing resources to perform large numbers of computer simulations quickly, building a database of calculations. This database can be interrogated by data analysis and machine learning techniques to refine the search space and to identify the optimum sets of numerical terms which result in an accurate replication of the target calculations.

This methodology allows for the automated creation of high-fidelity kinetic models using computational resources as opposed to expert knowledge. The MLOCK framework provides a template to which more sophisticated architecture can be incorporated to further improve the efficacy of the algorithm.

8.2 Applications

8.2.1 Methane/Air Combustion

The methane/air combustion system was the first application of the proposed methodology. This archetypal system is of critical importance to the gas turbine industry, as methane is the primary component of natural gas. It was demonstrated that MLOCK readily compacts two separate detailed kinetic models, NUIG1817C3 and NUIGMECH1.0. A virtual reaction

network was constructed by applying the path flux analysis (PFA) model reduction algorithm to reduce the detailed model to its minimum size. The kinetics component of the Overly-Reduced Model was then optimised using the MLOCK1.0 algorithm. This resulted in 15-node compact models and one 19-node compact model which retain a predictive fidelity of 75.0 – 95.0% to their respective detailed models' calculations. It is shown that the 15-node models outperform the state-of-art over a wide range of zero-dimensional (0-D) and one-dimensional (1-D) conditions identified by our industry partner, Siemens Energy, as crucial for their gas turbine design efforts.

8.2.2 Oxides of Nitrogen, NO_x

The method was extended to address the challenge of minimalistic NO_x modelling. Siemens Energy defined a detail-fidelity cost-benefit performance envelope consisting of a maximum of three additional nodes that retains at least a 75% fidelity to a range of 0-D and 1-D calculations.

To construct a virtual reaction network for NO_x of this simplicity, model reduction techniques are not suitable. Hence, a combinatorial method based on a Latin Square was employed. The virtual network, comprising N, NO, and NO₂, was then appended to a 15-node compact model for methane/air combustion. The MLOCK1.1 algorithm was then utilised to determine the optimal sets of virtual Arrhenius parameters for the NO_x network connections. MLOCK readily finds models with fidelities in excess of 80% to 0-D calculations across the performance envelope. However, it was discovered that a single model with a fidelity greater than 57% to NO_x mole fractions in 1-D simulations across the range of equivalence ratios could not be achieved using the present NO_x virtual reaction network. The three-node network lacks sufficient degrees of freedom to accurately replicate both extreme lean and rich conditions simultaneously. Nevertheless, it was demonstrated that three distinct compact models, each of which is valid within a limited range of equivalence ratios, can collectively meet the performance envelope set by Industry, while the best-performing model outperforms the current state-of-the-art. Siemens Energy engineers have extensively utilised this 18-node compact model in their combustor design process, with notable application in the study of thermoacoustic instabilities in the lean-premixed natural gas conditions of the Siemens Energy SGT-A20 gas turbine.

8.2.3 Liquid Fuels

A methodology to produce compact models for liquid fuels was proposed and demonstrated for the case of Arabian Extra Light (AXL) crude oil. This method begins with characterisation of AXL to obtain combustion property targets, followed by the creation of a surrogate definition for AXL using a surrogate formulator code. The resulting AXL surrogate definition is n-octadecane/iso-cetane/n-butyl cyclohexane/tetralin/ α -methyl naphthalene at a mole fraction mixture composition of 0.346/0.178/0.247/0.114/0.115. A detailed model containing over 6,000 species is identified, whose calculations will serve as performance, optimisation, and validation conditions for the compaction process. This model is then simplified using virtualisation. The physically authentic high-carbon fuel oxidation chemistry is replaced with eight virtual species that replicate the effect of distinct chemical functionalities by providing a path from the fuel molecule to important intermediates in the C₂-C₄ sub model. The virtual Arrhenius parameters of the new connections introduced by the virtualisation procedure are obtained through analogy or by MLOCK1.0, in the absence of analogous reactions. Path flux analysis (PFA) is used to reduce the 429-node model to a virtual reaction network of 35 nodes. The MLOCK1.2 algorithm is applied to optimise this Overly-Reduced Model to detailed model 0-D and 1-D calculations at high temperatures. This results in a 35-node compact model that retains a predictive fidelity of 79.6 - 89.1% to the 6,476-species detailed model calculations across the Industry-defined performance conditions. It is suspected that this model can be further simplified to reduce the number of nodes while retaining fidelities that are acceptable for Industry purposes.

The method was then extended to the task of low temperature chemistry. A virtual reaction network for low temperatures was created and one extra node was introduced to represent oxygen addition to fuel radical. The MLOCK1.2 algorithm was then used to optimise connections sensitive at low temperatures to detailed model 0-D and 1-D calculations. Ultimately, the most effective approach involved simplifying the virtual bin scheme from eight to four bins and optimising the model to low, intermediate, and high temperatures simultaneously. The resulting 32-node compact model has a high fidelity to detailed model 0-D calculations across the complete performance envelope and a high S_u fidelity at lean conditions, however the performance decreased at stoichiometric and rich conditions.

8.2.4 Other Applications

The concept of this thesis and the automated optimisation algorithm produced has been applied to produce kinetic models for other systems.

Kinetic Model for Biomass Pyrolysis

Lignocellulosic biomass is an abundant renewable resource that can be upgraded to chemical and fuel products through a range of thermal conversion processes such as pyrolysis. Key to maximising the potential of lignocellulosic biomass is the development of an accurate kinetic model detailing its reaction mechanism. Xylan is a major component of hemicellulose which is one of three major components of lignocellulosic biomass. Thus, comprehension of hemicellulose reactivity relies on our knowledge of the reaction mechanism of xylan.

A reaction mechanism for xylan was constructed by developing hierarchical reaction networks for xylopyranose, xylobiose and xylotriose, which are structural motifs for xylan. Potential energy surface calculations were used to construct the reaction mechanism and provide initial guesses for the activation energy, E_A , of the reaction pathways. The optimal Arrhenius parameters for these reactions were obtained using MLOCK1.0 to optimise to experimental data from thermogravimetric analysis (TGA) of xylopyranose, xylobiose and xylotriose. TGA of xylopyranose, xylobiose and xylotriose was simulated using each model candidate and the error between the calculations and experiment evaluated. The resulting Phase 1 Optimised model had a good replication of experimental TGA data of xylan.

This work is currently unpublished; however, it was presented at the 23rd edition of the International Conference on Analytical and Applied Pyrolysis in May 2022 by Dr. Stephen Dooley. This work forms the basis of a European Research Council (ERC) project titled “*Mod-L-T: Models for Lignocellulose Thermochemical Conversion*” that aims to develop the first detailed, elementary, mass- and energy-conserved chemical reaction model for lignocellulose pyrolysis.

Kinetic Model for Biomass Ethanolysis

MLOCK has also been applied to corn cob ethanolysis by group member Ailís O’Shea. Corn cob is a lignocellulosic biomass comprised of cellulose, hemicellulose, and lignin. Cellulose

is a biopolymer of glucose, which is converted to ethyl levulinate, an advanced biofuel, in the acid catalysed ethanolysis process.

A reaction mechanism was constructed hierarchically for glucose, cellulose, and corncob based on the complexity of the feedstock. Global reactions were proposed for the system based on the experimentally detected species. The Arrhenius parameters for these reactions were found using MLOCK1.0 Phase 1. The resulting kinetic model accurately replicated the experimental yields of the key products, ethyl levulinate and diethyl ether. The manuscript describing the method and findings is currently undergoing peer review.

8.3 Perspectives

Due to the novel nature of this work, numerous subjective decisions were necessary, and various alternative approaches could have been taken. While the current methodology may not represent the optimal solution, our results illustrate its efficacy in achieving our specific objectives. Nevertheless, certain aspects of the algorithm warrant further refinement. Thus, I present a list of potential avenues for future research to refine the MLOCK algorithm.

8.3.1 Improvement of Objective Error Functions

The selection and validation of objective error functions (OEF) is a critical aspect of any optimisation study. In this thesis, multiple OEFs were used, and for each one, numerous formulations were tested to assess their suitability. The task of formulating an OEF can be broken down into four general aspects:

- 1) Selection of the reactor physics (e.g., PSR, Constant UV, Freely propagating flame).
- 2) Selection of the optimisation calculation(s) (e.g., max OH mole fractions, CO mole fraction profile over time, ignition delay time, laminar burning velocity).
- 3) Selection of the conditions (i.e., selecting suitable temperatures, pressures, equivalence ratios).
- 4) Mathematical formulation of the error function (e.g., relative error).

Throughout the course of this thesis, I encountered many challenges in constructing an OEF that provides a fair evaluation of the goodness of the model calculations across the range of calculations in the optimisation targets. Despite the importance and intricacy of this

task, there is a surprising lack of discussion in the literature regarding the ideal OEF formulation for kinetic model optimisation.

One exception to this is the work from the “MOX” and “CRECK” research groups from Politecnico di Milano, who have delved into the issues with common OEF formulations that are routinely used in the literature and proposed an OEF that aims to address these [268]. This new method, termed *curve matching*, involves the use of transformations of experimental and numerical results into continuous functions. The similarity between the functions can then be computed using first derivatives, vertical dilations, vertical transformations, and horizontal shifts.

While this method appears to be quite effective for detailed model or skeletal model optimisation, its application to overly-reduced model optimisation may face unresolved issues due to the unusual and unphysical “shapes” that the IDT (as function of temperature), PSR profile (as function of time) and S_u (as function of equivalence ratio) functions can exhibit.

However, it would be useful to attempt to incorporate the method, or a similar method based on learnings from this work, to MLOCK and benchmark the results against the OEFs used in this thesis.

8.3.2 Improvement of Bound Refinement Algorithm

The bound refinement algorithm represents a critical component of MLOCK, as it guides the search algorithm towards regions of the bound space that are expected to yield higher-fidelity models. Therefore, the efficiency and effectiveness of our approach are highly sensitive to the precision of the bound refinement algorithm. Improvements in this algorithm could significantly enhance the overall performance of our methodology. To this end, a partial parameter study was conducted to identify optimal values for several variables within the bound refinement algorithm, such as the percentile value and the number of regions into which the bound space is partitioned and evaluated.

However, the current algorithm considers only the coupling between each virtual reaction rate constant and the objective error function in isolation. This does not account for the inter-connection coupling that arises due to competition between different connections.

As a result, a more sophisticated algorithm that incorporates the influence of one virtual reaction rate constant on others could yield further improvements in the quality of the models generated by our methodology. One potential method to do this would be using a correlation matrix to quantify the correlation between each region of the virtual reaction rate constant (k_v) bound space of one connection, with each region of every other connection.

Additionally, testing the effect of replacing the step-wise evaluation of each k_v region with a method that assesses overlapping k_v areas would be a worthwhile study.

8.3.3 Replacing Genetic Seed Scan

The Genetic Seed model is regarded as possessing desirable attributes that could facilitate the generation of a compact model with a high-fidelity to the optimisation targets. As such it is treated as an effective initial guess to the optimisation problem.

The Genetic Seed Scan samples the parameter bound space by employing a Gaussian distribution centred around the parameters of the Genetic Seed model, which enables comprehensive exploration of the bound space region occupied by this model. However, it would be intriguing to explore the possibility of replacing this Scan with a “smarter” alternative that employs an optimisation algorithm suitable for tasks where a good initial guess is available, such as Bayesian optimisation, gradient-based methods, or particle swarm optimisation.

By benchmarking the performance of these algorithms against the current Genetic Seed Scan based on the quality of the best model and the convergence rate to the minima, we could determine whether a more efficient and effective method exists for scanning the parameter bound space of the Genetic Seed model.

8.3.4 Implementation of Neural Networks

In recent years, neural networks have gained significant attention in the combustion community as a promising alternative to solve the chemical source terms, as discussed in Chapter 3. As our work requires adherence to the ChemKin form of reaction description using neural networks for this specific application is not feasible.

However, neural networks could be incorporated into MLOCK as an optimisation algorithm. These constructs require a large database of calculations to be trained and validated on. The Coarse Scan in MLOCK could serve as an ideal dataset for developing and training an artificial neural network (ANN). The ANN could utilise virtual Arrhenius parameters or even reaction rate constants at fixed temperatures as the inputs, with the objective error function (OEF) as the output. Once the ANN is trained and validated, it could be implemented in subsequent scans, such as the Refined Scan, to predict the objective error function, rather than performing a chemical kinetic simulation. This approach could significantly reduce the computational cost of the simulation. Alternatively, ANNs could be used in place of multiple linear regression in the prediction of the 1-D OEF in MLOCK.

8.3.5 Improving MLOCK1.2

In Phase 2 of MLOCK1.0, a S_u sensitivity analysis is performed, and the top fifteen most sensitive reactions are optimised with large bounds covering around fifteen orders of magnitude in the Coarse Scan. However, some of the connections selected for optimisation are also sensitive to 0-D calculations and have just been optimised in Phase 1. Optimisation of these connections across large bounds may not be necessary. Additionally, due to the Assessment steps, this model typically has a moderate laminar burning velocity (S_u) fidelity. Hence, it might not be essential to employ extensive bounds during the Coarse Scan of Phase 2. Therefore, an improved approach employed in MLOCK1.1 and MLOCK1.2 is to combine Phase 1 and Phase 2 and optimise to an average of 0-D and 1-D objective error functions. However, there is still room for improvement, such as incorporating a multiple linear regression model that is trained and validated on data from the Refined Scan. This would allow for its integration into the Genetic Seed Scan, leading to a considerable reduction in computational cost.

8.3.6 Improving Model Performance at Varying Pressures

Optimisation targets at multiple pressures were utilised in MLOCK1.0, MLOCK1.1 and MLOCK1.2 in Chapters 6 and 7. The errors at each pressure were combined to give an overall OEF, resulting in the lumping of the assessment of the suitability of the set of Arrhenius parameters at each pressure. A possible improvement to this method is to leverage

the PLOG reaction description, which was used in Phase 3 and Phase 4 in MLOCK1.0, to concurrently determine a set of virtual Arrhenius parameters for each discrete pressure. In this approach, each connection undergoing optimisation would be set to PLOG, with a set of virtual Arrhenius parameters declared for each pressure in the optimisation conditions. The OEFs at each pressure would be kept distinct, and the bound refinement algorithm would be carried out on the data from each pressure. This has potential to yield more accurate compact models, at the expense of an increased computational cost.

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Appendix A

C3_15sOp and C3_19sOp Validation

For more comprehensive validation, please see [269].

1. Constant UV: Ignition Delay Time

The compact model has good replication of IDT across the performance conditions (Table 5.1).

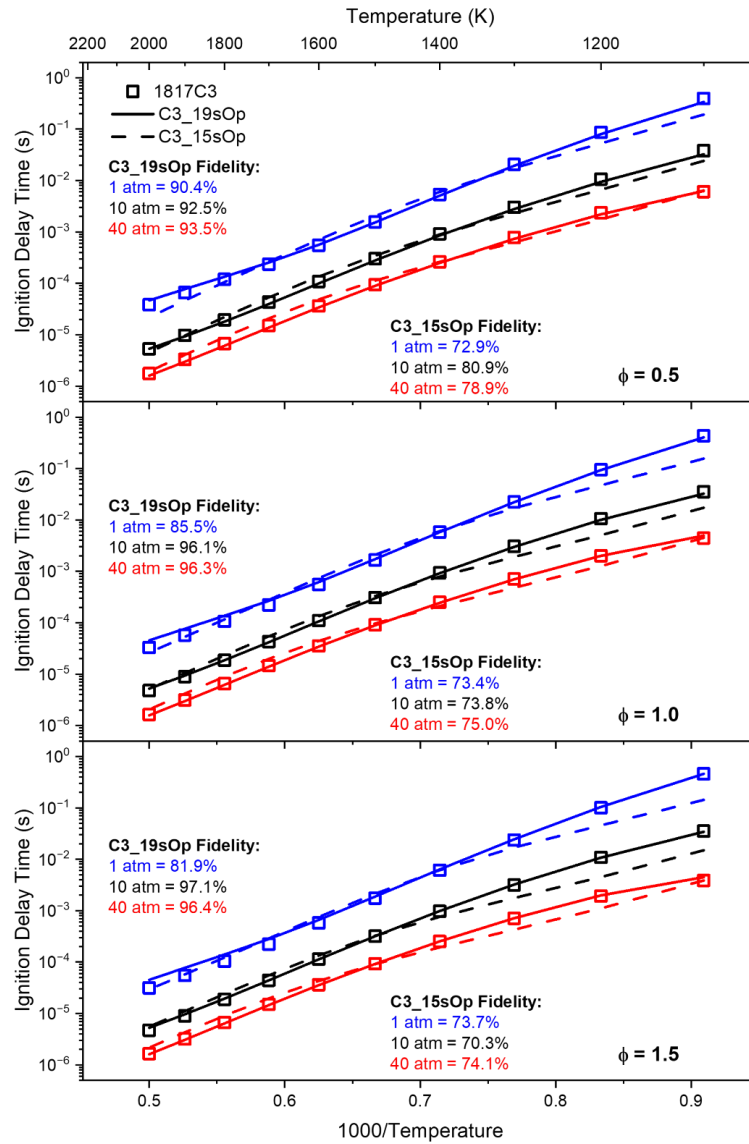


Figure A.1. Ignition delay time as a function of temperature for lean, stoichiometric, and rich methane/air mixtures at 1, 10 and 40 atm using the 1817C3 detailed model (symbols), C3_15sOp (dash lines) and C3_19sOp (solid lines)..

2. Perfectly Stirred Reactor: Speciation

Mole fractions of CO are used as validation for C3_15sOp and C3_19sOp. The compact models have a good replication across the performance conditions (Table 5.1). Representative temperature and equivalence ratio conditions are used here. C3_15sOp fidelity decreases at lower temperatures.

1200 K:

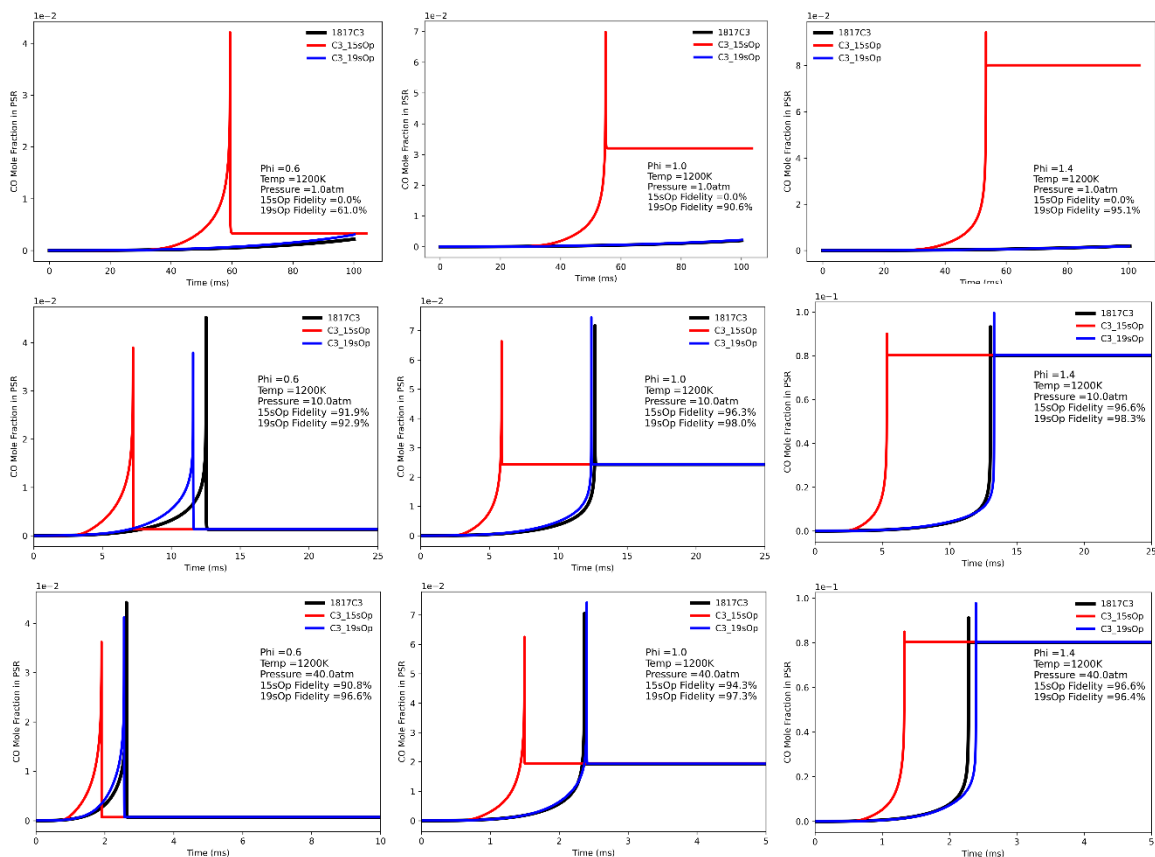


Figure A.2. CO mole fractions in PSR simulations at 1200 K using 1817C3 detailed model (black), C3_15sOp (red) and C3_19sOp (blue). Equivalence ratios 0.6 (left), 1.0 (middle) and 1.4 (right). C3_19sOp has excellent replication of detailed model CO mole fractions. C3_15sOp has a considerable error in the time of the onset of CO.

1600 K:

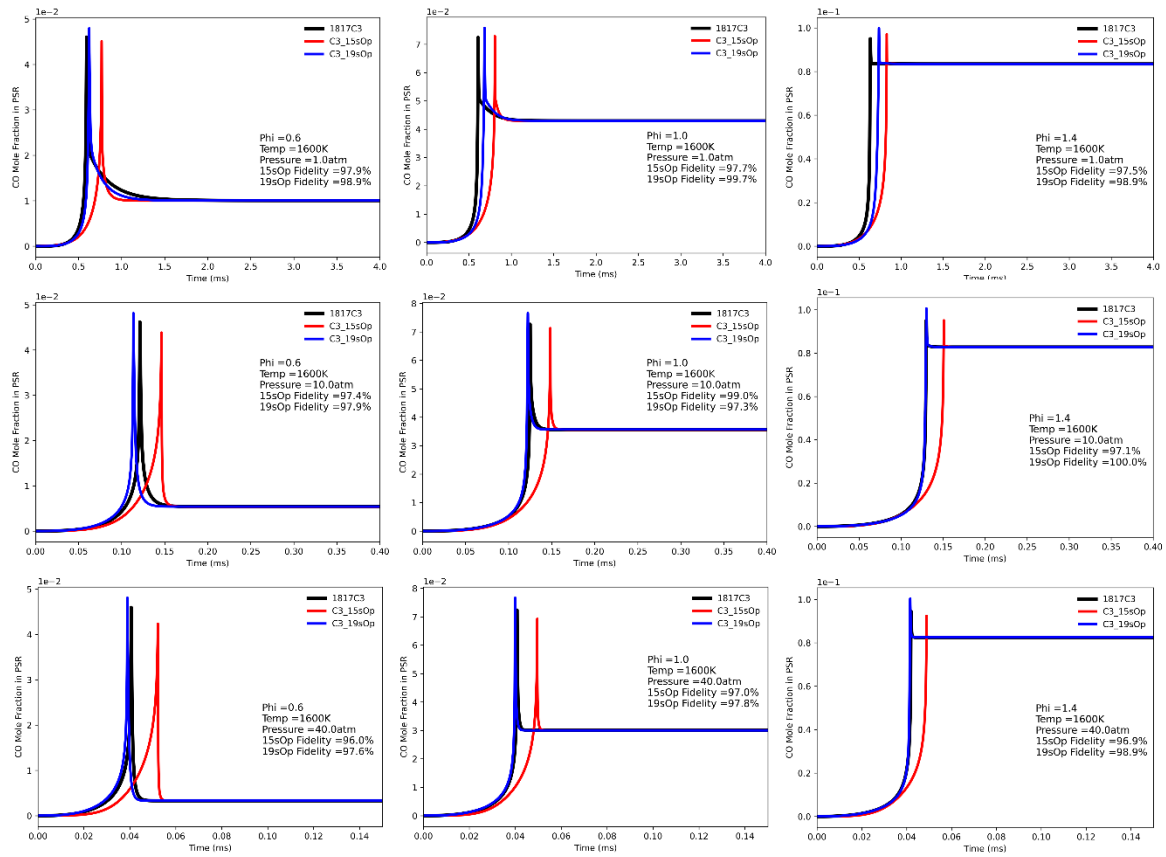


Figure A.3. CO mole fractions in PSR simulations at 1600 K using 1817C3 detailed model (black), C3_15sOp (red) and C3_19sOp (blue). Equivalence ratios 0.6 (left), 1.0 (middle) and 1.4 (right). Both compact models have an excellent replication of detailed model CO mole fractions.

2000 K:

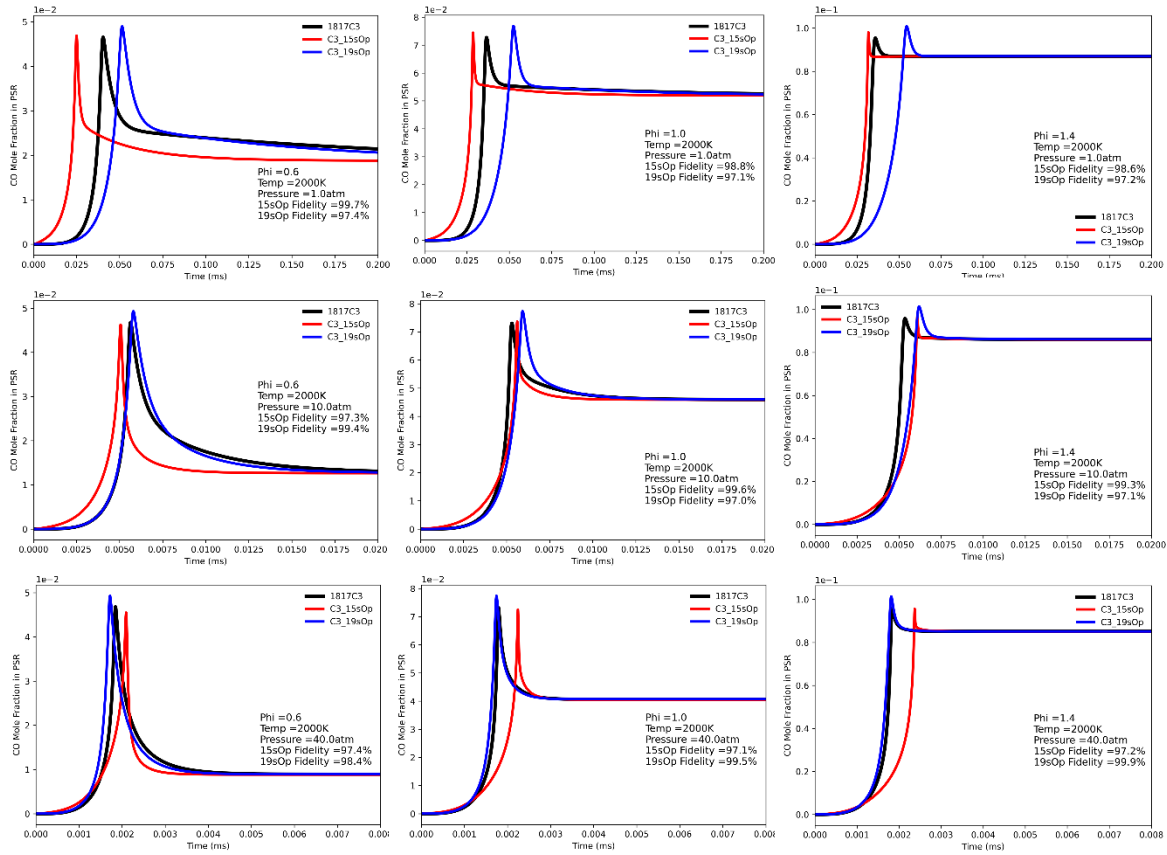


Figure A.4. CO mole fractions in PSR simulations at 2000 K using 1817C3 detailed model (black), C3_15sOp (red) and C3_19sOp (blue). Equivalence ratios 0.6 (left), 1.0 (middle) and 1.4 (right). Both compact models have an excellent replication of detailed model CO mole fractions.

3. Freely Propagating Flame: Laminar Burning Velocity

C3_19sOp has excellent fidelity across the complete performance conditions (Table 5.1). C3_15sOp has a good fidelity however the performance decreases at 1 atm.

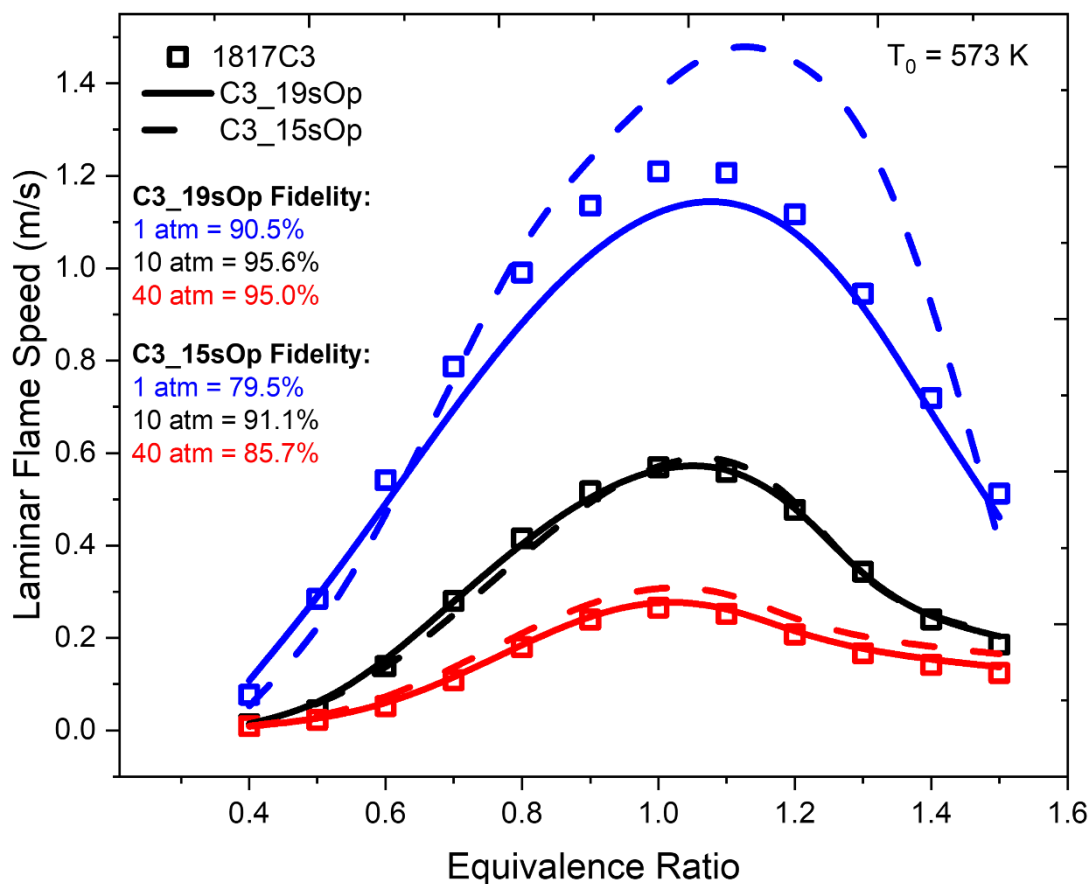


Figure A.5. Laminar burning velocity as a function of equivalence ratio at 1, 10 and 40 atm using the 1817C3 detailed model (symbols), C3_15sOp (dash lines) and C3_19sOp (solid lines).

4. Freely Propagating Flame: Speciation

Mole fractions of CO are used as validation for C3_15sOp and C3_19sOp. The compact models have a good replication across the performance conditions (Table 5.1). Representative temperature and equivalence ratio conditions are used here.

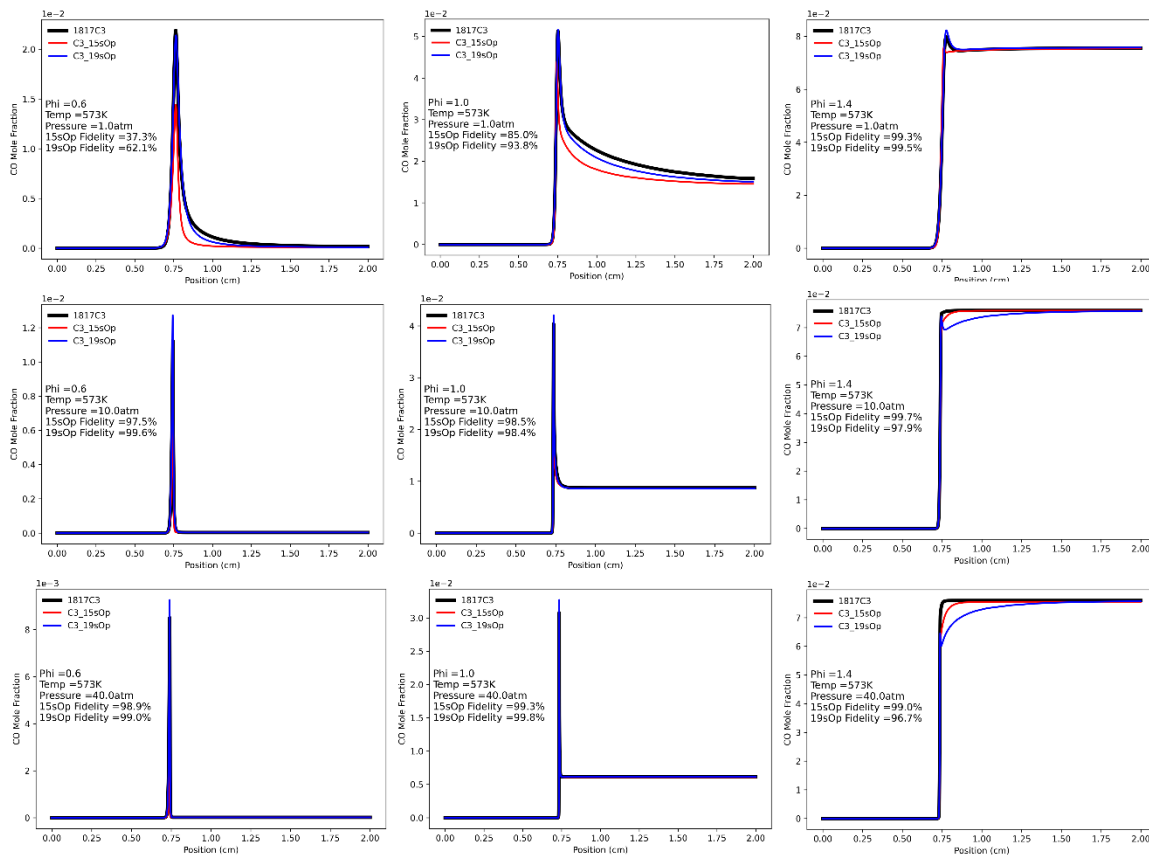


Figure A.6. CO mole fractions in freely propagating flame simulations at 573 K using 1817C3 detailed model (black), C3_15sOp (red) and C3_19sOp (blue) Equivalence ratios 0.6 (left), 1.0 (middle) and 1.4 (right). Both compact models have a good replication of detailed model CO mole fractions at all conditions.

Appendix B

C3_15sOp and C3_19sOp Files

C3_15sOp Cantera File:

```
units(length='cm', time='s', quantity='mol', act_energy='cal/mol')

ideal_gas(name='gas',
  elements="C H N O Ar He",
  species="""N2 H2 H O2 O H2O OH H2O2 HO2
          CO CO2 CH4 CH3 CH2O HCO""",
  reactions='all',
  transport='Mix',
  initial_state=state(temperature=300.0, pressure=OneAtm))

#-----
# Species data
#-----

species(name='N2',
  atoms='N:2',
  thermo=(NASA([200.00, 1000.00],
    [ 3.53100528E+00, -1.23660988E-04, -5.02999433E-07,
      2.43530612E-09, -1.40881235E-12, -1.04697628E+03,
      2.96747038E+00]),
    NASA([1000.00, 6000.00],
      [ 2.95257637E+00, 1.39690040E-03, -4.92631603E-07,
        7.86010195E-11, -4.60755204E-15, -9.23948688E+02,
        5.87188762E+00])),
  transport=gas_transport(geom='linear',
    diam=3.621,
    well_depth=97.53,
    polar=1.76,
    rot_relax=4.0),
  note='G8/02')

species(name='H2',
  atoms='H:2',
  thermo=(NASA([200.00, 1000.00],
    [ 2.34433112E+00, 7.98052075E-03, -1.94781510E-05,
      2.01572094E-08, -7.37611761E-12, -9.17935173E+02,
      6.83010238E-01]),
```

```
NASA([1000.00, 6000.00],
      [ 2.93286575E+00, 8.26608026E-04, -1.46402364E-07,
        1.54100414E-11, -6.88804800E-16, -8.13065581E+02,
        -1.02432865E+00])),
transport=gas_transport(geom='linear',
                        diam=2.92,
                        well_depth=38.0,
                        polar=0.79,
                        rot_relax=280.0),
note='TPIS78')
```

```
species(name='H',
        atoms='H:1',
        thermo=(NASA([200.00, 1000.00],
                      [ 2.50000000E+00, 0.00000000E+00, 0.00000000E+00,
                        0.00000000E+00, 0.00000000E+00, 2.54736600E+04,
                        -4.46682850E-01])),
              NASA([1000.00, 6000.00],
                    [ 2.50000000E+00, 0.00000000E+00, 0.00000000E+00,
                      0.00000000E+00, 0.00000000E+00, 2.54736600E+04,
                      -4.46682850E-01])),
        transport=gas_transport(geom='atom',
                                diam=2.05,
                                well_depth=145.0),
        note='L6/94')
```

```
species(name='O2',
        atoms='O:2',
        thermo=(NASA([200.00, 1000.00],
                      [ 3.78245636E+00, -2.99673416E-03, 9.84730201E-06,
                        -9.68129509E-09, 3.24372837E-12, -1.06394356E+03,
                        3.65767573E+00])),
              NASA([1000.00, 6000.00],
                    [ 3.66096065E+00, 6.56365811E-04, -1.41149627E-07,
                      2.05797935E-11, -1.29913436E-15, -1.21597718E+03,
                      3.41536279E+00])),
        transport=gas_transport(geom='linear',
                                diam=3.458,
                                well_depth=107.4,
                                polar=1.6,
                                rot_relax=3.8),
        note='RUS89')
```

```
species(name='O',
        atoms='O:1',
        thermo=(NASA([200.00, 1000.00],
                      [ 3.16826710E+00, -3.27931884E-03, 6.64306396E-06,
                        -6.12806624E-09, 2.11265971E-12, 2.91222592E+04,
                        2.05193346E+00])),
              NASA([1000.00, 6000.00],
                    [ 2.54363697E+00, -2.73162486E-05, -4.19029520E-09,
```

```
4.95481845E-12, -4.79553694E-16, 2.92260120E+04,
4.92229457E+00])),
transport=gas_transport(geom='atom',
    diam=2.75,
    well_depth=80.0),
note='L1/90')

species(name='H2O',
    atoms='H:2 O:1',
    thermo=(NASA([200.00, 1000.00],
        [ 4.19863520E+00, -2.03640170E-03, 6.52034160E-06,
        -5.48792690E-09, 1.77196800E-12, -3.02937260E+04,
        -8.49009010E-01]),
        NASA([1000.00, 6000.00],
        [ 2.67703890E+00, 2.97318160E-03, -7.73768890E-07,
        9.44335140E-11, -4.26899910E-15, -2.98858940E+04,
        6.88255000E+00])),
    transport=gas_transport(geom='nonlinear',
        diam=2.605,
        well_depth=572.4,
        dipole=1.844,
        rot_relax=4.0),
    note='L5/89')

species(name='OH',
    atoms='H:1 O:1',
    thermo=(NASA([200.00, 1000.00],
        [ 3.99198424E+00, -2.40106655E-03, 4.61664033E-06,
        -3.87916306E-09, 1.36319502E-12, 3.36889836E+03,
        -1.03998477E-01]),
        NASA([1000.00, 6000.00],
        [ 2.83853033E+00, 1.10741289E-03, -2.94000209E-07,
        4.20698729E-11, -2.42289890E-15, 3.69780808E+03,
        5.84494652E+00])),
    transport=gas_transport(geom='linear',
        diam=2.75,
        well_depth=80.0),
    note='IU3/03')

species(name='H2O2',
    atoms='H:2 O:2',
    thermo=(NASA([200.00, 1000.00],
        [ 4.31515149E+00, -8.47390622E-04, 1.76404323E-05,
        -2.26762944E-08, 9.08950158E-12, -1.77067437E+04,
        3.27373319E+00]),
        NASA([1000.00, 6000.00],
        [ 4.57977305E+00, 4.05326003E-03, -1.29844730E-06,
        1.98211400E-10, -1.13968792E-14, -1.80071775E+04,
        6.64970694E-01])),
    transport=gas_transport(geom='nonlinear',
        diam=3.458,
```

```
        well_depth=107.4,  
        rot_relax=3.8),  
note='T8/03')
```

```
species(name='HO2',  
        atoms='H:1 O:2',  
        thermo=(NASA([200.00, 1000.00],  
                      [ 4.30179807E+00, -4.74912097E-03, 2.11582905E-05,  
                        -2.42763914E-08, 9.29225225E-12, 2.64018485E+02,  
                        3.71666220E+00])),  
              NASA([1000.00, 5000.00],  
                    [ 4.17228741E+00, 1.88117627E-03, -3.46277286E-07,  
                      1.94657549E-11, 1.76256905E-16, 3.10206839E+01,  
                      2.95767672E+00])),  
        transport=gas_transport(geom='nonlinear',  
                                diam=3.458,  
                                well_depth=107.4,  
                                rot_relax=1.0),  
note='T1/09')
```

```
species(name='CO',  
        atoms='C:1 O:1',  
        thermo=(NASA([200.00, 1000.00],  
                      [ 3.57953350E+00, -6.10353690E-04, 1.01681430E-06,  
                        9.07005860E-10, -9.04424490E-13, -1.43440860E+04,  
                        3.50840930E+00])),  
              NASA([1000.00, 6000.00],  
                    [ 3.04848590E+00, 1.35172810E-03, -4.85794050E-07,  
                      7.88536440E-11, -4.69807460E-15, -1.42661170E+04,  
                      6.01709770E+00])),  
        transport=gas_transport(geom='linear',  
                                diam=3.65,  
                                well_depth=98.1,  
                                polar=1.95,  
                                rot_relax=1.8),  
note='RUS79')
```

```
species(name='CO2',  
        atoms='C:1 O:2',  
        thermo=(NASA([200.00, 1000.00],  
                      [ 2.35681300E+00, 8.98412990E-03, -7.12206320E-06,  
                        2.45730080E-09, -1.42885480E-13, -4.83719710E+04,  
                        9.90090350E+00])),  
              NASA([1000.00, 6000.00],  
                    [ 4.63651110E+00, 2.74145690E-03, -9.95897590E-07,  
                      1.60386660E-10, -9.16198570E-15, -4.90249040E+04,  
                      -1.93489550E+00])),  
        transport=gas_transport(geom='linear',  
                                diam=3.763,  
                                well_depth=244.0,  
                                polar=2.65,
```



```

        rot_relax=2.1),
note='L7/88')

species(name='CH4',
  atoms='C:1 H:4',
  thermo=(NASA([200.00, 1000.00],
    [ 5.14911468E+00, -1.36622009E-02, 4.91453921E-05,
      -4.84246767E-08, 1.66603441E-11, -1.02465983E+04,
      -4.63848842E+00]),
    NASA([1000.00, 6000.00],
      [ 1.65326226E+00, 1.00263099E-02, -3.31661238E-06,
        5.36483138E-10, -3.14696758E-14, -1.00095936E+04,
        9.90506283E+00])),
  transport=gas_transport(geom='nonlinear',
    diam=3.746,
    well_depth=141.4,
    polar=2.6,
    rot_relax=13.0),
note='G8/99')

species(name='CH3',
  atoms='C:1 H:3',
  thermo=(NASA([200.00, 1000.00],
    [ 3.65717970E+00, 2.12659790E-03, 5.45838830E-06,
      -6.61810030E-09, 2.46570740E-12, 1.64227160E+04,
      1.67353540E+00]),
    NASA([1000.00, 6000.00],
      [ 2.97812060E+00, 5.79785200E-03, -1.97558000E-06,
        3.07297900E-10, -1.79174160E-14, 1.65095130E+04,
        4.72247990E+00])),
  transport=gas_transport(geom='linear',
    diam=3.8,
    well_depth=144.0),
note='IU0702')

species(name='CH2O',
  atoms='C:1 H:2 O:1',
  thermo=(NASA([200.00, 1000.00],
    [ 4.79372312E+00, -9.90833322E-03, 3.73219990E-05,
      -3.79285237E-08, 1.31772641E-11, -1.43791953E+04,
      6.02798058E-01]),
    NASA([1000.00, 6000.00],
      [ 3.16952665E+00, 6.19320560E-03, -2.25056366E-06,
        3.65975660E-10, -2.20149458E-14, -1.45486831E+04,
        6.04207898E+00])),
  transport=gas_transport(geom='nonlinear',
    diam=3.59,
    well_depth=498.0,
    rot_relax=2.0),
note='T5/11')
```

```
species(name='HCO',
  atoms='C:1 H:1 O:1',
  thermo=(NASA([200.00, 1000.00],
    [ 4.23754610E+00, -3.32075257E-03, 1.40030264E-05,
      -1.34239995E-08, 4.37416208E-12, 3.87241185E+03,
        3.30834869E+00]),
    NASA([1000.00, 6000.00],
      [ 3.92001542E+00, 2.52279324E-03, -6.71004164E-07,
        1.05615948E-10, -7.43798261E-15, 3.65342928E+03,
          3.58077056E+00])),
  transport=gas_transport(geom='nonlinear',
    diam=3.59,
    well_depth=498.0),
  note='T5/03')

#-----
# Reaction data
#-----

# Reaction 1
three_body_reaction('H2 + M <=> H + H + M', [4.577e+19, -1.4, 104400.0],
  efficiencies='CH4:2.0 CO:1.9 CO2:3.8 H2:2.5 H2O:12.0')

# Reaction 2
reaction('H2 + O <=> H + OH', [5.416e+04, 2.569, 5583.9])

# Reaction 3
reaction('H2 + OH <=> H + H2O', [3.340e+13, 0.020, 6855.8])

# Reaction 4
three_body_reaction('O + O + M <=> O2 + M', [6.165e+15, -0.5, 0.0],
  efficiencies='CH4:2.0 CO:1.9 CO2:3.8 H2:2.5 H2O:12.0')

# Reaction 5
reaction('O2 + H <=> O + OH', [7.370e+14, -0.062, 15763.7])

# Reaction 6
three_body_reaction('H + OH + M <=> H2O + M', [6.520e+22, -2.296, 0.03],
  efficiencies='CH4:2.0 H2:0.73 H2O:3.65')

# Reaction 7
reaction('O + H2O <=> OH + OH', [5.929e+06, 1.898, 13988.5])

# Reaction 8
three_body_reaction('O + H + M <=> OH + M', [4.714e+18, -1.0, 0.0],
  efficiencies='CH4:2.0 CO:1.5 CO2:2.0 H2:2.5 H2O:12.0')

# Reaction 9
falloff_reaction('H2O2 (+ M) <=> OH + OH (+ M)',
  kf=[2.000e+12, 0.9, 48749.0],
  kf0=[2.353e+24, -2.293, 48743.4],
```

```
efficiencies='CO:2.8 CO2:1.06 H2:3.7 H2O:5.1 H2O2:5.2 N2:1.5 O2:0.79',  
falloff=Troe(A=0.43, T3=1e-30, T1=1e+30))
```

```
# Reaction 10
```

```
reaction('H2O2 + H <=> H2O + OH', [2.410e+13, 0.0, 3970.0])
```

```
# Reaction 11
```

```
reaction('H2O2 + H <=> H2 + HO2', [2.150e+10, 1.0, 6000.0])
```

```
# Reaction 12
```

```
reaction('H2O2 + O <=> OH + HO2', [9.550e+06, 2.0, 3970.0])
```

```
# Reaction 13
```

```
reaction('H2O2 + OH <=> H2O + HO2', [1.740e+12, 0.0, 318.0],  
options='duplicate')
```

```
# Reaction 14
```

```
reaction('H2O2 + OH <=> H2O + HO2', [7.590e+13, 0.0, 7269.0],  
options='duplicate')
```

```
# Reaction 15
```

```
reaction('HO2 + H <=> OH + OH', [3.320e+11, 0.894, -59.6])
```

```
# Reaction 16
```

```
reaction('HO2 + H <=> H2 + O2', [1.733e+08, 1.798, -512.3])
```

```
# Reaction 17
```

```
reaction('HO2 + O <=> OH + O2', [2.790e+13, -0.008, -0.06])
```

```
# Reaction 18
```

```
reaction('HO2 + OH <=> H2O + O2', [1.800e+13, -0.033, -644.4])
```

```
# Reaction 19
```

```
reaction('HO2 + HO2 <=> H2O2 + O2', [1.214e+10, 0.422, -1480.5],  
options='duplicate')
```

```
# Reaction 20
```

```
reaction('HO2 + HO2 <=> H2O2 + O2', [1.688e+16, -0.681, 12931.7],  
options='duplicate')
```

```
# Reaction 21
```

```
falloff_reaction('H + O2 (+ M) <=> HO2 (+ M)',  
kf=[4.650e+12, 0.44, 0.0],  
kf0=[1.850e+21, -1.433, -0.008],  
efficiencies='CH4:2.0 CO:1.9 CO2:3.8 H2:1.3 H2O:10.0',  
falloff=Troe(A=0.67, T3=1e-30, T1=1e+30, T2=1e+30))
```

```
# Reaction 22
```

```
falloff_reaction('CO + O (+ M) <=> CO2 (+ M)',  
kf=[1.362e+10, 0.0, 2384.0],  
kf0=[1.173e+24, -2.79, 4191.0],  
efficiencies='CO:1.75 CO2:3.6 H2:2.0 H2O:12.0')
```

Reaction 23

reaction('CO + OH <=> CO2 + H', [1.601e+07, 1.573, 710.4])

Reaction 24

reaction('CO + HO2 <=> CO2 + OH', [8.550e+03, 2.52, 15560.0])

Reaction 25

reaction('CO + O2 <=> CO2 + O', [1.119e+12, 0.0, 47700.0])

Reaction 26

falloff_reaction('CH3 + H (+ M) <=> CH4 (+ M)',
kf=[6.470e+13, 0.185, -54.0],
kf0=[1.110e+34, -4.589, 1511.5],
efficiencies='CH4:2.0 CO:1.5 CO2:2.0 H2:2.0 H2O:6.0 N2:1.4',
falloff=Troe(A=0.516194, T3=3637.8482, T1=1.0, T2=1e+30))

Reaction 27

reaction('CH4 + H <=> CH3 + H2', [3.780e+03, 3.185, 4660.9])

Reaction 28

reaction('CH4 + O <=> CH3 + OH', [4.431e+06, 2.045, 9995.9])

Reaction 29

reaction('CH4 + OH <=> CH3 + H2O', [5.830e+04, 2.6, 2190.0])

Reaction 30

reaction('CH4 + HO2 <=> CH3 + H2O2', [1.647e+00, 3.935, 18142.6])

Reaction 31

reaction('CH3 + HO2 <=> CH4 + O2', [7.434e+01, 2.531, -9381.6])

Reaction 32

reaction('CH3 + O2 <=> CH2O + OH', [9.60e+01, 2.823, 11579.6])

Reaction 33

reaction('CH3 + O <=> CH2O + H', [2.428e-01, 3.635, 4412.8])

Reaction 34

reaction('CH3 + O <=> HCO + H2', [6.970e+14, 0.04, -120.3])

Reaction 35

pdep_arrhenius('CH3 + OH <=> CH2O + H2',
[(0.01, 'atm'), 3.502e+05, 1.441, -3244.0],
[(0.1, 'atm'), 8.854e+05, 1.327, -2975.0],
[(1.0, 'atm'), 1.650e+07, 0.973, -2010.0],
[(10.0, 'atm'), 5.374e+09, 0.287, 280.0],
[(100.0, 'atm'), 9.494e+18, -2.199, 9769.0])

Reaction 36

falloff_reaction('CH2O (+ M) <=> HCO + H (+ M)',

```
kf=[8.000e+15, 0.0, 87726.0],  
kf0=[1.300e+36, -5.5, 93932.0],  
efficiencies='CH4:2.0 CO:1.5 CO2:2.0 H2:2.0 H2O:6.0')
```

```
# Reaction 37
```

```
falloff_reaction('CH2O (+ M) <=> CO + H2 (+ M)',  
kf=[3.700e+13, 0.0, 71969.0],  
kf0=[4.400e+38, -6.1, 93932.0],  
efficiencies='CH4:2.0 CO:1.5 CO2:2.0 H2:2.0 H2O:6.0')
```

```
# Reaction 38
```

```
reaction('CH2O + O2 <=> HCO + HO2', [9.290e+13, -0.010, 60822.6])
```

```
# Reaction 39
```

```
reaction('CH2O + O <=> HCO + OH', [6.260e+09, 1.15, 2260.0])
```

```
# Reaction 40
```

```
reaction('CH2O + H <=> HCO + H2', [1.322e+12, 0.516, 4136.3])
```

```
# Reaction 41
```

```
reaction('CH2O + OH <=> HCO + H2O', [2.185e+09, 1.178, -576.0])
```

```
# Reaction 42
```

```
reaction('CH2O + HO2 <=> HCO + H2O2', [2.109e+03, 2.669, 11047.0])
```

```
# Reaction 43
```

```
reaction('CH2O + CH3 <=> HCO + CH4', [2.930e-02, 4.3, 2831.0])
```

```
# Reaction 44
```

```
reaction('CH2O + OH => H + CO + H2O', [2.565e+11, 0.693, 9368.7])
```

```
# Reaction 45
```

```
reaction('CH2O + H => H + CO + H2', [1.470e+10, 1.417, 13100.2])
```

```
# Reaction 46
```

```
three_body_reaction('HCO + M <=> H + CO + M', [5.970e+12, 0.594, 13235.5],  
efficiencies='CH4:2.0 CO:1.5 CO2:2.0 H2:2.0 H2O:6.0')
```

```
# Reaction 47
```

```
reaction('HCO + O2 <=> CO + HO2', [4.885e+06, 1.599, -1463.8])
```

```
# Reaction 48
```

```
reaction('HCO + O <=> CO + OH', [3.020e+13, 0.0, 0.0])
```

```
# Reaction 49
```

```
reaction('HCO + H <=> CO + H2', [4.760e+14, -0.018, 0.01])
```

```
# Reaction 50
```

```
reaction('HCO + OH <=> CO + H2O', [3.011e+13, 0.0, 0.0])
```

```
# Reaction 51
```

reaction('HCO + CH3 <=> CO + CH4', [4.588e+07, -0.009, 0.03])

Reaction 52

reaction('HCO + HCO <=> CO + CH2O', [2.700e+13, 0.0, 0.0])

Reaction 53

reaction('HCO + O <=> CO2 + H', [3.000e+13, 0.0, 0.0])

Reaction 54

reaction('HCO + HO2 => CO2 + H + OH', [3.000e+13, 0.0, 0.0])

Reaction 55

reaction('HCO + HCO => H2 + CO + CO', [3.000e+12, 0.0, 0.0])

C3_19sOp Cantera File:

```

units(length='cm', time='s', quantity='mol', act_energy='cal/mol')

ideal_gas(name='gas',
  elements="C H N O Ar He",
  species="""N2  H2  H   O2  O   H2O  OH   H2O2
           HO2  CO   CO2  CH4  CH3  CH2  CH3O2  CH3O
           CH2O  HCO   C2H6""",
  reactions='all',
  transport='Mix',
  initial_state=state(temperature=300.0, pressure=OneAtm))

#-----
# Species data
#-----

species(name='N2',
  atoms='N:2',
  thermo=(NASA([200.00, 1000.00],
    [ 3.53100528E+00, -1.23660988E-04, -5.02999433E-07,
      2.43530612E-09, -1.40881235E-12, -1.04697628E+03,
      2.96747038E+00]),
    NASA([1000.00, 6000.00],
      [ 2.95257637E+00, 1.39690040E-03, -4.92631603E-07,
        7.86010195E-11, -4.60755204E-15, -9.23948688E+02,
        5.87188762E+00])),
  transport=gas_transport(geom='linear',
    diam=3.621,
    well_depth=97.53,
    polar=1.76,
    rot_relax=4.0),
  note='G8/02')

species(name='H2',
  atoms='H:2',
  thermo=(NASA([200.00, 1000.00],
    [ 2.34433112E+00, 7.98052075E-03, -1.94781510E-05,
      2.01572094E-08, -7.37611761E-12, -9.17935173E+02,
      6.83010238E-01]),
    NASA([1000.00, 6000.00],
      [ 2.93286575E+00, 8.26608026E-04, -1.46402364E-07,
        1.54100414E-11, -6.88804800E-16, -8.13065581E+02,
        -1.02432865E+00])),
  transport=gas_transport(geom='linear',
    diam=2.92,
    well_depth=38.0,
    polar=0.79,
    rot_relax=280.0),
  note='TPIS78')

```

```
species(name='H',
  atoms='H:1',
  thermo=(NASA([200.00, 1000.00],
    [ 2.50000000E+00, 0.00000000E+00, 0.00000000E+00,
      0.00000000E+00, 0.00000000E+00, 2.54736600E+04,
      -4.46682850E-01]),
    NASA([1000.00, 6000.00],
      [ 2.50000000E+00, 0.00000000E+00, 0.00000000E+00,
        0.00000000E+00, 0.00000000E+00, 2.54736600E+04,
        -4.46682850E-01])),
  transport=gas_transport(geom='atom',
    diam=2.05,
    well_depth=145.0),
  note='L6/94')
```

```
species(name='O2',
  atoms='O:2',
  thermo=(NASA([200.00, 1000.00],
    [ 3.78245636E+00, -2.99673416E-03, 9.84730201E-06,
      -9.68129509E-09, 3.24372837E-12, -1.06394356E+03,
      3.65767573E+00]),
    NASA([1000.00, 6000.00],
      [ 3.66096065E+00, 6.56365811E-04, -1.41149627E-07,
        2.05797935E-11, -1.29913436E-15, -1.21597718E+03,
        3.41536279E+00])),
  transport=gas_transport(geom='linear',
    diam=3.458,
    well_depth=107.4,
    polar=1.6,
    rot_relax=3.8),
  note='RUS89')
```

```
species(name='O',
  atoms='O:1',
  thermo=(NASA([200.00, 1000.00],
    [ 3.16826710E+00, -3.27931884E-03, 6.64306396E-06,
      -6.12806624E-09, 2.11265971E-12, 2.91222592E+04,
      2.05193346E+00]),
    NASA([1000.00, 6000.00],
      [ 2.54363697E+00, -2.73162486E-05, -4.19029520E-09,
        4.95481845E-12, -4.79553694E-16, 2.92260120E+04,
        4.92229457E+00])),
  transport=gas_transport(geom='atom',
    diam=2.75,
    well_depth=80.0),
  note='L1/90')
```

```
species(name='H2O',
  atoms='H:2 O:1',
  thermo=(NASA([200.00, 1000.00],
```



```
[ 4.19863520E+00, -2.03640170E-03, 6.52034160E-06,
-5.48792690E-09, 1.77196800E-12, -3.02937260E+04,
-8.49009010E-01]),
NASA([1000.00, 6000.00],
[ 2.67703890E+00, 2.97318160E-03, -7.73768890E-07,
9.44335140E-11, -4.26899910E-15, -2.98858940E+04,
6.88255000E+00])),
transport=gas_transport(geom='nonlinear',
    diam=2.605,
    well_depth=572.4,
    dipole=1.844,
    rot_relax=4.0),
note='L5/89')

species(name='OH',
    atoms='H:1 O:1',
    thermo=(NASA([200.00, 1000.00],
        [ 3.99198424E+00, -2.40106655E-03, 4.61664033E-06,
        -3.87916306E-09, 1.36319502E-12, 3.36889836E+03,
        -1.03998477E-01]),
        NASA([1000.00, 6000.00],
        [ 2.83853033E+00, 1.10741289E-03, -2.94000209E-07,
        4.20698729E-11, -2.42289890E-15, 3.69780808E+03,
        5.84494652E+00])),
    transport=gas_transport(geom='linear',
        diam=2.75,
        well_depth=80.0),
    note='IU3/03')

species(name='H2O2',
    atoms='H:2 O:2',
    thermo=(NASA([200.00, 1000.00],
        [ 4.31515149E+00, -8.47390622E-04, 1.76404323E-05,
        -2.26762944E-08, 9.08950158E-12, -1.77067437E+04,
        3.27373319E+00]),
        NASA([1000.00, 6000.00],
        [ 4.57977305E+00, 4.05326003E-03, -1.29844730E-06,
        1.98211400E-10, -1.13968792E-14, -1.80071775E+04,
        6.64970694E-01])),
    transport=gas_transport(geom='nonlinear',
        diam=3.458,
        well_depth=107.4,
        rot_relax=3.8),
    note='T8/03')

species(name='HO2',
    atoms='H:1 O:2',
    thermo=(NASA([200.00, 1000.00],
        [ 4.30179807E+00, -4.74912097E-03, 2.11582905E-05,
        -2.42763914E-08, 9.29225225E-12, 2.64018485E+02,
        3.71666220E+00]),
```

```
NASA([1000.00, 5000.00],
      [ 4.17228741E+00, 1.88117627E-03, -3.46277286E-07,
        1.94657549E-11, 1.76256905E-16, 3.10206839E+01,
        2.95767672E+00])),
transport=gas_transport(geom='nonlinear',
                        diam=3.458,
                        well_depth=107.4,
                        rot_relax=1.0),
note='T1/09')

species(name='CO',
        atoms='C:1 O:1',
        thermo=(NASA([200.00, 1000.00],
                      [ 3.57953350E+00, -6.10353690E-04, 1.01681430E-06,
                        9.07005860E-10, -9.04424490E-13, -1.43440860E+04,
                        3.50840930E+00])),
              NASA([1000.00, 6000.00],
                    [ 3.04848590E+00, 1.35172810E-03, -4.85794050E-07,
                      7.88536440E-11, -4.69807460E-15, -1.42661170E+04,
                      6.01709770E+00])),
              transport=gas_transport(geom='linear',
                                      diam=3.65,
                                      well_depth=98.1,
                                      polar=1.95,
                                      rot_relax=1.8),
              note='RUS79')

species(name='CO2',
        atoms='C:1 O:2',
        thermo=(NASA([200.00, 1000.00],
                      [ 2.35681300E+00, 8.98412990E-03, -7.12206320E-06,
                        2.45730080E-09, -1.42885480E-13, -4.83719710E+04,
                        9.90090350E+00])),
              NASA([1000.00, 6000.00],
                    [ 4.63651110E+00, 2.74145690E-03, -9.95897590E-07,
                      1.60386660E-10, -9.16198570E-15, -4.90249040E+04,
                      -1.93489550E+00])),
              transport=gas_transport(geom='linear',
                                      diam=3.763,
                                      well_depth=244.0,
                                      polar=2.65,
                                      rot_relax=2.1),
              note='L7/88')

species(name='CH4',
        atoms='C:1 H:4',
        thermo=(NASA([200.00, 1000.00],
                      [ 5.14911468E+00, -1.36622009E-02, 4.91453921E-05,
                        -4.84246767E-08, 1.66603441E-11, -1.02465983E+04,
                        -4.63848842E+00])),
              NASA([1000.00, 6000.00],
```

```
[ 1.65326226E+00, 1.00263099E-02, -3.31661238E-06,
  5.36483138E-10, -3.14696758E-14, -1.00095936E+04,
  9.90506283E+00]],
transport=gas_transport(geom='nonlinear',
  diam=3.746,
  well_depth=141.4,
  polar=2.6,
  rot_relax=13.0),
note='G8/99')

species(name='CH3',
  atoms='C:1 H:3',
  thermo=(NASA([200.00, 1000.00],
    [ 3.65717970E+00, 2.12659790E-03, 5.45838830E-06,
      -6.61810030E-09, 2.46570740E-12, 1.64227160E+04,
      1.67353540E+00]),
    NASA([1000.00, 6000.00],
      [ 2.97812060E+00, 5.79785200E-03, -1.97558000E-06,
        3.07297900E-10, -1.79174160E-14, 1.65095130E+04,
        4.72247990E+00])),
  transport=gas_transport(geom='linear',
    diam=3.8,
    well_depth=144.0),
  note='IU0702')

species(name='CH2',
  atoms='C:1 H:2',
  thermo=(NASA([200.00, 1000.00],
    [ 3.71757846E+00, 1.27391260E-03, 2.17347251E-06,
      -3.48858500E-09, 1.65208866E-12, 4.58723866E+04,
      1.75297945E+00]),
    NASA([1000.00, 6000.00],
      [ 3.14631886E+00, 3.03671259E-03, -9.96474439E-07,
        1.50483580E-10, -8.57335515E-15, 4.60412605E+04,
        4.72341711E+00])),
  transport=gas_transport(geom='linear',
    diam=3.8,
    well_depth=144.0),
  note='IU3/03')

species(name='CH3O2',
  atoms='C:1 H:3 O:2',
  thermo=(NASA([300.00, 1374.00],
    [ 1.97339205E+00, 1.53542340E-02, -6.37314891E-06,
      3.19930565E-10, 2.82193915E-13, 2.54278835E+02,
      1.69194215E+01]),
    NASA([1374.00, 5000.00],
      [ 6.47970487E+00, 7.44401080E-03, -2.52348555E-06,
        3.89577296E-10, -2.25182399E-14, -1.56285441E+03,
        -8.19477074E+00])),
  transport=gas_transport(geom='nonlinear',
```

```
diam=3.626,  
well_depth=481.8,  
rot_relax=1.0))
```

```
species(name='CH3O',  
atoms='C:1 H:3 O:1',  
thermo=(NASA([200.00, 1000.00],  
[ 3.71180502E+00, -2.80463306E-03, 3.76550971E-05,  
-4.73072089E-08, 1.86588420E-11, 1.29569760E+03,  
6.57240864E+00]),  
NASA([1000.00, 6000.00],  
[ 4.75779238E+00, 7.44142474E-03, -2.69705176E-06,  
4.38090504E-10, -2.63537098E-14, 3.78111940E+02,  
-1.96680028E+00])),  
transport=gas_transport(geom='nonlinear',  
diam=3.69,  
well_depth=417.0,  
dipole=1.7,  
rot_relax=2.0),  
note='IU1/03')
```

```
species(name='CH2O',  
atoms='C:1 H:2 O:1',  
thermo=(NASA([200.00, 1000.00],  
[ 4.79372312E+00, -9.90833322E-03, 3.73219990E-05,  
-3.79285237E-08, 1.31772641E-11, -1.43791953E+04,  
6.02798058E-01]),  
NASA([1000.00, 6000.00],  
[ 3.16952665E+00, 6.19320560E-03, -2.25056366E-06,  
3.65975660E-10, -2.20149458E-14, -1.45486831E+04,  
6.04207898E+00])),  
transport=gas_transport(geom='nonlinear',  
diam=3.59,  
well_depth=498.0,  
rot_relax=2.0),  
note='T5/11')
```

```
species(name='HCO',  
atoms='C:1 H:1 O:1',  
thermo=(NASA([200.00, 1000.00],  
[ 4.23754610E+00, -3.32075257E-03, 1.40030264E-05,  
-1.34239995E-08, 4.37416208E-12, 3.87241185E+03,  
3.30834869E+00]),  
NASA([1000.00, 6000.00],  
[ 3.92001542E+00, 2.52279324E-03, -6.71004164E-07,  
1.05615948E-10, -7.43798261E-15, 3.65342928E+03,  
3.58077056E+00])),  
transport=gas_transport(geom='nonlinear',  
diam=3.59,  
well_depth=498.0),  
note='T5/03')
```

```

species(name='C2H6',
        atoms='C:2 H:6',
        thermo=(NASA([200.00, 1000.00],
                      [ 4.29142572E+00, -5.50154901E-03, 5.99438458E-05,
                        -7.08466469E-08, 2.68685836E-11, -1.15222056E+04,
                        2.66678994E+00]),
                NASA([1000.00, 6000.00],
                      [ 4.04666411E+00, 1.53538802E-02, -5.47039485E-06,
                        8.77826544E-10, -5.23167531E-14, -1.24473499E+04,
                        -9.68698313E-01])),
        transport=gas_transport(geom='nonlinear',
                                diam=4.35,
                                well_depth=247.5,
                                rot_relax=1.5),
        note='G8/88')

#-----
# Reaction data
#-----

# Reaction 1
three_body_reaction('H2 + M <=> H + H + M', [4.577e+19, -1.4, 104400.0],
                   efficiencies='C2H6:3.0 CH4:2.0 CO:1.9 CO2:3.8 H2:2.5 H2O:12.0')

# Reaction 2
reaction('H2 + O <=> H + OH', [5.416e+4, 2.569, 5583.9])

# Reaction 3
reaction('H2 + OH <=> H + H2O', [4.359e+13, 0.019, 6624.4])

# Reaction 4
three_body_reaction('O + O + M <=> O2 + M', [6.165e+15, -0.5, 0.0],
                   efficiencies='C2H6:3.0 CH4:2.0 CO:1.9 CO2:3.8 H2:2.5 H2O:12.0')

# Reaction 5
reaction('O2 + H <=> O + OH', [2.688e+13, 0.011, 10201.4])

# Reaction 6
three_body_reaction('H + OH + M <=> H2O + M', [3.500e+22, -2.0, 0.0],
                   efficiencies='C2H6:3.0 CH4:2.0 H2:0.73 H2O:3.65')

# Reaction 7
reaction('O + H2O <=> OH + OH', [5.929094e+6, 1.898, 13988.5])

# Reaction 8
three_body_reaction('O + H + M <=> OH + M', [4.714e+18, -1.0, 0.0],
                   efficiencies='C2H6:3.0 CH4:2.0 CO:1.5 CO2:2.0 H2:2.5 H2O:12.0')

# Reaction 9
falloff_reaction('H2O2 (+ M) <=> OH + OH (+ M)',

```

```
kf=[2.00e+12, 0.9, 48749.0],  
kf0=[2.353e+24, -2.293, 48743.4],  
efficiencies='CO:2.8 CO2:1.06 H2:3.7 H2O:5.1 H2O2:5.2 N2:1.5 O2:0.79',  
falloff=Troe(A=0.43, T3=1e-30, T1=1e+30))
```

```
# Reaction 11
```

```
reaction('H2O2 + H <=> H2 + HO2', [2.150e+10, 1.0, 6000.0])
```

```
# Reaction 14
```

```
reaction('H2O2 + OH <=> H2O + HO2', [7.590e+13, 0.0, 7269.0],)
```

```
# Reaction 15
```

```
reaction('HO2 + H <=> OH + OH', [2.200e+11, 0.88, -64.5])
```

```
# Reaction 16
```

```
reaction('HO2 + H <=> H2 + O2', [6.700e+07, 1.77, -569.0])
```

```
# Reaction 17
```

```
reaction('HO2 + O <=> OH + O2', [3.250e+13, 0.0, 0.0])
```

```
# Reaction 18
```

```
reaction('HO2 + OH <=> H2O + O2', [2.456e+13, 0.0, -497.0])
```

```
# Reaction 19
```

```
reaction('HO2 + HO2 <=> H2O2 + O2', [1.214e+10, 0.422, -1480.5],  
options='duplicate')
```

```
# Reaction 20
```

```
reaction('HO2 + HO2 <=> H2O2 + O2', [1.688e+16, -0.681, 12931.7],  
options='duplicate')
```

```
# Reaction 21
```

```
falloff_reaction('H + O2 (+ M) <=> HO2 (+ M)',  
kf=[4.650e+12, 0.44, 0.0],  
kf0=[3.272e+19, -1.178, -0.02],  
efficiencies='C2H6:3.0 CH4:2.0 CO:1.9 CO2:3.8 H2:1.3 H2O:10.0',  
falloff=Troe(A=0.67, T3=1e-30, T1=1e+30, T2=1e+30))
```

```
# Reaction 23
```

```
pdep_arrhenius('CO + OH <=> CO2 + H',  
[(0.01315, 'atm'), 2.10e+05, 1.9, -1064.0],  
[(0.1315, 'atm'), 2.50e+05, 1.88, -1043.0],  
[(1.315, 'atm'), 8.700e+05, 1.73, -685.0],  
[(13.158, 'atm'), 1.131e+7, 1.403, 52.0],  
[(131.58, 'atm'), 2.300e+07, 1.35, 974.0])
```

```
# Reaction 24
```

```
reaction('CO + HO2 <=> CO2 + OH', [8.550e+03, 2.52, 15560.0])
```

```
# Reaction 26
```

```
falloff_reaction('CH3 + H (+ M) <=> CH4 (+ M)',  
kf=[6.470e+13, 0.185, -54.0],  
kf0=[6.842e+32, -4.665, 2145.4],  
efficiencies='C2H6:3.0 CH4:2.0 CO:1.5 CO2:2.0 H2:2.0 H2O:6.0 N2:1.4',  
falloff=Troe(A=0.516194, T3=3637.8482, T1=1.0, T2=1e+30))
```

```
# Reaction 27
```

```
reaction('CH4 + H <=> CH3 + H2', [1.766e+3, 3.238, 9440.6])
```

```
# Reaction 28
```

```
reaction('CH4 + O <=> CH3 + OH', [4.900e+06, 2.2, 7591.0])
```

```
# Reaction 29
```

```
reaction('CH4 + OH <=> CH3 + H2O', [5.830e+04, 2.6, 2190.0])
```

```
# Reaction 30
```

```
reaction('CH4 + HO2 <=> CH3 + H2O2', [1.120e+01, 3.74, 21009.0])
```

```
# Reaction 31
```

```
reaction('CH3 + HO2 <=> CH4 + O2', [1.200e+05, 2.227, -3021.36])
```

```
# Reaction 34
```

```
reaction('CH2 + O2 => CO2 + H + H', [1.805e+9, 0.982, -295.6])
```

```
# Reaction 36
```

```
reaction('CH2 + O2 <=> CH2O + O', [1.702e+5, 2.509, 1409.5])
```

```
# Reaction 38
```

```
reaction('CH3 + H <=> CH2 + H2', [6.030e+13, 0.9, 15100.0])
```

```
# Reaction 39
```

```
falloff_reaction('CH3 + O2 (+ M) <=> CH3O2 (+ M)',  
kf=[7.812e+09, 0.9, 0.0],  
kf0=[6.850e+24, -3.0, 0.0],  
falloff=Troe(A=0.6, T3=1000.0, T1=70.0, T2=1700.0))
```

```
# Reaction 40
```

```
reaction('CH3 + O2 <=> CH3O + O', [7.546e+12, 0.0, 28320.0])
```

```
# Reaction 41
```

```
reaction('CH3 + O2 <=> CH2O + OH', [2.641e+00, 3.283, 8105.0])
```

```
# Reaction 42
```

```
reaction('CH3 + O <=> CH2O + H', [3.324e+13, 0.05, -136.0])
```

```
# Reaction 43
```

```
reaction('CH3 + O <=> HCO + H2', [3.655e+13, 0.049, -147.9])
```

```
# Reaction 47
```

```
reaction('CH3 + HO2 <=> CH3O + OH', [9.854e+11, 0.302, -846.8])
```

Reaction 48

reaction('CH3O2 + O <=> CH3O + O2', [3.60e+13, 0.0, 0.0])

Reaction 49

reaction('CH3O2 + H <=> CH3O + OH', [9.600e+13, 0.0, 0.0])

Reaction 50

reaction('CH3O2 + CH3 <=> CH3O + CH3O', [5.080e+12, 0.0, -1411.0])

Reaction 53

reaction('CH3O + O2 <=> CH2O + HO2', [4.380e-19, 9.5, -5501.0])

Reaction 59

reaction('CH2O + O2 <=> HCO + HO2', [8.070e+15, 0.0, 53420.0])

Reaction 60

reaction('CH2O + O <=> HCO + OH', [6.260e+09, 1.15, 2260.0])

Reaction 61

reaction('CH2O + H <=> HCO + H2', [1.322e+12, 0.516, 4136.26])

Reaction 62

reaction('CH2O + OH <=> HCO + H2O', [2.185e+09, 1.178, -576.02])

Reaction 63

reaction('CH2O + HO2 <=> HCO + H2O2', [1.88e+04, 2.7, 11520.0])

Reaction 64

reaction('CH2O + CH3 <=> HCO + CH4', [2.930e-02, 4.3, 2831.0])

Reaction 65

reaction('CH2O + OH => H + CO + H2O', [2.565e+11, 0.693, 9368.7])

Reaction 66

reaction('CH2O + H => H + CO + H2', [1.470e+10, 1.417, 13100.2])

Reaction 67

three_body_reaction('HCO + M <=> H + CO + M', [4.635e+11, 0.702, 15607.7],
efficiencies='C2H6:3.0 CH4:2.0 CO:1.5 CO2:2.0 H2:2.0 H2O:6.0')

Reaction 68

reaction('HCO + O2 <=> CO + HO2', [9.145e+5, 1.642, -1118.1])

Reaction 69

reaction('HCO + O <=> CO + OH', [3.020e+13, 0.0, 0.0])

Reaction 70

reaction('HCO + H <=> CO + H2', [7.219e+14, 0.006, 0.02])

Reaction 71

reaction('HCO + OH <=> CO + H2O', [3.011e+13, 0.0, 0.0])

Reaction 72

reaction('HCO + CH3 <=> CO + CH4', [2.650e+13, 0.0, 0.0])

Reaction 77

pdep_arrhenius('CH3O <=> CH2O + H',
[(1.0, 'atm'), 3.170e+24, -4.25, 26042.1],
[(100.0, 'atm'), 8.500e+28, -5.09, 28584.9])

Reaction 78

falloff_reaction('CH3 + CH3 (+ M) <=> C2H6 (+ M)',
kf=[2.350e+14, -0.337, -4.9],
kf0=[2.210 e+50, -9.983, 4341.0],
efficiencies='C2H6:3.0 CH4:2.0 CO:1.5 CO2:2.0 H2:2.0 H2O:6.0 N2:1.4',
falloff=Troe(A=0.865, T3=454.5, T1=1e+30, T2=1e+30))

Appendix C

NUIGMECH_15sOp Validation

For more comprehensive validation, please see [180].

1. Constant UV: Ignition Delay Time

The compact model has good replication of IDT across the performance conditions (Table 5.1).

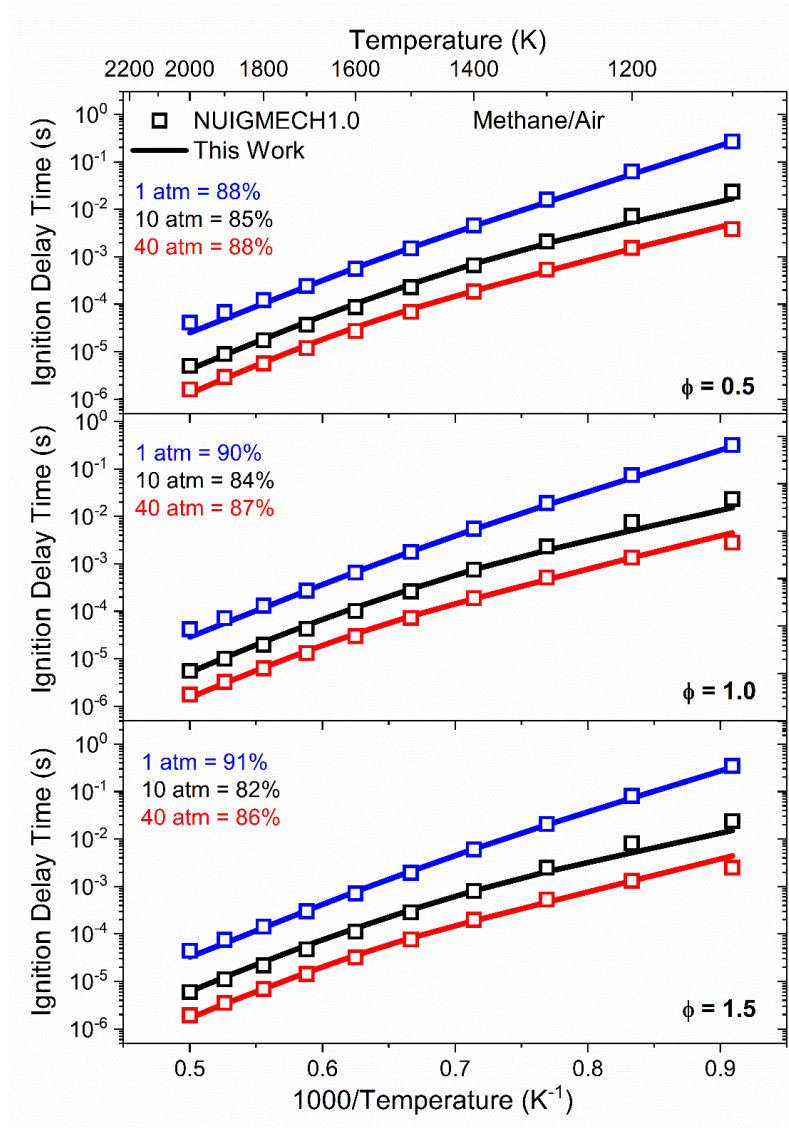


Figure C.1. Ignition delay time as a function of temperature for lean, stoichiometric and rich methane/air mixtures at 1, 10 and 40 atm using the NUIGMECH1.0 detailed model (symbols) and NUIGMECH_15sOp (lines).

2. Perfectly Stirred Reactor: Speciation

Mole fractions of CO are used as validation for NUIGMECH_15sOp. The compact model has good replication across the performance conditions (Table 5.1). Representative temperature and equivalence ratio conditions are used here.

1200 K:

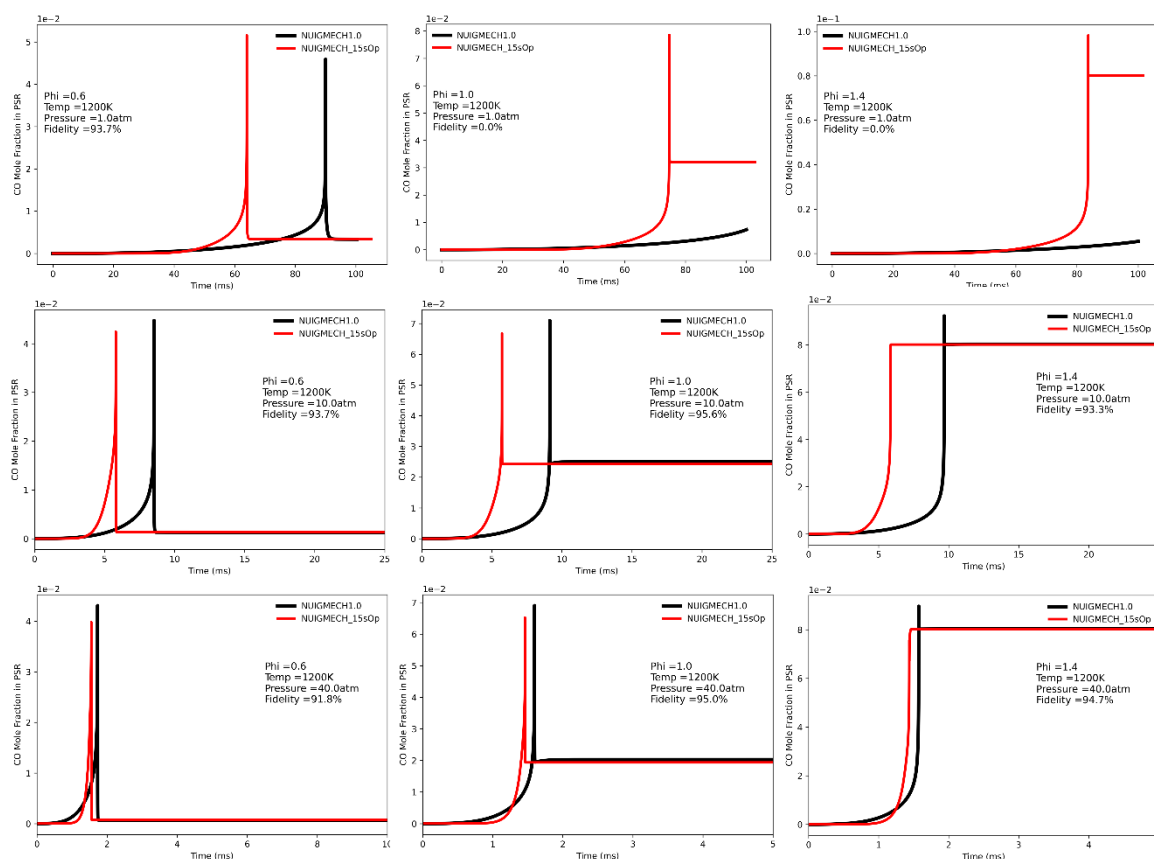


Figure C.2. CO mole fractions in PSR simulations at 1200 K using NUIGMECH1.0 detailed model (black) and NUIGMECH_15sOp (red). Equivalence ratios 0.6 (left), 1.0 (middle) and 1.4 (right). NUIGMECH_15sOp has excellent replication of detailed model CO mole fractions at 40 atm, however fidelity decreases as pressure decreases to 1 atm.

1600 K:

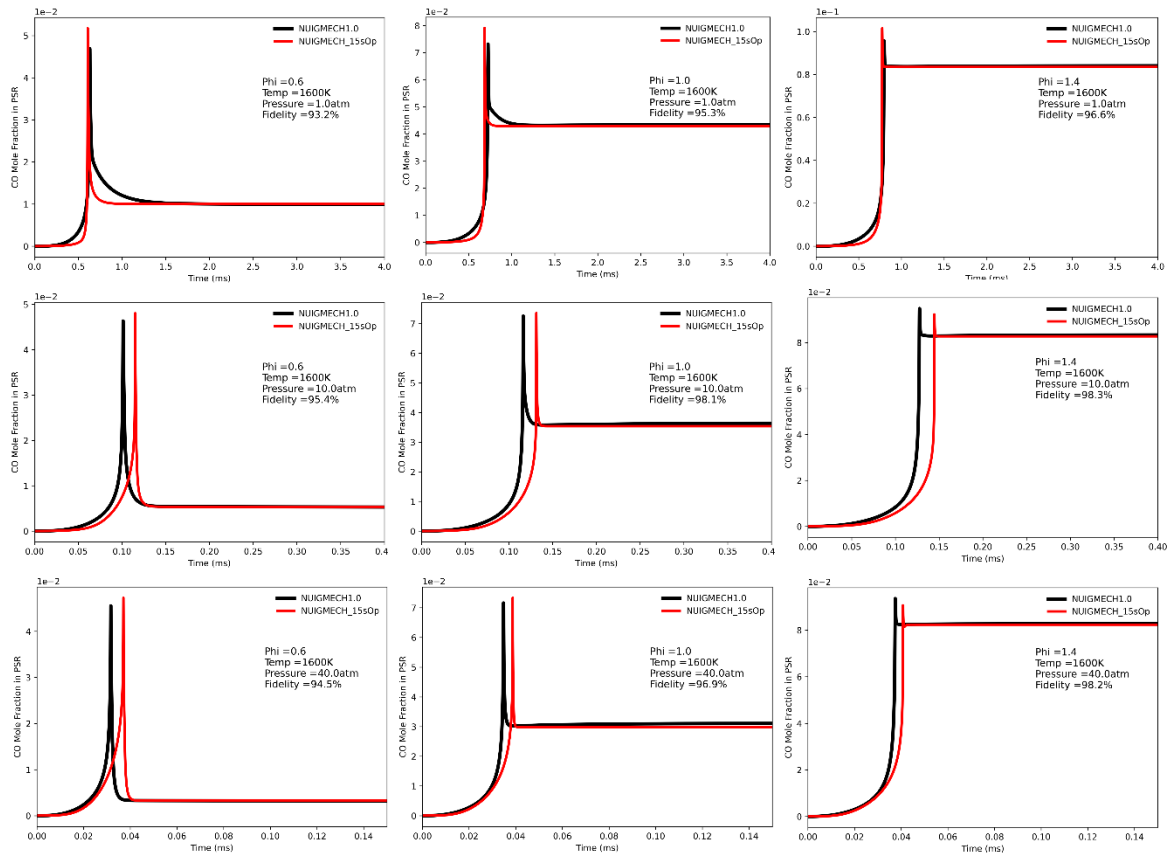


Figure C.3. CO mole fractions in PSR simulations at 1600 K using NUIGMECH1.0 detailed model (black) and NUIGMECH_15sOp (red). Equivalence ratios 0.6 (left), 1.0 (middle) and 1.4 (right). NUIGMECH_15sOp has excellent replication of detailed model CO mole fractions at all conditions.

2000 K:

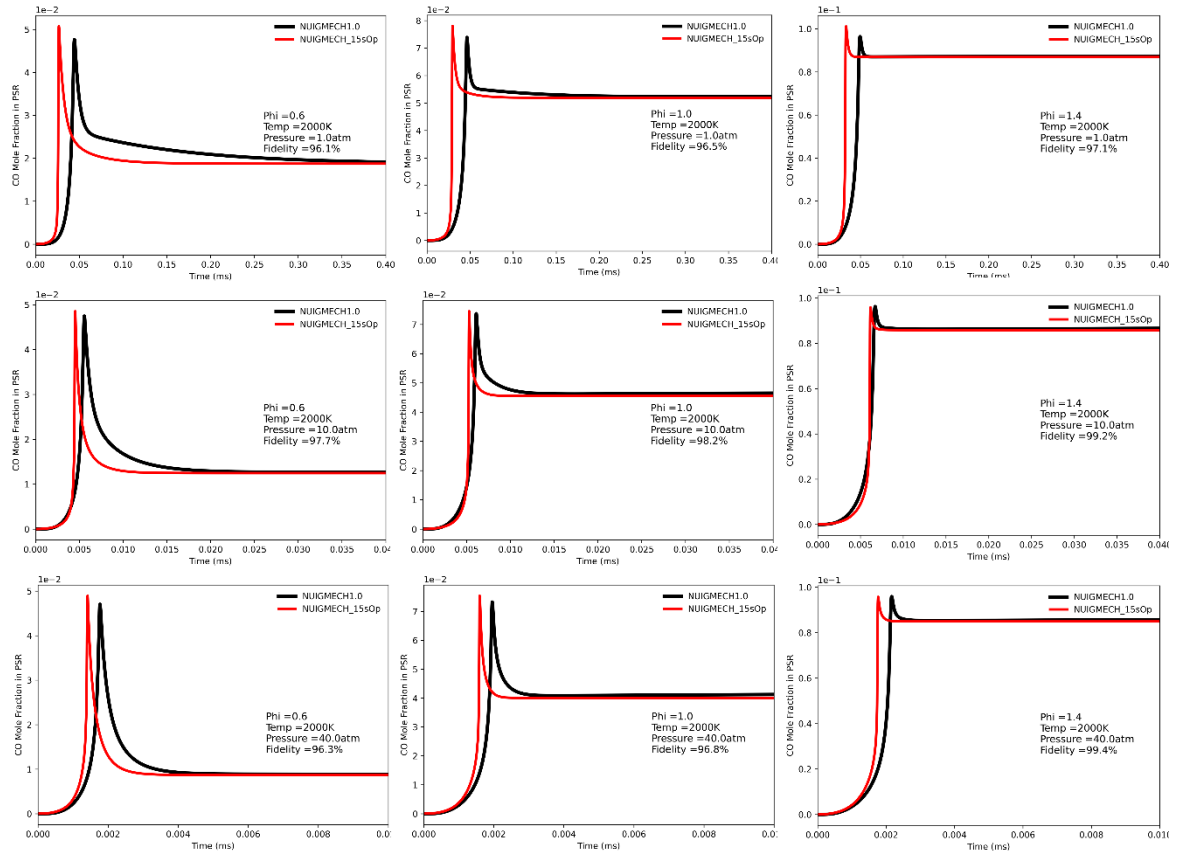


Figure C.4. CO mole fractions in PSR simulations at 2000 K using NUIGMECH1.0 detailed model (black) and NUIGMECH_15sOp (red). Equivalence ratios 0.6 (left), 1.0 (middle) and 1.4 (right). NUIGMECH_15sOp has excellent replication of detailed model CO mole fractions at all conditions.

3. Freely Propagating Flame: Laminar Burning Velocity

The compact model has good replication of laminar burning velocity across the performance conditions (Table 5.1). The fidelity decreases at 1 atm.

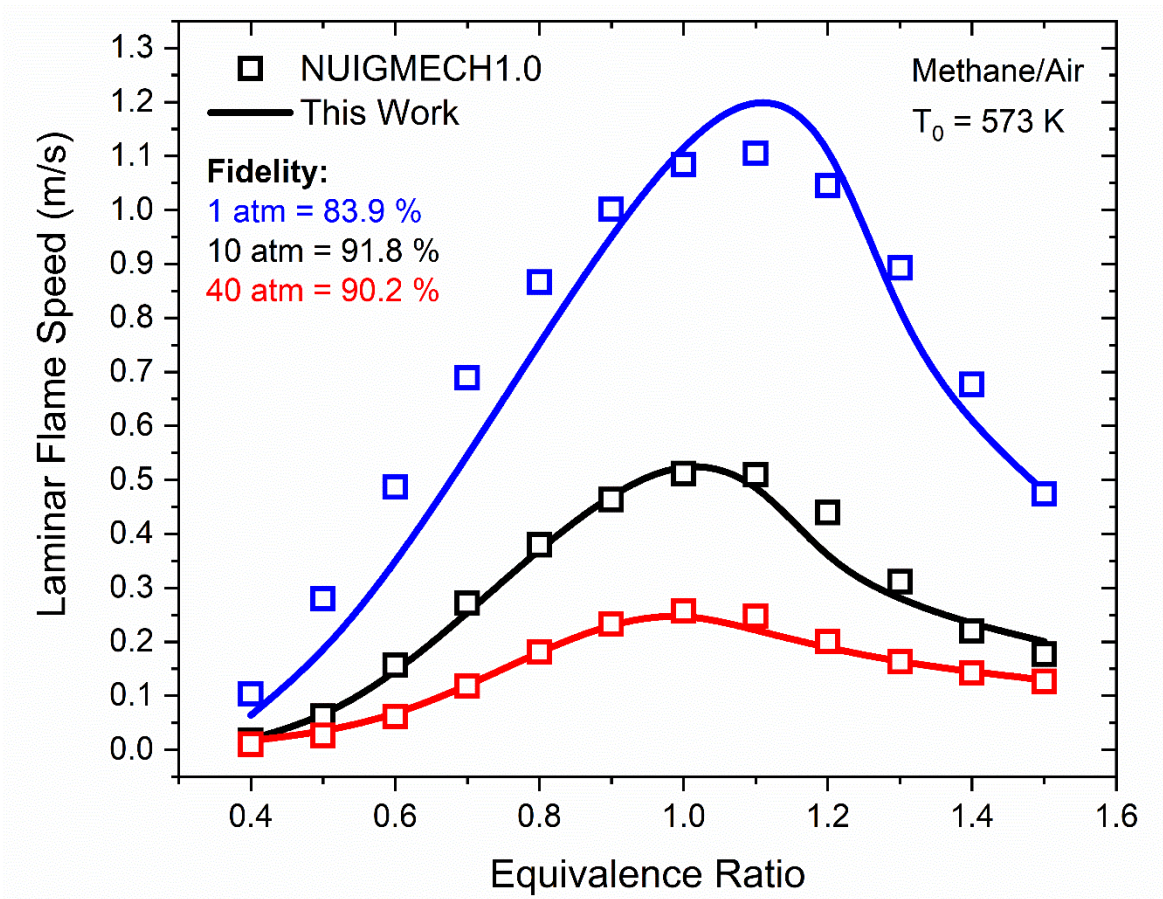


Figure C.5. Laminar burning velocity as a function of equivalence ratio at 1, 10 and 40 atm using the NUIGMECH1.0 detailed model (symbols) and NUIGMECH_15sOp (lines).

4. Freely Propagating Flame: Speciation

Mole fractions of CO are used as validation for NUIGMECH_15sOp. The compact model has good replication across the performance conditions (Table 5.1). Representative temperature and equivalence ratio conditions are used here.

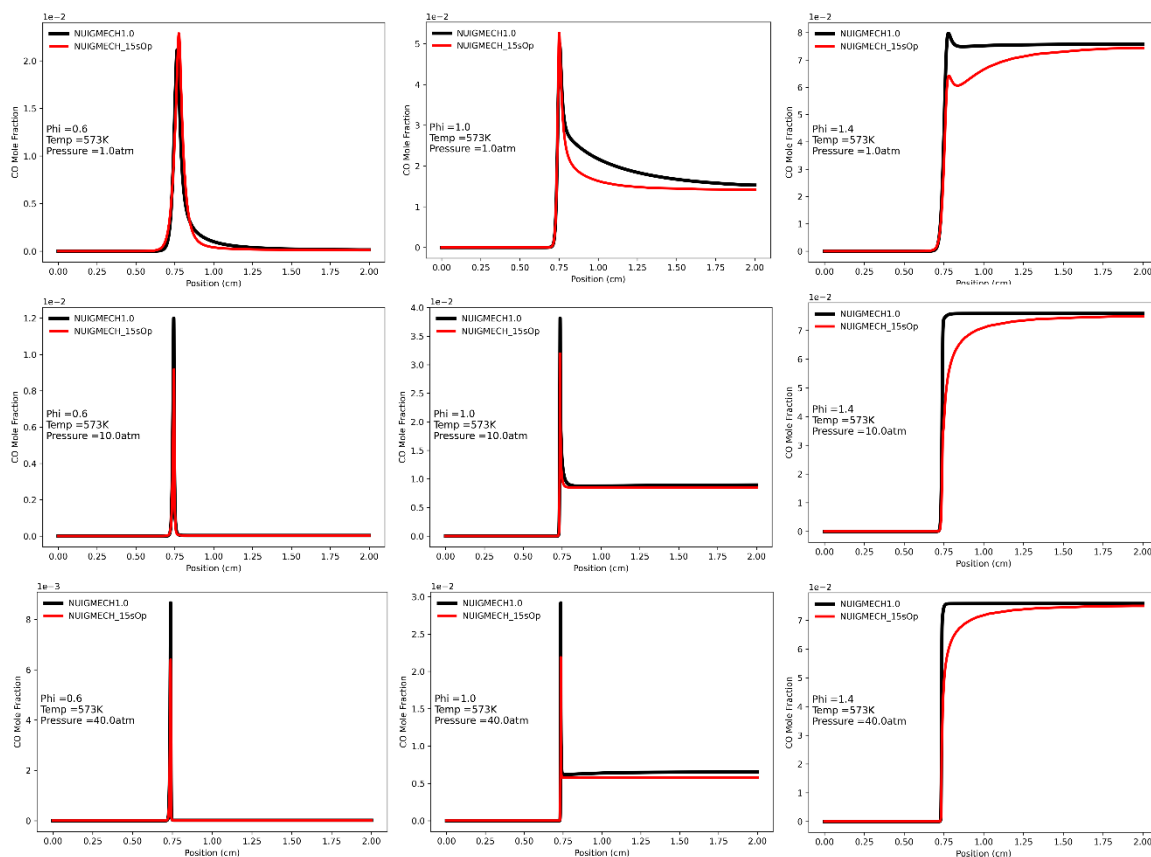


Figure C.6. CO mole fractions in freely propagating flame simulations at 573 K using NUIGMECH1.0 detailed model (black) and NUIGMECH_15sOp (red). Equivalence ratios 0.6 (left), 1.0 (middle) and 1.4 (right). NUIGMECH_15sOp has good replication of detailed model CO mole fractions at all conditions.

Appendix D

NUIGMECH_15sOp Files

NUIGMECH_15sOp Cantera File:

```
units(length='cm', time='s', quantity='mol', act_energy='cal/mol')
```

```
ideal_gas(name='gas',  
  elements="C H N O Ar He",  
  species="""CH2O CH3 CH4 CO CO2 H H2 H2O H2O2  
    HCO HO2 N2 O O2 OH """,  
  reactions='all',  
  transport='Mix',  
  initial_state=state(temperature=300.0, pressure=OneAtm))
```

```
#-----  
# Species data  
#-----
```

```
species(name='CH2O',  
  atoms='C:1 H:2 O:1',  
  thermo=(NASA([200.00, 1000.00],  
    [ 4.79372312E+00, -9.90833322E-03, 3.73219990E-05,  
      -3.79285237E-08, 1.31772641E-11, -1.43791953E+04,  
      6.02798058E-01]),  
    NASA([1000.00, 6000.00],  
      [ 3.16952665E+00, 6.19320560E-03, -2.25056366E-06,  
        3.65975660E-10, -2.20149458E-14, -1.45486831E+04,  
        6.04207898E+00])),  
  transport=gas_transport(geom='nonlinear',  
    diam=3.59,  
    well_depth=498.0,  
    rot_relax=2.0))
```

```
species(name='CH3',  
  atoms='C:1 H:3',  
  thermo=(NASA([200.00, 1000.00],  
    [ 3.65717970E+00, 2.12659790E-03, 5.45838830E-06,  
      -6.61810030E-09, 2.46570740E-12, 1.64227160E+04,  
      1.67353540E+00]),  
    NASA([1000.00, 6000.00],  
      [ 2.97812060E+00, 5.79785200E-03, -1.97558000E-06,  
        3.07297900E-10, -1.79174160E-14, 1.65095130E+04,
```



```
4.72247990E+00])),
transport=gas_transport(geom='linear',
    diam=3.8,
    well_depth=144.0))

species(name='CH4',
    atoms='C:1 H:4',
    thermo=(NASA([200.00, 1000.00],
        [ 5.14911468E+00, -1.36622009E-02, 4.91453921E-05,
          -4.84246767E-08, 1.66603441E-11, -1.02465983E+04,
          -4.63848842E+00])),
        NASA([1000.00, 6000.00],
            [ 1.65326226E+00, 1.00263099E-02, -3.31661238E-06,
              5.36483138E-10, -3.14696758E-14, -1.00095936E+04,
              9.90506283E+00])),
    transport=gas_transport(geom='nonlinear',
        diam=3.746,
        well_depth=141.4,
        polar=2.6,
        rot_relax=13.0))

species(name='CO',
    atoms='C:1 O:1',
    thermo=(NASA([200.00, 1000.00],
        [ 3.57953350E+00, -6.10353690E-04, 1.01681430E-06,
          9.07005860E-10, -9.04424490E-13, -1.43440860E+04,
          3.50840930E+00])),
        NASA([1000.00, 6000.00],
            [ 3.04848590E+00, 1.35172810E-03, -4.85794050E-07,
              7.88536440E-11, -4.69807460E-15, -1.42661170E+04,
              6.01709770E+00])),
    transport=gas_transport(geom='linear',
        diam=3.65,
        well_depth=98.1,
        polar=1.95,
        rot_relax=1.8))

species(name='CO2',
    atoms='C:1 O:2',
    thermo=(NASA([200.00, 1000.00],
        [ 2.35681300E+00, 8.98412990E-03, -7.12206320E-06,
          2.45730080E-09, -1.42885480E-13, -4.83719710E+04,
          9.90090350E+00])),
        NASA([1000.00, 6000.00],
            [ 4.63651110E+00, 2.74145690E-03, -9.95897590E-07,
              1.60386660E-10, -9.16198570E-15, -4.90249040E+04,
              -1.93489550E+00])),
    transport=gas_transport(geom='linear',
        diam=3.763,
        well_depth=244.0,
        polar=2.65,
```

```
rot_relax=2.1))
```

```
species(name='H',  
  atoms='H:1',  
  thermo=(NASA([200.00, 1000.00],  
    [ 2.50000000E+00, 0.00000000E+00, 0.00000000E+00,  
      0.00000000E+00, 0.00000000E+00, 2.54736600E+04,  
      -4.46682850E-01]),  
    NASA([1000.00, 6000.00],  
      [ 2.50000000E+00, 0.00000000E+00, 0.00000000E+00,  
        0.00000000E+00, 0.00000000E+00, 2.54736600E+04,  
        -4.46682850E-01])),  
  transport=gas_transport(geom='atom',  
    diam=1.53,  
    well_depth=541.672,  
    polar=0.666))
```

```
species(name='H2',  
  atoms='H:2',  
  thermo=(NASA([200.00, 1000.00],  
    [ 2.34433112E+00, 7.98052075E-03, -1.94781510E-05,  
      2.01572094E-08, -7.37611761E-12, -9.17935173E+02,  
      6.83010238E-01]),  
    NASA([1000.00, 6000.00],  
      [ 2.93286575E+00, 8.26608026E-04, -1.46402364E-07,  
        1.54100414E-11, -6.88804800E-16, -8.13065581E+02,  
        -1.02432865E+00])),  
  transport=gas_transport(geom='linear',  
    diam=2.19,  
    well_depth=304.69,  
    polar=0.775,  
    rot_relax=280.0))
```

```
species(name='H2O',  
  atoms='H:2 O:1',  
  thermo=(NASA([200.00, 1000.00],  
    [ 4.19863520E+00, -2.03640170E-03, 6.52034160E-06,  
      -5.48792690E-09, 1.77196800E-12, -3.02937260E+04,  
      -8.49009010E-01]),  
    NASA([1000.00, 6000.00],  
      [ 2.67703890E+00, 2.97318160E-03, -7.73768890E-07,  
        9.44335140E-11, -4.26899910E-15, -2.98858940E+04,  
        6.88255000E+00])),  
  transport=gas_transport(geom='nonlinear',  
    diam=2.943,  
    well_depth=637.056,  
    dipole=1.851,  
    polar=1.407,  
    rot_relax=4.0))
```

```
species(name='H2O2',
```

```
atoms='H:2 O:2',
thermo=(NASA([200.00, 1000.00],
  [ 4.31515149E+00, -8.47390622E-04, 1.76404323E-05,
    -2.26762944E-08, 9.08950158E-12, -1.77067437E+04,
    3.27373319E+00]),
  NASA([1000.00, 6000.00],
    [ 4.57977305E+00, 4.05326003E-03, -1.29844730E-06,
      1.98211400E-10, -1.13968792E-14, -1.80071775E+04,
      6.64970694E-01])),
transport=gas_transport(geom='nonlinear',
  diam=3.179,
  well_depth=1361.148,
  dipole=1.702,
  polar=2.239,
  rot_relax=3.8))

species(name='HCO',
atoms='C:1 H:1 O:1',
thermo=(NASA([200.00, 1000.00],
  [ 4.23754610E+00, -3.32075257E-03, 1.40030264E-05,
    -1.34239995E-08, 4.37416208E-12, 3.87241185E+03,
    3.30834869E+00]),
  NASA([1000.00, 6000.00],
    [ 3.92001542E+00, 2.52279324E-03, -6.71004164E-07,
      1.05615948E-10, -7.43798261E-15, 3.65342928E+03,
      3.58077056E+00])),
transport=gas_transport(geom='nonlinear',
  diam=3.59,
  well_depth=498.0))

species(name='HO2',
atoms='H:1 O:2',
thermo=(NASA([200.00, 1000.00],
  [ 4.30179807E+00, -4.74912097E-03, 2.11582905E-05,
    -2.42763914E-08, 9.29225225E-12, 2.64018485E+02,
    3.71666220E+00]),
  NASA([1000.00, 5000.00],
    [ 4.17228741E+00, 1.88117627E-03, -3.46277286E-07,
      1.94657549E-11, 1.76256905E-16, 3.10206839E+01,
      2.95767672E+00])),
transport=gas_transport(geom='nonlinear',
  diam=3.129,
  well_depth=963.003,
  dipole=2.146,
  polar=1.959,
  rot_relax=3.8))

species(name='N2',
atoms='N:2',
thermo=(NASA([200.00, 1000.00],
  [ 3.53100528E+00, -1.23660988E-04, -5.02999433E-07,
```

```
2.43530612E-09, -1.40881235E-12, -1.04697628E+03,  
2.96747038E+00)),  
NASA([1000.00, 6000.00],  
[ 2.95257637E+00, 1.39690040E-03, -4.92631603E-07,  
7.86010195E-11, -4.60755204E-15, -9.23948688E+02,  
5.87188762E+00])),  
transport=gas_transport(geom='linear',  
diam=3.61,  
well_depth=97.839,  
polar=1.756,  
rot_relax=4.0))
```

```
species(name='O',  
atoms='O:1',  
thermo=(NASA([200.00, 1000.00],  
[ 3.16826710E+00, -3.27931884E-03, 6.64306396E-06,  
-6.12806624E-09, 2.11265971E-12, 2.91222592E+04,  
2.05193346E+00])),  
NASA([1000.00, 6000.00],  
[ 2.54363697E+00, -2.73162486E-05, -4.19029520E-09,  
4.95481845E-12, -4.79553694E-16, 2.92260120E+04,  
4.92229457E+00])),  
transport=gas_transport(geom='atom',  
diam=2.485,  
well_depth=235.686,  
polar=0.744))
```

```
species(name='O2',  
atoms='O:2',  
thermo=(NASA([200.00, 1000.00],  
[ 3.78245636E+00, -2.99673416E-03, 9.84730201E-06,  
-9.68129509E-09, 3.24372837E-12, -1.06394356E+03,  
3.65767573E+00])),  
NASA([1000.00, 6000.00],  
[ 3.66096065E+00, 6.56365811E-04, -1.41149627E-07,  
2.05797935E-11, -1.29913436E-15, -1.21597718E+03,  
3.41536279E+00])),  
transport=gas_transport(geom='linear',  
diam=3.069,  
well_depth=676.424,  
polar=1.487,  
rot_relax=3.8))
```

```
species(name='OH',  
atoms='H:1 O:1',  
thermo=(NASA([200.00, 1000.00],  
[ 3.99198424E+00, -2.40106655E-03, 4.61664033E-06,  
-3.87916306E-09, 1.36319502E-12, 3.36889836E+03,  
-1.03998477E-01])),  
NASA([1000.00, 6000.00],  
[ 2.83853033E+00, 1.10741289E-03, -2.94000209E-07,
```

```
4.20698729E-11, -2.42289890E-15, 3.69780808E+03,
5.84494652E+00))),
transport=gas_transport(geom='linear',
    diam=2.582,
    well_depth=514.598,
    dipole=1.635,
    polar=1.077))
#-----
# Reaction data
#-----

# Reaction 1
three_body_reaction('H2 + M <=> H + H + M', [4.577e+19, -1.4, 104400.0],
    efficiencies='CH4:2.0 CO:1.9 CO2:3.8 H2:2.5 H2O:12.0')

# Reaction 2
reaction('O + H2 <=> OH + H', [3.800e+12, 0.0, 7948.0],
    options='duplicate')

# Reaction 3
reaction('O + H2 <=> OH + H', [5.531e+14, -0.021, 21049.2],
    options='duplicate')

# Reaction 4
reaction('H2 + OH <=> H + H2O', [8.468e+7, 1.455, 4406.0])

# Reaction 5
reaction('H + O2 + H <=> H2 + O2', [8.800e+22, -1.835, 800.0])

# Reaction 6
reaction('H + O2 + H <=> OH + OH', [4.000e+22, -1.835, 800.0])

# Reaction 7
reaction('H + O2 + O <=> OH + O2', [7.350e+22, -1.835, 800.0])

# Reaction 8
reaction('H + O2 + OH <=> H2O + O2', [2.560e+22, -1.835, 800.0])

# Reaction 9
three_body_reaction('O + O + M <=> O2 + M', [6.165e+15, -0.5, 0.0],
    efficiencies='CH4:2.0 CO:1.9 CO2:3.8 H2:2.5 H2O:12.0')

# Reaction 10
pdep_arrhenius('O2 + H <=> O + OH',
    [(1.00, 'atm'), 7.559e+14, 0.025, 15977.7],
    [(10.00, 'atm'), 2.65e+16, 0.023, 30724.0],
    [(40.00, 'atm'), 2.63e+17, 0.020, 42330.2])

# Reaction 11
falloff_reaction('H + OH (+ M) <=> H2O (+ M)',
    kf=[2.500e+13, 0.234, -114.0],
```

```
kf0=[2.580e+22, -1.887, 512.8],  
efficiencies='H2:1.5 H2O:13.0 N2:1.0 O2:1.0',  
falloff=Troe(A=0.73, T3=1e-30, T1=1e+30, T2=1e+30))
```

```
# Reaction 12
```

```
reaction('OH + OH <=> H2O + O', [2.226e+05, 1.875, -1477.1])
```

```
# Reaction 13
```

```
three_body_reaction('O + H + M <=> OH + M', [4.714e+18, -1.0, 0.0],  
    efficiencies='CH4:2.0 CO:1.5 CO2:2.0 H2:2.5 H2O:12.0')
```

```
# Reaction 14
```

```
falloff_reaction('H2O2 (+ M) <=> OH + OH (+ M)',  
    kf=[2.000e+12, 0.9, 48749.0],  
    kf0=[2.353e+24, -2.293, 48743.4],  
    efficiencies='CO:2.8 CO2:1.06 H2:3.7 H2O:5.1 H2O2:5.2 N2:1.5 O2:0.79',  
    falloff=Troe(A=0.43, T3=1e-30, T1=1e+30))
```

```
# Reaction 15
```

```
reaction('H2O2 + H <=> H2O + OH', [2.410e+13, 0.0, 3970.0])
```

```
# Reaction 16
```

```
reaction('H2O2 + H <=> HO2 + H2', [5.020e+06, 2.07, 4300.0])
```

```
# Reaction 17
```

```
reaction('H2O2 + O <=> OH + HO2', [9.550e+06, 2.0, 3970.0])
```

```
# Reaction 18
```

```
reaction('H2O2 + OH <=> H2O + HO2', [1.740e+12, 0.0, 318.0],  
    options='duplicate')
```

```
# Reaction 19
```

```
reaction('H2O2 + OH <=> H2O + HO2', [7.590e+13, 0.0, 7269.0],  
    options='duplicate')
```

```
# Reaction 20
```

```
reaction('HO2 + H <=> H2 + O2', [3.259e+05, 2.055, -1896.6])
```

```
# Reaction 21
```

```
reaction('HO2 + H <=> OH + OH', [3.529e+14, -0.009, 382.6])
```

```
# Reaction 22
```

```
reaction('HO2 + O <=> OH + O2', [3.553e+12, -0.012, -0.02])
```

```
# Reaction 23
```

```
reaction('OH + HO2 <=> H2O + O2', [1.930e+20, -2.49, 584.2],  
    options='duplicate')
```

```
# Reaction 24
```

```
reaction('OH + HO2 <=> H2O + O2', [8.766e+7, 1.195, -1319.5],  
    options='duplicate')
```

```
# Reaction 25
reaction('HO2 + HO2 <=> H2O2 + O2', [1.214e+10, 0.422, -1480.5],
        options='duplicate')

# Reaction 26
reaction('HO2 + HO2 <=> H2O2 + O2', [2.365e+16, -0.732, 20003.5],
        options='duplicate')

# Reaction 27
falloff_reaction('H + O2 (+ M) <=> HO2 (+ M)',
                kf=[4.660e+12, 0.44, 0.0],
                kf0=[7.521e+20, -1.140, -0.02],
                efficiencies='CH4:2.0 CO2:3.25 H2:1.35 H2O:16.6 N2:1.0 O2:0.9',
                falloff=Troe(A=0.5, T3=1.0, T1=10000000000.0))

# Reaction 28
falloff_reaction('CO + O (+ M) <=> CO2 (+ M)',
                kf=[1.362e+10, 0.0, 2384.0],
                kf0=[1.173e+24, -2.79, 4191.0],
                efficiencies='CO:1.75 CO2:3.6 H2:2.0 H2O:12.0')

# Reaction 29
pdep_arrhenius('CO + OH <=> CO2 + H',
               [(0.01315, 'atm'), 2.100e+05, 1.9, -1064.0],
               [(0.1315, 'atm'), 2.500e+05, 1.88, -1043.0],
               [(1.315, 'atm'), 8.700e+05, 1.73, -685.0],
               [(13.158, 'atm'), 5.812e+7, 1.271, 28.6],
               [(131.58, 'atm'), 2.300e+07, 1.35, 974.0])

# Reaction 30
reaction('CO + HO2 <=> CO2 + OH', [8.550e+03, 2.52, 15560.0])

# Reaction 31
reaction('CO + O2 <=> CO2 + O', [1.119e+12, 0.0, 47700.0])

# Reaction 32
falloff_reaction('CH3 + H (+ M) <=> CH4 (+ M)',
                kf=[6.470e+13, 0.185, -54.0],
                kf0=[4.910e+37, -5.815, 907.6],
                efficiencies='CH4:5.0 CO:2.3 CO2:4.0 H2:4.0 H2O:12.0 N2:1.5 O2:1.5',
                falloff=Troe(A=0.516194, T3=3637.8482, T1=1.0, T2=1e+30))

# Reaction 33
reaction('CH4 + H <=> CH3 + H2', [1.625e+03, 3.609, 8818.5])

# Reaction 34
reaction('CH4 + O <=> CH3 + OH', [5.172749e+6, 2.409, 9236.5])

# Reaction 35
reaction('CH4 + OH <=> CH3 + H2O', [1.944e+8, 1.747, 3369.3])
```

Reaction 36

reaction('CH4 + HO2 <=> CH3 + H2O2', [3.122e-01, 2.975, 12865.3])

Reaction 37

reaction('CH3 + HO2 <=> CH4 + O2', [3.185e+02, 2.421, -3089.6])

Reaction 38

pdep_arrhenius('CH3 + O2 <=> CH2O + OH',
[(1.00, 'atm'), 0.0125, 4.125, 18761.8],
[(10.00, 'atm'), 2.882, 3.346, 15266.3],
[(40.00, 'atm'), 2.109, 3.644, 19400.7])

Reaction 39

reaction('CH3 + O <=> CH2O + H', [4.875e+13, 0.048, -150.9])

Reaction 40

pdep_arrhenius('CH3 + OH <=> CH2O + H2',
[(0.01, 'atm'), 3.502e+05, 1.441, -3244.0],
[(0.1, 'atm'), 8.854e+05, 1.327, -2975.0],
[(1.0, 'atm'), 1.650e+07, 0.973, -2010.0],
[(10.0, 'atm'), 2.943e+9, 0.285, 245.2],
[(100.0, 'atm'), 9.494e+18, -2.199, 9769.0])

Reaction 41

falloff_reaction('HCO + H (+ M) <=> CH2O (+ M)',
kf=[1.090e+12, 0.48, -260.0],
kf0=[1.350e+24, -2.57, 1425.0],
falloff=Troe(A=0.7824, T3=271.0, T1=2755.0, T2=6570.0))

Reaction 42

falloff_reaction('CO + H2 (+ M) <=> CH2O (+ M)',
kf=[4.300e+07, 1.5, 79600.0],
kf0=[5.070e+27, -3.42, 84348.0],
falloff=Troe(A=0.932, T3=197.0, T1=1540.0, T2=10300.0))

Reaction 43

reaction('CH2O + O2 <=> HCO + HO2', [1.760e+17, 0.017, 35587.6])

Reaction 44

reaction('CH2O + O <=> HCO + OH', [2.313e+09, 1.035, 1816.5])

Reaction 45

reaction('CH2O + H <=> HCO + H2', [4.069e+03, 2.717, 1963.4])

Reaction 46

reaction('CH2O + OH <=> HCO + H2O', [2.422e+11, 0.982, -503.3])

Reaction 47

reaction('CH2O + HO2 <=> HCO + H2O2', [2.632e-10, 4.342, 4465.8])

Reaction 48

reaction('CH2O + CH3 <=> HCO + CH4', [3.430e-05, 4.344, 3216.4])

Reaction 49

reaction('CH2O + OH => H + CO + H2O', [2.565e+11, 0.693, 9368.7])

Reaction 50

reaction('CH2O + H => H + CO + H2', [1.940e+07, 2.192, 11740.3])

Reaction 51

three_body_reaction('HCO + M <=> H + CO + M', [8.993e+11, 0.691, 14221.72],
efficiencies='CH4:2.0 CO:1.5 CO2:2.0 H2:2.0 H2O:6.0')

Reaction 52

reaction('HCO + O2 <=> CO + HO2', [7.567e+04, 0.765, -412.1383])

Reaction 53

reaction('HCO + O <=> CO + OH', [3.020e+13, 0.0, 0.0])

Reaction 54

reaction('HCO + H <=> CO + H2', [1.121e+12, 0.385, -144.4])

Reaction 55

reaction('HCO + OH <=> CO + H2O', [1.196e+13, 0.019, -0.013])

Reaction 56

reaction('HCO + CH3 <=> CO + CH4', [1.423e+12, -0.017, -0.014])

Reaction 57

reaction('HCO + HCO <=> CO + CH2O', [2.700e+13, 0.0, 0.0])

Reaction 58

reaction('HCO + O <=> CO2 + H', [3.000e+13, 0.0, 0.0])

Reaction 59

reaction('HCO + HO2 => CO2 + H + OH', [3.000e+13, 0.0, 0.0])

Reaction 60

reaction('HCO + HCO => H2 + CO + CO', [3.000e+12, 0.0, 0.0])

Appendix E

15sOp_NOx Validation

For more comprehensive validation, please see [172].

1. Constant UV: Ignition Delay Time

15sOp_NOx has identical IDT calculations to the NUIGMECH_15sOp model across the performance conditions (Table 6.1).

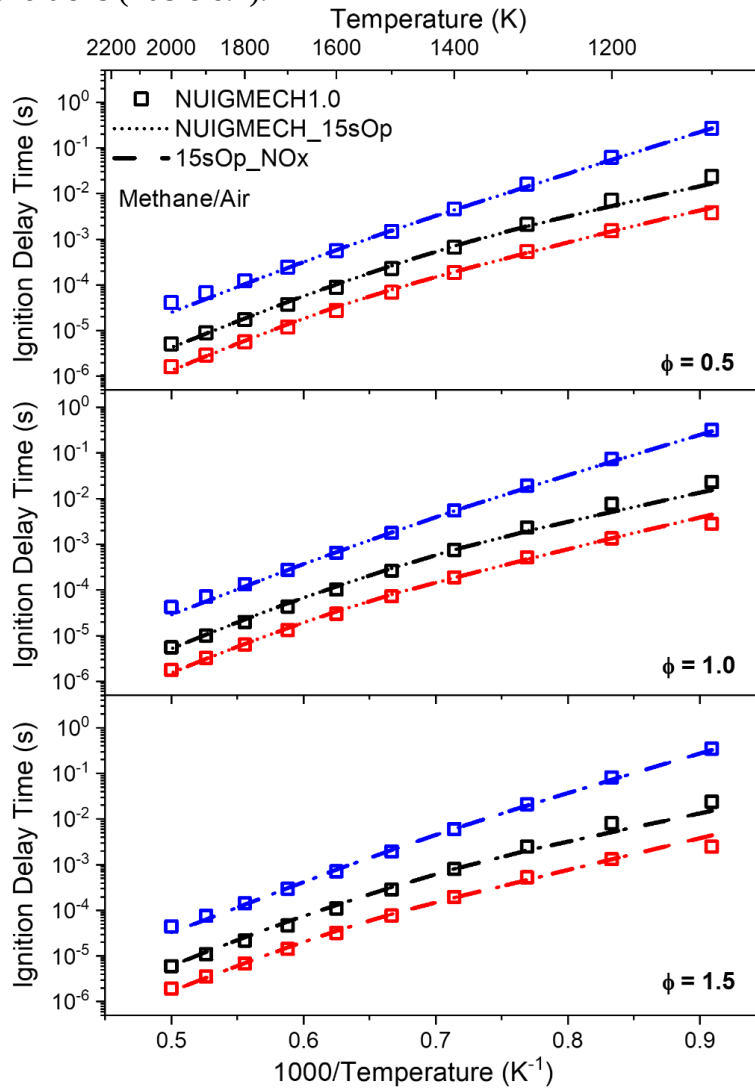


Figure E.1. Ignition delay time as a function of temperature for lean, stoichiometric, and rich methane/air mixtures at 1, 10 and 40 atm using the NUIGMECH1.0 detailed model (symbols), NUIGMECH_15sOp (dot lines) and 15sOp_NOx (dash lines). 15sOp_NOx and NUIGMECH_15sOp identical IDT calculations.

2. Perfectly Stirred Reactor: Speciation

Mole fractions of NO are used as validation for 15sOp_NOx models. The compact model has a good replication across the performance conditions (Table 6.1). The performance of the compact model decreases at 1200 K. Representative temperature and equivalence ratio conditions are used here.

1200 K:

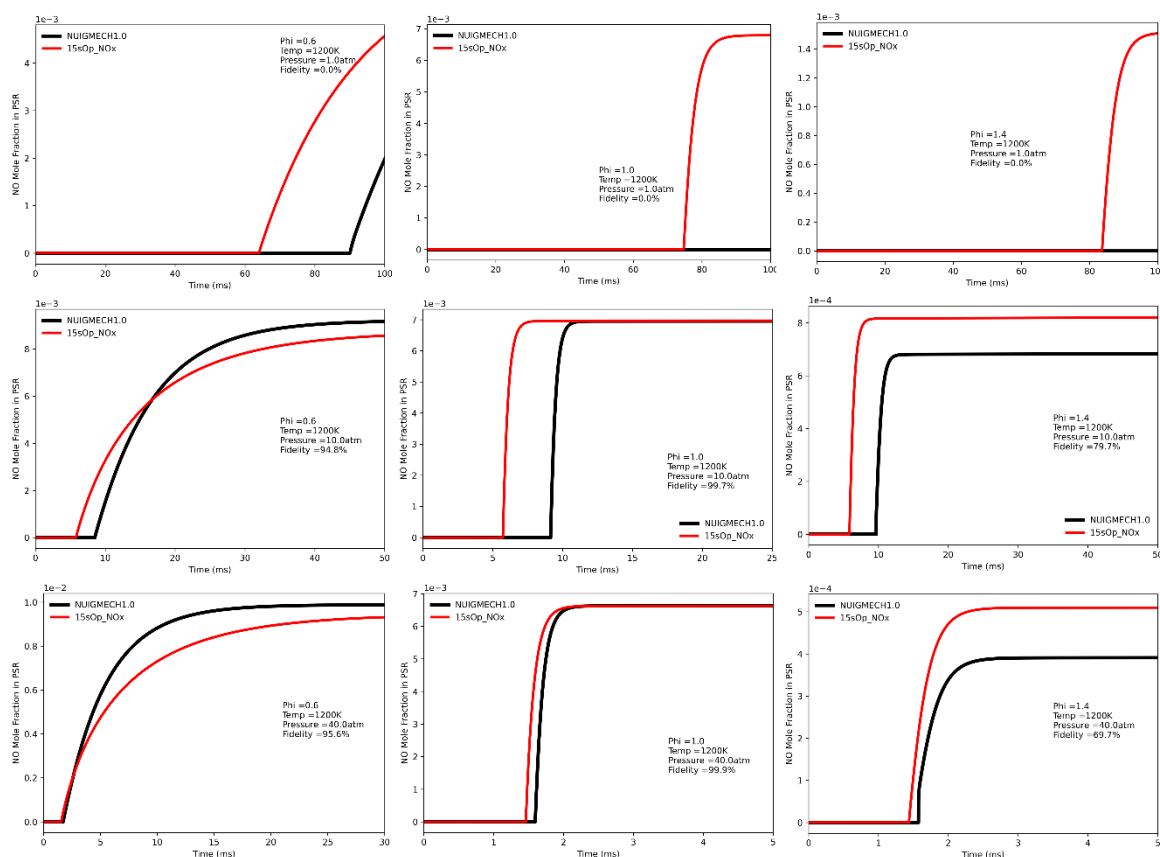


Figure E.2. CO mole fractions in PSR simulations at 1200 K using NUIGMECH1.0 detailed model (black) and 15sOp_NOx (red). Equivalence ratios 0.6 (left), 1.0 (middle) and 1.4 (right). 15sOp_NOx has a decent replication of detailed model NO mole fractions.

1600 K:

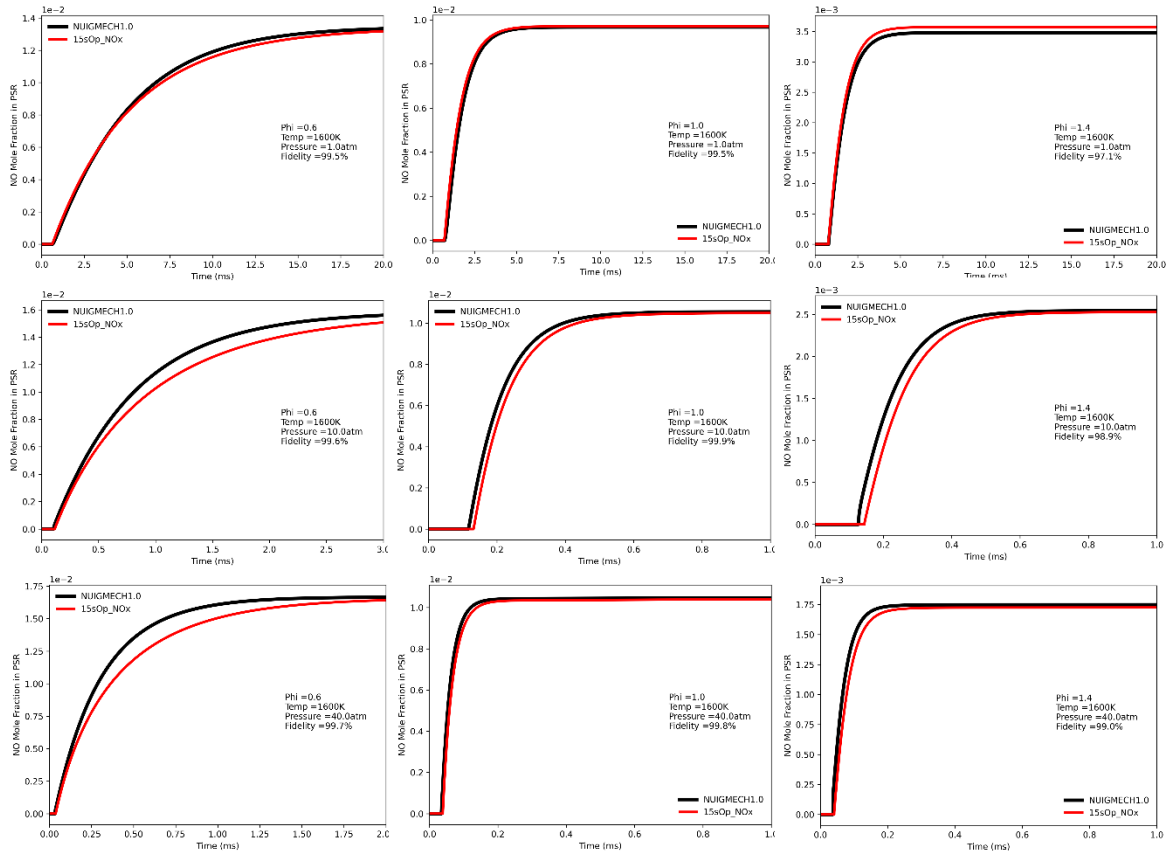


Figure E.3. CO mole fractions in PSR simulations at 1600 K using NUIGMECH1.0 detailed model (black) and 15sOp_NOx (red). Equivalence ratios 0.6 (left), 1.0 (middle) and 1.4 (right). 15sOp_NOx has a decent replication of detailed model NO mole fractions.

2000 K:

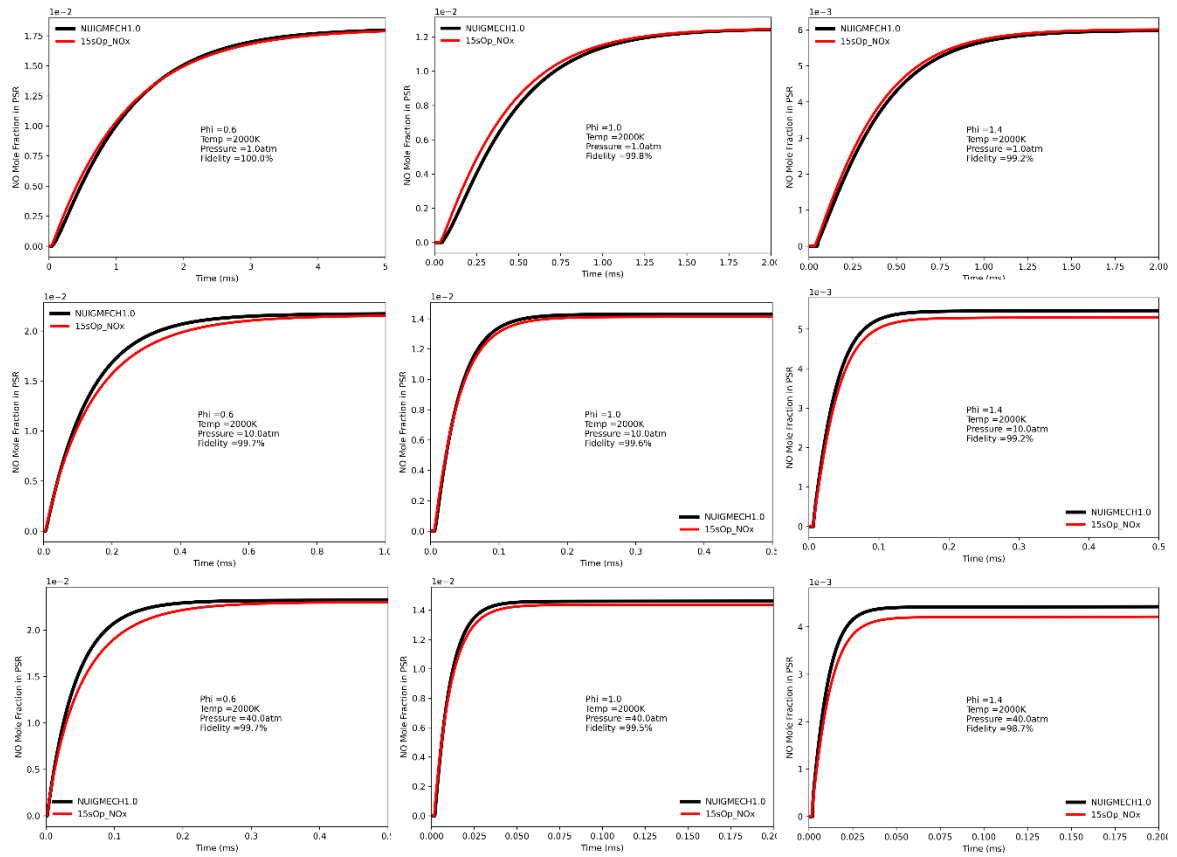


Figure E.4. CO mole fractions in PSR simulations at 2000 K using NUIGMECH1.0 detailed model (black) and 15sOp_NOx (red). Equivalence ratios 0.6 (left), 1.0 (middle) and 1.4 (right). 15sOp_NOx has a decent replication of detailed model NO mole fractions.

3. Freely Propagating Flame: Laminar Burning Velocity

C3_19sOp has excellent fidelity across the complete performance conditions (Table 5.1). C3_15sOp has a good fidelity however the performance decreases at 1 atm.

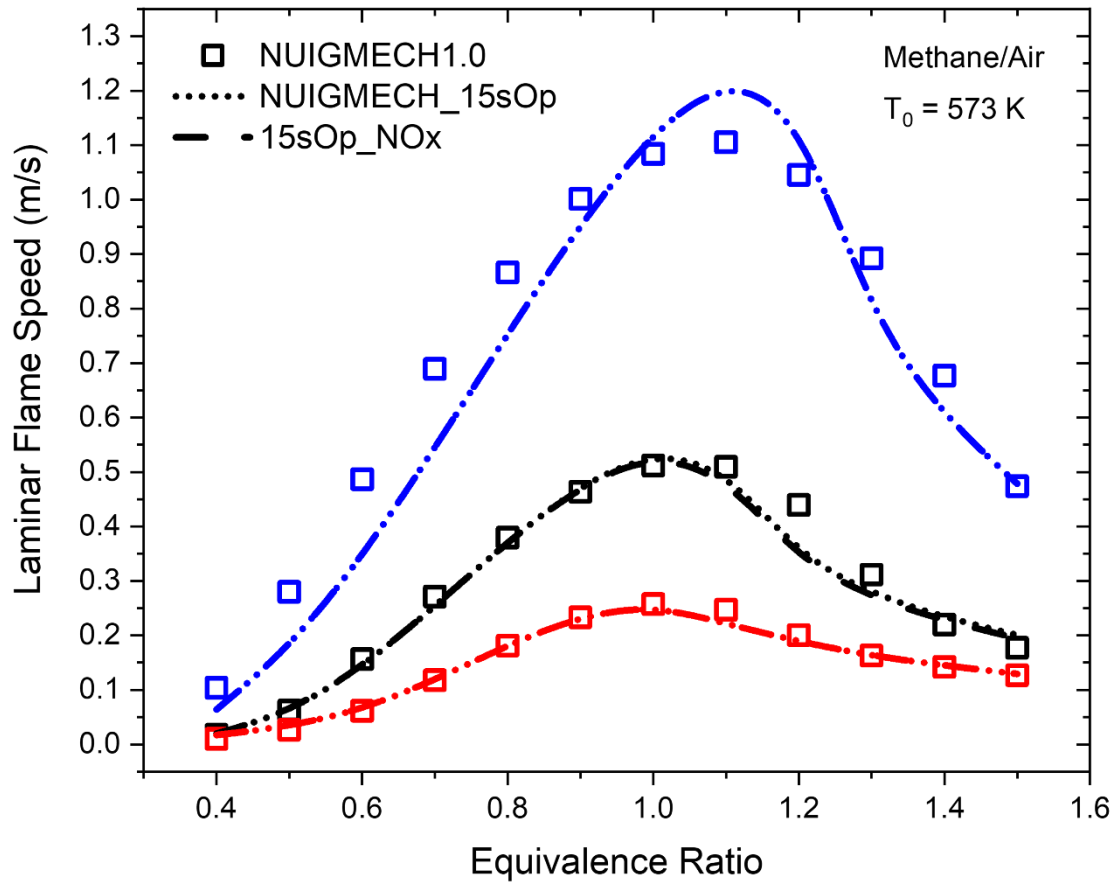


Figure E.5. Laminar burning velocity as a function of equivalence ratio at 1, 10 and 40 atm using the NUIGMECH1.0 detailed model (symbols), NUIGMECH_15sOp (dot lines) and 15sOp_NOx (dash lines). 15sOp_NOx and NUIGMECH_15sOp identical laminar burning velocity calculations.

4. Freely Propagating Flame: Speciation

The compact model has a good replication of detailed model NO and NO₂ mole fractions at lean and rich conditions, however fidelity deteriorates at rich conditions as described in text. Representative temperature and equivalence ratio conditions are used here.

NO:

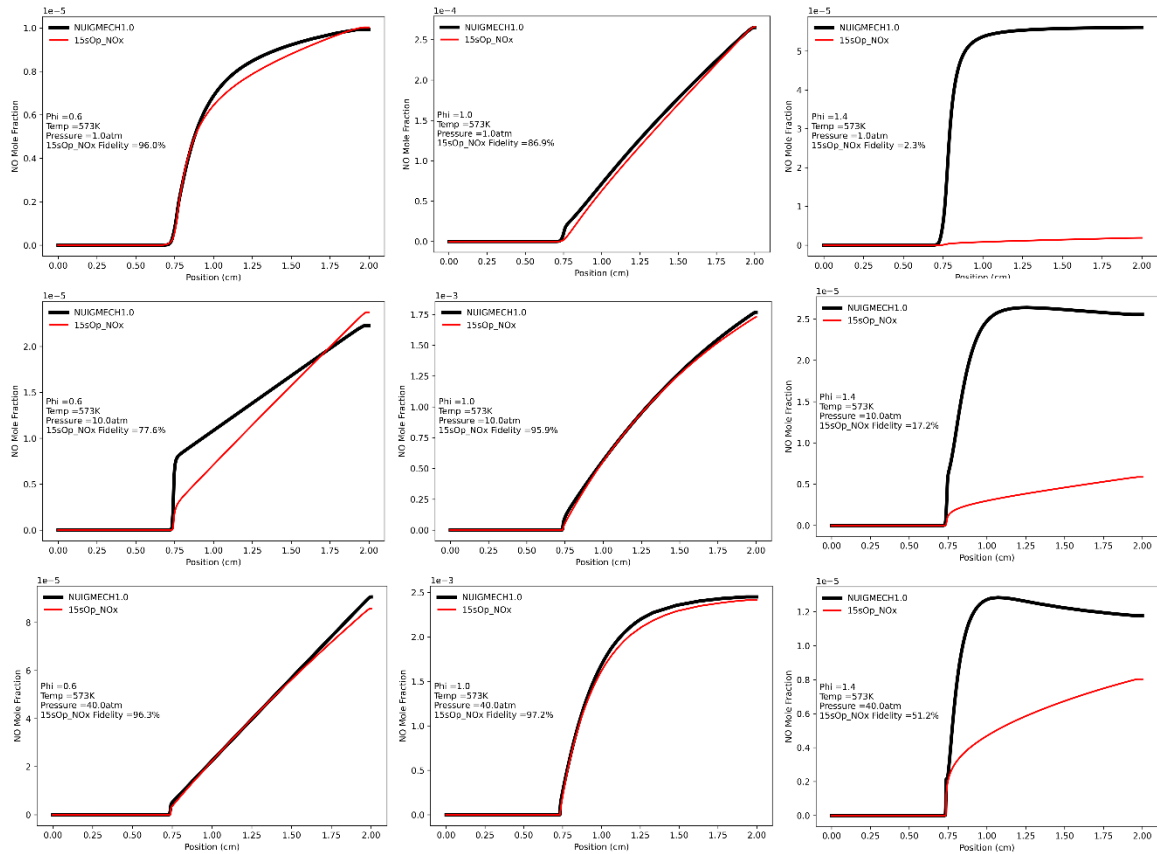


Figure E.6. NO mole fractions in freely propagating flame simulations at 573 K using NUIGMECH1.0 detailed model (black) and 15sOp_NOx (red). Equivalence ratios 0.6 (left), 1.0 (middle) and 1.4 (right). The compact model has a good replication of detailed model NO mole fractions at lean and rich conditions, however fidelity deteriorates at rich conditions as described in text.

NO₂:

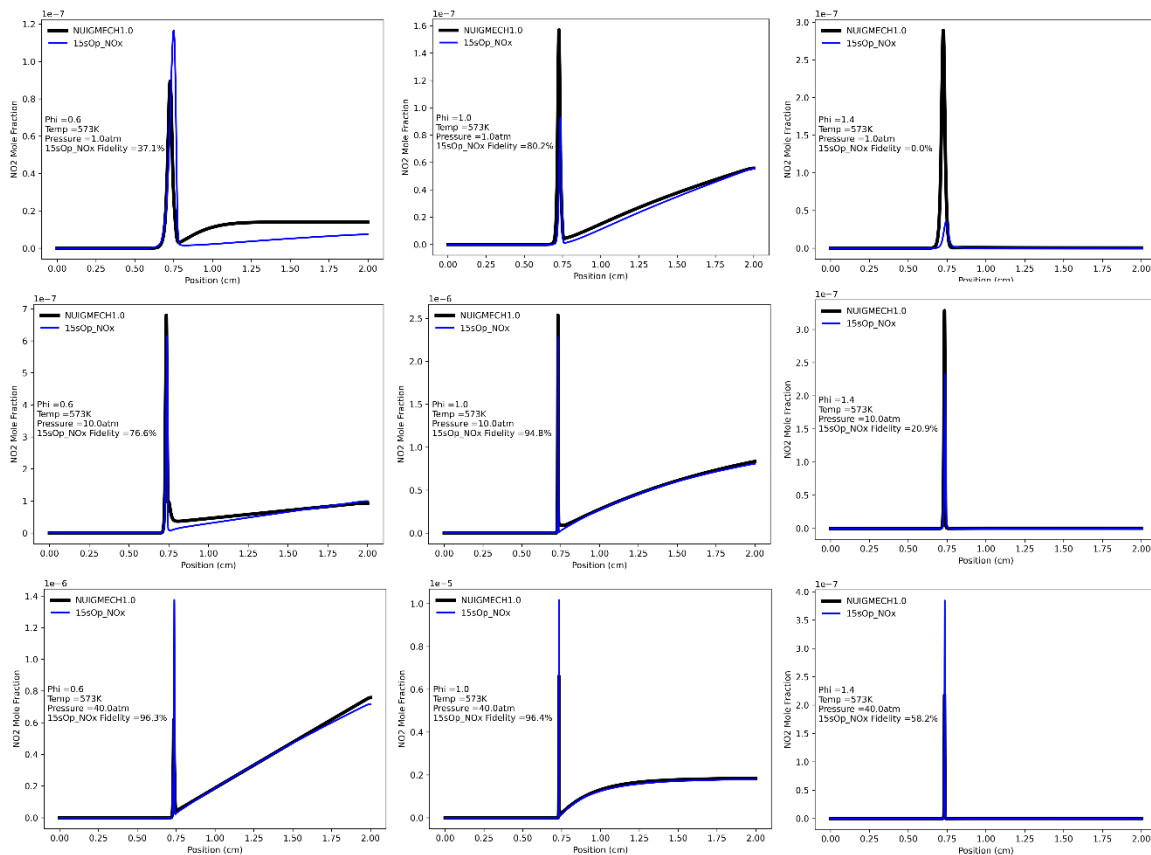


Figure E.7. NO₂ mole fractions in freely propagating flame simulations at 573 K using NUIGMECH1.0 detailed model (black) and 15sOp_NOx (red). Equivalence ratios 0.6 (left), 1.0 (middle) and 1.4 (right). The compact model has a good replication of detailed model NO₂ mole fractions at lean and rich conditions, however fidelity decreases at rich conditions as described in text.

Appendix F

15sOp_NOx, 15sOp_NOx_1 and 15sOp_NOx_2 Files

15sOp_NOx Cantera File:

```
units(length='cm', time='s', quantity='mol', act_energy='cal/mol')

ideal_gas(name='gas',
  elements="C H N O",
  species="""CH2O CH3 CH4 CO CO2 H H2 H2O H2O2
          HCO HO2 N2 O O2 OH N NO NO2""",
  reactions='all',
  transport='Mix',
  initial_state=state(temperature=300.0, pressure=OneAtm))

#-----
# Species data
#-----

species(name='CH2O',
  atoms='C:1 H:2 O:1',
  thermo=(NASA([200.00, 1000.00],
    [ 4.79372312E+00, -9.90833322E-03, 3.73219990E-05,
      -3.79285237E-08, 1.31772641E-11, -1.43791953E+04,
      6.02798058E-01]),
    NASA([1000.00, 6000.00],
      [ 3.16952665E+00, 6.19320560E-03, -2.25056366E-06,
        3.65975660E-10, -2.20149458E-14, -1.45486831E+04,
        6.04207898E+00])),
  transport=gas_transport(geom='nonlinear',
    diam=3.59,
    well_depth=498.0,
    rot_relax=2.0),
  note='T5/11')

species(name='CH3',
  atoms='C:1 H:3',
  thermo=(NASA([200.00, 1000.00],
    [ 3.65717970E+00, 2.12659790E-03, 5.45838830E-06,
      -6.61810030E-09, 2.46570740E-12, 1.64227160E+04,
```

```
1.67353540E+00]),  
NASA([1000.00, 6000.00],  
[ 2.97812060E+00, 5.79785200E-03, -1.97558000E-06,  
3.07297900E-10, -1.79174160E-14, 1.65095130E+04,  
4.72247990E+00])),  
transport=gas_transport(geom='linear',  
diam=3.8,  
well_depth=144.0),  
note='IU0702')
```

```
species(name='CH4',  
atoms='C:1 H:4',  
thermo=(NASA([200.00, 1000.00],  
[ 5.14911468E+00, -1.36622009E-02, 4.91453921E-05,  
-4.84246767E-08, 1.66603441E-11, -1.02465983E+04,  
-4.63848842E+00]),  
NASA([1000.00, 6000.00],  
[ 1.65326226E+00, 1.00263099E-02, -3.31661238E-06,  
5.36483138E-10, -3.14696758E-14, -1.00095936E+04,  
9.90506283E+00])),  
transport=gas_transport(geom='nonlinear',  
diam=3.746,  
well_depth=141.4,  
polar=2.6,  
rot_relax=13.0),  
note='G8/99')
```

```
species(name='CO',  
atoms='C:1 O:1',  
thermo=(NASA([200.00, 1000.00],  
[ 3.57953350E+00, -6.10353690E-04, 1.01681430E-06,  
9.07005860E-10, -9.04424490E-13, -1.43440860E+04,  
3.50840930E+00]),  
NASA([1000.00, 6000.00],  
[ 3.04848590E+00, 1.35172810E-03, -4.85794050E-07,  
7.88536440E-11, -4.69807460E-15, -1.42661170E+04,  
6.01709770E+00])),  
transport=gas_transport(geom='linear',  
diam=3.65,  
well_depth=98.1,  
polar=1.95,  
rot_relax=1.8),  
note='RUS79')
```

```
species(name='CO2',  
atoms='C:1 O:2',  
thermo=(NASA([200.00, 1000.00],  
[ 2.35681300E+00, 8.98412990E-03, -7.12206320E-06,  
2.45730080E-09, -1.42885480E-13, -4.83719710E+04,  
9.90090350E+00]),  
NASA([1000.00, 6000.00],
```

```
[ 4.63651110E+00, 2.74145690E-03, -9.95897590E-07,
 1.60386660E-10, -9.16198570E-15, -4.90249040E+04,
-1.93489550E+00)),
transport=gas_transport(geom='linear',
    diam=3.763,
    well_depth=244.0,
    polar=2.65,
    rot_relax=2.1),
note='L7/88')

species(name='H',
    atoms='H:1',
    thermo=(NASA([200.00, 1000.00],
        [ 2.50000000E+00, 0.00000000E+00, 0.00000000E+00,
          0.00000000E+00, 0.00000000E+00, 2.54736600E+04,
          -4.46682850E-01]),
        NASA([1000.00, 6000.00],
            [ 2.50000000E+00, 0.00000000E+00, 0.00000000E+00,
              0.00000000E+00, 0.00000000E+00, 2.54736600E+04,
              -4.46682850E-01])),
    transport=gas_transport(geom='atom',
        diam=1.53,
        well_depth=541.672,
        polar=0.666),
    note='L6/94')

species(name='H2',
    atoms='H:2',
    thermo=(NASA([200.00, 1000.00],
        [ 2.34433112E+00, 7.98052075E-03, -1.94781510E-05,
          2.01572094E-08, -7.37611761E-12, -9.17935173E+02,
          6.83010238E-01]),
        NASA([1000.00, 6000.00],
            [ 2.93286575E+00, 8.26608026E-04, -1.46402364E-07,
              1.54100414E-11, -6.88804800E-16, -8.13065581E+02,
              -1.02432865E+00])),
    transport=gas_transport(geom='linear',
        diam=2.19,
        well_depth=304.69,
        polar=0.775,
        rot_relax=280.0),
    note='TPIS78')

species(name='H2O',
    atoms='H:2 O:1',
    thermo=(NASA([200.00, 1000.00],
        [ 4.19863520E+00, -2.03640170E-03, 6.52034160E-06,
          -5.48792690E-09, 1.77196800E-12, -3.02937260E+04,
          -8.49009010E-01]),
        NASA([1000.00, 6000.00],
            [ 2.67703890E+00, 2.97318160E-03, -7.73768890E-07,
```

```
9.44335140E-11, -4.26899910E-15, -2.98858940E+04,  
6.88255000E+00]]),  
transport=gas_transport(geom='nonlinear',  
    diam=2.943,  
    well_depth=637.056,  
    dipole=1.851,  
    polar=1.407,  
    rot_relax=4.0),  
note='L5/89')
```

```
species(name='H2O2',  
    atoms='H:2 O:2',  
    thermo=(NASA([200.00, 1000.00],  
        [ 4.31515149E+00, -8.47390622E-04, 1.76404323E-05,  
        -2.26762944E-08, 9.08950158E-12, -1.77067437E+04,  
        3.27373319E+00])),  
        NASA([1000.00, 6000.00],  
            [ 4.57977305E+00, 4.05326003E-03, -1.29844730E-06,  
            1.98211400E-10, -1.13968792E-14, -1.80071775E+04,  
            6.64970694E-01])),  
    transport=gas_transport(geom='nonlinear',  
        diam=3.179,  
        well_depth=1361.148,  
        dipole=1.702,  
        polar=2.239,  
        rot_relax=3.8),  
    note='T8/03')
```

```
species(name='HCO',  
    atoms='C:1 H:1 O:1',  
    thermo=(NASA([200.00, 1000.00],  
        [ 4.23754610E+00, -3.32075257E-03, 1.40030264E-05,  
        -1.34239995E-08, 4.37416208E-12, 3.87241185E+03,  
        3.30834869E+00])),  
        NASA([1000.00, 6000.00],  
            [ 3.92001542E+00, 2.52279324E-03, -6.71004164E-07,  
            1.05615948E-10, -7.43798261E-15, 3.65342928E+03,  
            3.58077056E+00])),  
    transport=gas_transport(geom='nonlinear',  
        diam=3.59,  
        well_depth=498.0),  
    note='T5/03')
```

```
species(name='HO2',  
    atoms='H:1 O:2',  
    thermo=(NASA([200.00, 1000.00],  
        [ 4.30179807E+00, -4.74912097E-03, 2.11582905E-05,  
        -2.42763914E-08, 9.29225225E-12, 2.64018485E+02,  
        3.71666220E+00])),  
        NASA([1000.00, 5000.00],  
            [ 4.17228741E+00, 1.88117627E-03, -3.46277286E-07,
```

```
1.94657549E-11, 1.76256905E-16, 3.10206839E+01,
2.95767672E+00))),
transport=gas_transport(geom='nonlinear',
    diam=3.129,
    well_depth=963.003,
    dipole=2.146,
    polar=1.959,
    rot_relax=3.8),
note='T1/09')

species(name='N2',
    atoms='N:2',
    thermo=(NASA([200.00, 1000.00],
        [ 3.53100528E+00, -1.23660988E-04, -5.02999433E-07,
          2.43530612E-09, -1.40881235E-12, -1.04697628E+03,
          2.96747038E+00])),
        NASA([1000.00, 6000.00],
            [ 2.95257637E+00, 1.39690040E-03, -4.92631603E-07,
              7.86010195E-11, -4.60755204E-15, -9.23948688E+02,
              5.87188762E+00])),
    transport=gas_transport(geom='linear',
        diam=3.61,
        well_depth=97.839,
        polar=1.756,
        rot_relax=4.0),
    note='G8/02')

species(name='O',
    atoms='O:1',
    thermo=(NASA([200.00, 1000.00],
        [ 3.16826710E+00, -3.27931884E-03, 6.64306396E-06,
          -6.12806624E-09, 2.11265971E-12, 2.91222592E+04,
          2.05193346E+00])),
        NASA([1000.00, 6000.00],
            [ 2.54363697E+00, -2.73162486E-05, -4.19029520E-09,
              4.95481845E-12, -4.79553694E-16, 2.92260120E+04,
              4.92229457E+00])),
    transport=gas_transport(geom='atom',
        diam=2.485,
        well_depth=235.686,
        polar=0.744),
    note='L1/90')

species(name='O2',
    atoms='O:2',
    thermo=(NASA([200.00, 1000.00],
        [ 3.78245636E+00, -2.99673416E-03, 9.84730201E-06,
          -9.68129509E-09, 3.24372837E-12, -1.06394356E+03,
          3.65767573E+00])),
        NASA([1000.00, 6000.00],
            [ 3.66096065E+00, 6.56365811E-04, -1.41149627E-07,
```

```
2.05797935E-11, -1.29913436E-15, -1.21597718E+03,  
3.41536279E+00]]),  
transport=gas_transport(geom='linear',  
    diam=3.069,  
    well_depth=676.424,  
    polar=1.487,  
    rot_relax=3.8),  
note='RUS89')
```

```
species(name='OH',  
    atoms='H:1 O:1',  
    thermo=(NASA([200.00, 1000.00],  
        [ 3.99198424E+00, -2.40106655E-03, 4.61664033E-06,  
        -3.87916306E-09, 1.36319502E-12, 3.36889836E+03,  
        -1.03998477E-01]),  
        NASA([1000.00, 6000.00],  
            [ 2.83853033E+00, 1.10741289E-03, -2.94000209E-07,  
            4.20698729E-11, -2.42289890E-15, 3.69780808E+03,  
            5.84494652E+00])),  
    transport=gas_transport(geom='linear',  
        diam=2.582,  
        well_depth=514.598,  
        dipole=1.635,  
        polar=1.077),  
    note='IU3/03')
```

```
species(name='N',  
    atoms='N:1',  
    thermo=(NASA([200.00, 1000.00],  
        [ 2.49976643E+00, 5.02149594E-07, 1.93091211E-09,  
        -4.94632629E-12, 2.74089506E-15, 5.60760710E+04,  
        4.19499326E+00]),  
        NASA([1000.00, 6000.00],  
            [ 2.41604245E+00, 1.74663766E-04, -1.18864562E-07,  
            3.01850054E-11, -2.03260159E-15, 5.61051512E+04,  
            4.64905706E+00])),  
    transport=gas_transport(geom='atom',  
        diam=3.298,  
        well_depth=71.4),  
    note='ATcT3E')
```

```
species(name='NO',  
    atoms='N:1 O:1',  
    thermo=(NASA([298.15, 1000.00],  
        [ 4.15036687E+00, -4.08890008E-03, 9.38071726E-06,  
        -7.50908901E-09, 2.11742798E-12, 9.77018679E+03,  
        2.53971032E+00]),  
        NASA([1000.00, 3000.00],  
            [ 2.79462839E+00, 2.12260586E-03, -1.11936971E-06,  
            2.79521018E-10, -2.68625363E-14, 1.00019069E+04,  
            8.88322674E+00])),  
    transport=gas_transport(geom='linear',  
        diam=3.069,  
        well_depth=676.424,  
        polar=1.487,  
        rot_relax=3.8),  
    note='RUS89')
```

```

        transport=gas_transport(geom='linear',
                                diam=3.339,
                                well_depth=139.32,
                                dipole=0.2,
                                polar=1.76,
                                rot_relax=4.0))

species(name='NO2',
        atoms='N:1 O:2',
        thermo=(NASA([298.15, 1000.00],
                      [ 3.39100918E+00, 2.62448348E-03, 5.09790306E-06,
                        -7.62120493E-09, 2.79960135E-12, 2.78130679E+03,
                        8.57220275E+00]),
                NASA([1000.00, 3000.00],
                      [ 3.65239279E+00, 4.71632310E-03, -2.74591748E-06,
                        7.45382834E-10, -7.63891108E-14, 2.57216137E+03,
                        6.52683440E+00])),
        transport=gas_transport(geom='nonlinear',
                                diam=3.852,
                                well_depth=333.59,
                                dipole=0.4,
                                rot_relax=1.0))

#-----
# Reaction data
#-----

# Reaction 1
three_body_reaction('H2 + M <=> H + H + M', [4.577e+19, -1.4, 104400.0],
                    efficiencies='CH4:2.0 CO:1.9 CO2:3.8 H2:2.5 H2O:12.0')

# Reaction 2
reaction('O + H2 <=> OH + H', [3.800e+12, 0.0, 7948.0],
        options='duplicate')

# Reaction 3
reaction('O + H2 <=> OH + H', [5.531e+14, -0.021, 21049.2],
        options='duplicate')

# Reaction 4
reaction('H2 + OH <=> H + H2O', [8.468e+7, 1.455, 4406.0])

# Reaction 5
reaction('H + O2 + H <=> H2 + O2', [8.800e+22, -1.835, 800.0])

# Reaction 6
reaction('H + O2 + H <=> OH + OH', [4.000e+22, -1.835, 800.0])

# Reaction 7
reaction('H + O2 + O <=> OH + O2', [7.350e+22, -1.835, 800.0])

```

Reaction 8

reaction('H + O2 + OH <=> H2O + O2', [2.560e+22, -1.835, 800.0])

Reaction 9

three_body_reaction('O + O + M <=> O2 + M', [6.165e+15, -0.5, 0.0],
efficiencies='CH4:2.0 CO:1.9 CO2:3.8 H2:2.5 H2O:12.0')

Reaction 10

pdep_arrhenius('O2 + H <=> O + OH',
[(1.00, 'atm'), 7.559e+14, 0.025, 15977.7],
[(10.00, 'atm'), 2.65e+16, 0.023, 30724.0],
[(40.00, 'atm'), 2.63e+17, 0.020, 42330.2])

Reaction 11

falloff_reaction('H + OH (+ M) <=> H2O (+ M)',
kf=[2.500e+13, 0.234, -114.0],
kf0=[2.580e+22, -1.887, 512.8],
efficiencies='H2:1.5 H2O:13.0 N2:1.0 O2:1.0',
falloff=Troe(A=0.73, T3=1e-30, T1=1e+30, T2=1e+30))

Reaction 12

reaction('OH + OH <=> H2O + O', [2.226e+05, 1.875, -1477.1])

Reaction 13

three_body_reaction('O + H + M <=> OH + M', [4.714e+18, -1.0, 0.0],
efficiencies='CH4:2.0 CO:1.5 CO2:2.0 H2:2.5 H2O:12.0')

Reaction 14

falloff_reaction('H2O2 (+ M) <=> OH + OH (+ M)',
kf=[2.000e+12, 0.9, 48749.0],
kf0=[2.353e+24, -2.293, 48743.4],
efficiencies='CO:2.8 CO2:1.06 H2:3.7 H2O:5.1 H2O2:5.2 N2:1.5 O2:0.79',
falloff=Troe(A=0.43, T3=1e-30, T1=1e+30))

Reaction 15

reaction('H2O2 + H <=> H2O + OH', [2.410e+13, 0.0, 3970.0])

Reaction 16

reaction('H2O2 + H <=> HO2 + H2', [5.020e+06, 2.07, 4300.0])

Reaction 17

reaction('H2O2 + O <=> OH + HO2', [9.550e+06, 2.0, 3970.0])

Reaction 18

reaction('H2O2 + OH <=> H2O + HO2', [1.740e+12, 0.0, 318.0],
options='duplicate')

Reaction 19

reaction('H2O2 + OH <=> H2O + HO2', [7.590e+13, 0.0, 7269.0],
options='duplicate')

Reaction 20

reaction('HO2 + H <=> H2 + O2', [3.259e+05, 2.055, -1896.6])

Reaction 21

reaction('HO2 + H <=> OH + OH', [3.529e+14, -0.009, 382.6])

Reaction 22

reaction('HO2 + O <=> OH + O2', [3.553e+12, -0.012, -0.02])

Reaction 23

reaction('OH + HO2 <=> H2O + O2', [1.930e+20, -2.49, 584.2],
options='duplicate')

Reaction 24

reaction('OH + HO2 <=> H2O + O2', [8.766e+7, 1.195, -1319.5],
options='duplicate')

Reaction 25

reaction('HO2 + HO2 <=> H2O2 + O2', [1.214e+10, 0.422, -1480.5],
options='duplicate')

Reaction 26

reaction('HO2 + HO2 <=> H2O2 + O2', [2.365e+16, -0.732, 20003.5],
options='duplicate')

Reaction 27

falloff_reaction('H + O2 (+ M) <=> HO2 (+ M)',
kf=[4.660e+12, 0.44, 0.0],
kf0=[7.521e+20, -1.140, -0.02],
efficiencies='CH4:2.0 CO2:3.25 H2:1.35 H2O:16.6 N2:1.0 O2:0.9',
falloff=Troe(A=0.5, T3=1.0, T1=10000000000.0))

Reaction 28

falloff_reaction('CO + O (+ M) <=> CO2 (+ M)',
kf=[1.362e+10, 0.0, 2384.0],
kf0=[1.173e+24, -2.79, 4191.0],
efficiencies='CO:1.75 CO2:3.6 H2:2.0 H2O:12.0')

Reaction 29

pdep_arrhenius('CO + OH <=> CO2 + H',
[(0.01315, 'atm'), 2.100e+05, 1.9, -1064.0],
[(0.1315, 'atm'), 2.500e+05, 1.88, -1043.0],
[(1.315, 'atm'), 8.700e+05, 1.73, -685.0],
[(13.158, 'atm'), 5.812e+7, 1.271, 28.6],
[(131.58, 'atm'), 2.300e+07, 1.35, 974.0])

Reaction 30

reaction('CO + HO2 <=> CO2 + OH', [8.550e+03, 2.52, 15560.0])

Reaction 31

reaction('CO + O2 <=> CO2 + O', [1.119e+12, 0.0, 47700.0])

Reaction 32

```
falloff_reaction('CH3 + H (+ M) <=> CH4 (+ M)',  
    kf=[6.470e+13, 0.185, -54.0],  
    kf0=[4.910e+37, -5.815, 907.6],  
    efficiencies='CH4:5.0 CO:2.3 CO2:4.0 H2:4.0 H2O:12.0 N2:1.5 O2:1.5',  
    falloff=Troe(A=0.516194, T3=3637.8482, T1=1.0, T2=1e+30))
```

Reaction 33

```
reaction('CH4 + H <=> CH3 + H2', [1.625e+03, 3.609, 8818.5])
```

Reaction 34

```
reaction('CH4 + O <=> CH3 + OH', [5.172749e+6, 2.409, 9236.5])
```

Reaction 35

```
reaction('CH4 + OH <=> CH3 + H2O', [1.944e+8, 1.747, 3369.3])
```

Reaction 36

```
reaction('CH4 + HO2 <=> CH3 + H2O2', [3.122e-01, 2.975, 12865.3])
```

Reaction 37

```
reaction('CH3 + HO2 <=> CH4 + O2', [3.185e+02, 2.421, -3089.6])
```

Reaction 38

```
pdep_arrhenius('CH3 + O2 <=> CH2O + OH',  
    [(1.00, 'atm'), 0.0125, 4.125, 18761.8],  
    [(10.00, 'atm'), 2.882, 3.346, 15266.3],  
    [(40.00, 'atm'), 2.109, 3.644, 19400.7])
```

Reaction 39

```
reaction('CH3 + O <=> CH2O + H', [4.875e+13, 0.048, -150.9])
```

Reaction 40

```
pdep_arrhenius('CH3 + OH <=> CH2O + H2',  
    [(0.01, 'atm'), 3.502e+05, 1.441, -3244.0],  
    [(0.1, 'atm'), 8.854e+05, 1.327, -2975.0],  
    [(1.0, 'atm'), 1.650e+07, 0.973, -2010.0],  
    [(10.0, 'atm'), 2.943e+9, 0.285, 245.2],  
    [(100.0, 'atm'), 9.494e+18, -2.199, 9769.0])
```

Reaction 41

```
falloff_reaction('HCO + H (+ M) <=> CH2O (+ M)',  
    kf=[1.090e+12, 0.48, -260.0],  
    kf0=[1.350e+24, -2.57, 1425.0],  
    falloff=Troe(A=0.7824, T3=271.0, T1=2755.0, T2=6570.0))
```

Reaction 42

```
falloff_reaction('CO + H2 (+ M) <=> CH2O (+ M)',  
    kf=[4.300e+07, 1.5, 79600.0],  
    kf0=[5.070e+27, -3.42, 84348.0],
```

falloff=Troe(A=0.932, T3=197.0, T1=1540.0, T2=10300.0))

Reaction 43

reaction('CH2O + O2 <=> HCO + HO2', [1.760e+17, 0.017, 35587.6])

Reaction 44

reaction('CH2O + O <=> HCO + OH', [2.313e+09, 1.035, 1816.5])

Reaction 45

reaction('CH2O + H <=> HCO + H2', [4.069e+03, 2.717, 1963.4])

Reaction 46

reaction('CH2O + OH <=> HCO + H2O', [2.422e+11, 0.982, -503.3])

Reaction 47

reaction('CH2O + HO2 <=> HCO + H2O2', [2.632e-10, 4.342, 4465.8])

Reaction 48

reaction('CH2O + CH3 <=> HCO + CH4', [3.430e-05, 4.344, 3216.4])

Reaction 49

reaction('CH2O + OH => H + CO + H2O', [2.565e+11, 0.693, 9368.7])

Reaction 50

reaction('CH2O + H => H + CO + H2', [1.940e+07, 2.192, 11740.3])

Reaction 51

three_body_reaction('HCO + M <=> H + CO + M', [8.993e+11, 0.691, 14221.72],
efficiencies='CH4:2.0 CO:1.5 CO2:2.0 H2:2.0 H2O:6.0')

Reaction 52

reaction('HCO + O2 <=> CO + HO2', [7.567e+04, 0.765, -412.1383])

Reaction 53

reaction('HCO + O <=> CO + OH', [3.020e+13, 0.0, 0.0])

Reaction 54

reaction('HCO + H <=> CO + H2', [1.121e+12, 0.385, -144.4])

Reaction 55

reaction('HCO + OH <=> CO + H2O', [1.196e+13, 0.019, -0.013])

Reaction 56

reaction('HCO + CH3 <=> CO + CH4', [1.423e+12, -0.017, -0.014])

Reaction 57

reaction('HCO + HCO <=> CO + CH2O', [2.700e+13, 0.0, 0.0])

Reaction 58

reaction('HCO + O <=> CO2 + H', [3.000e+13, 0.0, 0.0])

Reaction 59

reaction('HCO + HO2 => CO2 + H + OH', [3.000e+13, 0.0, 0.0])

Reaction 60

reaction('HCO + HCO => H2 + CO + CO', [3.000e+12, 0.0, 0.0])

!!!! NOx !!!!!!!

Reaction 61

reaction('N + OH <=> NO + H', [2.997e+13, 0.0172, -0.02])

Reaction 62

reaction('N + O2 <=> NO + O', [1.524e+04, 1.185, 8639.0])

Reaction 63

reaction('N + NO <=> N2 + O', [1.695e+13, 0.120, -0.01])

Reaction 64

reaction('NO + HO2 <=> NO2 + OH', [9.000e+11, 0.02, -483.2])

Reaction 65

reaction('NO + O <=> NO2 ', [5.137e-06, 3.257, 2124.8])

Reaction 66

reaction('NO2 + O <=> NO + O2', [7.314e+13, -0.01969697, -187.6813627])

Reaction 67

reaction('NO2 + NO2 <=> NO + NO + O2', [3.708e+03, -0.006, 19525.9])

Reaction 68

reaction('CO + NO2 <=> NO + CO2', [5.470e+06, -0.015, 36069.1])

Reaction 69

reaction('CO2 + N <=> NO + CO', [1.17157916e+08, 0.026, -0.018])

Reaction 70

reaction('N2 + OH => NO + N + H', [1.312e+00, 0.002, 0])

Reaction 71

reaction('N2 + O => 2 N + O', [5.388e+04, -0.03, -0.02])

15sOp_NOx_1 Cantera File:

```

units(length='cm', time='s', quantity='mol', act_energy='cal/mol')

ideal_gas(name='gas',
  elements="C H N O",
  species="CH2O CH3 CH4 CO CO2 H H2 H2O H2O2
          HCO HO2 N2 O O2 OH N NO NO2",
  reactions='all',
  transport='Mix',
  initial_state=state(temperature=300.0, pressure=OneAtm))

#-----
# Species data
#-----

species(name='CH2O',
  atoms='C:1 H:2 O:1',
  thermo=(NASA([200.00, 1000.00],
    [ 4.79372312E+00, -9.90833322E-03, 3.73219990E-05,
      -3.79285237E-08, 1.31772641E-11, -1.43791953E+04,
      6.02798058E-01]),
    NASA([1000.00, 6000.00],
      [ 3.16952665E+00, 6.19320560E-03, -2.25056366E-06,
        3.65975660E-10, -2.20149458E-14, -1.45486831E+04,
        6.04207898E+00])),
  transport=gas_transport(geom='nonlinear',
    diam=3.59,
    well_depth=498.0,
    rot_relax=2.0),
  note='T5/11')

species(name='CH3',
  atoms='C:1 H:3',
  thermo=(NASA([200.00, 1000.00],
    [ 3.65717970E+00, 2.12659790E-03, 5.45838830E-06,
      -6.61810030E-09, 2.46570740E-12, 1.64227160E+04,
      1.67353540E+00]),
    NASA([1000.00, 6000.00],
      [ 2.97812060E+00, 5.79785200E-03, -1.97558000E-06,
        3.07297900E-10, -1.79174160E-14, 1.65095130E+04,
        4.72247990E+00])),
  transport=gas_transport(geom='linear',
    diam=3.8,
    well_depth=144.0),
  note='IU0702')

species(name='CH4',
  atoms='C:1 H:4',
  thermo=(NASA([200.00, 1000.00],
    [ 5.14911468E+00, -1.36622009E-02, 4.91453921E-05,

```

```
-4.84246767E-08, 1.66603441E-11, -1.02465983E+04,  
-4.63848842E+00]],  
NASA([1000.00, 6000.00],  
[ 1.65326226E+00, 1.00263099E-02, -3.31661238E-06,  
5.36483138E-10, -3.14696758E-14, -1.00095936E+04,  
9.90506283E+00])),  
transport=gas_transport(geom='nonlinear',  
diam=3.746,  
well_depth=141.4,  
polar=2.6,  
rot_relax=13.0),  
note='G8/99')
```

```
species(name='CO',  
atoms='C:1 O:1',  
thermo=(NASA([200.00, 1000.00],  
[ 3.57953350E+00, -6.10353690E-04, 1.01681430E-06,  
9.07005860E-10, -9.04424490E-13, -1.43440860E+04,  
3.50840930E+00])),  
NASA([1000.00, 6000.00],  
[ 3.04848590E+00, 1.35172810E-03, -4.85794050E-07,  
7.88536440E-11, -4.69807460E-15, -1.42661170E+04,  
6.01709770E+00])),  
transport=gas_transport(geom='linear',  
diam=3.65,  
well_depth=98.1,  
polar=1.95,  
rot_relax=1.8),  
note='RUS79')
```

```
species(name='CO2',  
atoms='C:1 O:2',  
thermo=(NASA([200.00, 1000.00],  
[ 2.35681300E+00, 8.98412990E-03, -7.12206320E-06,  
2.45730080E-09, -1.42885480E-13, -4.83719710E+04,  
9.90090350E+00])),  
NASA([1000.00, 6000.00],  
[ 4.63651110E+00, 2.74145690E-03, -9.95897590E-07,  
1.60386660E-10, -9.16198570E-15, -4.90249040E+04,  
-1.93489550E+00])),  
transport=gas_transport(geom='linear',  
diam=3.763,  
well_depth=244.0,  
polar=2.65,  
rot_relax=2.1),  
note='L7/88')
```

```
species(name='H',  
atoms='H:1',  
thermo=(NASA([200.00, 1000.00],  
[ 2.50000000E+00, 0.00000000E+00, 0.00000000E+00,
```

```
0.00000000E+00, 0.00000000E+00, 2.54736600E+04,
-4.46682850E-01]),
NASA([1000.00, 6000.00],
[ 2.50000000E+00, 0.00000000E+00, 0.00000000E+00,
0.00000000E+00, 0.00000000E+00, 2.54736600E+04,
-4.46682850E-01])),
transport=gas_transport(geom='atom',
diam=1.53,
well_depth=541.672,
polar=0.666),
note='L6/94')

species(name='H2',
atoms='H:2',
thermo=(NASA([200.00, 1000.00],
[ 2.34433112E+00, 7.98052075E-03, -1.94781510E-05,
2.01572094E-08, -7.37611761E-12, -9.17935173E+02,
6.83010238E-01]),
NASA([1000.00, 6000.00],
[ 2.93286575E+00, 8.26608026E-04, -1.46402364E-07,
1.54100414E-11, -6.88804800E-16, -8.13065581E+02,
-1.02432865E+00])),
transport=gas_transport(geom='linear',
diam=2.19,
well_depth=304.69,
polar=0.775,
rot_relax=280.0),
note='TPIS78')

species(name='H2O',
atoms='H:2 O:1',
thermo=(NASA([200.00, 1000.00],
[ 4.19863520E+00, -2.03640170E-03, 6.52034160E-06,
-5.48792690E-09, 1.77196800E-12, -3.02937260E+04,
-8.49009010E-01]),
NASA([1000.00, 6000.00],
[ 2.67703890E+00, 2.97318160E-03, -7.73768890E-07,
9.44335140E-11, -4.26899910E-15, -2.98858940E+04,
6.88255000E+00])),
transport=gas_transport(geom='nonlinear',
diam=2.943,
well_depth=637.056,
dipole=1.851,
polar=1.407,
rot_relax=4.0),
note='L5/89')

species(name='H2O2',
atoms='H:2 O:2',
thermo=(NASA([200.00, 1000.00],
[ 4.31515149E+00, -8.47390622E-04, 1.76404323E-05,
```

```
-2.26762944E-08, 9.08950158E-12, -1.77067437E+04,  
3.27373319E+00]],  
NASA([1000.00, 6000.00],  
[ 4.57977305E+00, 4.05326003E-03, -1.29844730E-06,  
1.98211400E-10, -1.13968792E-14, -1.80071775E+04,  
6.64970694E-01])),  
transport=gas_transport(geom='nonlinear',  
diam=3.179,  
well_depth=1361.148,  
dipole=1.702,  
polar=2.239,  
rot_relax=3.8),  
note='T8/03')
```

```
species(name='HCO',  
atoms='C:1 H:1 O:1',  
thermo=(NASA([200.00, 1000.00],  
[ 4.23754610E+00, -3.32075257E-03, 1.40030264E-05,  
-1.34239995E-08, 4.37416208E-12, 3.87241185E+03,  
3.30834869E+00])),  
NASA([1000.00, 6000.00],  
[ 3.92001542E+00, 2.52279324E-03, -6.71004164E-07,  
1.05615948E-10, -7.43798261E-15, 3.65342928E+03,  
3.58077056E+00])),  
transport=gas_transport(geom='nonlinear',  
diam=3.59,  
well_depth=498.0),  
note='T5/03')
```

```
species(name='HO2',  
atoms='H:1 O:2',  
thermo=(NASA([200.00, 1000.00],  
[ 4.30179807E+00, -4.74912097E-03, 2.11582905E-05,  
-2.42763914E-08, 9.29225225E-12, 2.64018485E+02,  
3.71666220E+00])),  
NASA([1000.00, 5000.00],  
[ 4.17228741E+00, 1.88117627E-03, -3.46277286E-07,  
1.94657549E-11, 1.76256905E-16, 3.10206839E+01,  
2.95767672E+00])),  
transport=gas_transport(geom='nonlinear',  
diam=3.129,  
well_depth=963.003,  
dipole=2.146,  
polar=1.959,  
rot_relax=3.8),  
note='T1/09')
```

```
species(name='N2',  
atoms='N:2',  
thermo=(NASA([200.00, 1000.00],  
[ 3.53100528E+00, -1.23660988E-04, -5.02999433E-07,
```



```
2.43530612E-09, -1.40881235E-12, -1.04697628E+03,
2.96747038E+00]),
NASA([1000.00, 6000.00],
[ 2.95257637E+00, 1.39690040E-03, -4.92631603E-07,
7.86010195E-11, -4.60755204E-15, -9.23948688E+02,
5.87188762E+00])),
transport=gas_transport(geom='linear',
diam=3.61,
well_depth=97.839,
polar=1.756,
rot_relax=4.0),
note='G8/02')

species(name='O',
atoms='O:1',
thermo=(NASA([200.00, 1000.00],
[ 3.16826710E+00, -3.27931884E-03, 6.64306396E-06,
-6.12806624E-09, 2.11265971E-12, 2.91222592E+04,
2.05193346E+00]),
NASA([1000.00, 6000.00],
[ 2.54363697E+00, -2.73162486E-05, -4.19029520E-09,
4.95481845E-12, -4.79553694E-16, 2.92260120E+04,
4.92229457E+00])),
transport=gas_transport(geom='atom',
diam=2.485,
well_depth=235.686,
polar=0.744),
note='L1/90')

species(name='O2',
atoms='O:2',
thermo=(NASA([200.00, 1000.00],
[ 3.78245636E+00, -2.99673416E-03, 9.84730201E-06,
-9.68129509E-09, 3.24372837E-12, -1.06394356E+03,
3.65767573E+00]),
NASA([1000.00, 6000.00],
[ 3.66096065E+00, 6.56365811E-04, -1.41149627E-07,
2.05797935E-11, -1.29913436E-15, -1.21597718E+03,
3.41536279E+00])),
transport=gas_transport(geom='linear',
diam=3.069,
well_depth=676.424,
polar=1.487,
rot_relax=3.8),
note='RUS89')

species(name='OH',
atoms='H:1 O:1',
thermo=(NASA([200.00, 1000.00],
[ 3.99198424E+00, -2.40106655E-03, 4.61664033E-06,
-3.87916306E-09, 1.36319502E-12, 3.36889836E+03,
```

```
-1.03998477E-01]),
NASA([1000.00, 6000.00],
[ 2.83853033E+00, 1.10741289E-03, -2.94000209E-07,
 4.20698729E-11, -2.42289890E-15, 3.69780808E+03,
 5.84494652E+00])),
transport=gas_transport(geom='linear',
  diam=2.582,
  well_depth=514.598,
  dipole=1.635,
  polar=1.077),
note='IU3/03')
```

```
species(name='N',
  atoms='N:1',
  thermo=(NASA([200.00, 1000.00],
[ 2.49976643E+00, 5.02149594E-07, 1.93091211E-09,
-4.94632629E-12, 2.74089506E-15, 5.60760710E+04,
 4.19499326E+00])),
  NASA([1000.00, 6000.00],
[ 2.41604245E+00, 1.74663766E-04, -1.18864562E-07,
 3.01850054E-11, -2.03260159E-15, 5.61051512E+04,
 4.64905706E+00])),
  transport=gas_transport(geom='atom',
    diam=3.298,
    well_depth=71.4),
  note='ATcT3E')
```

```
species(name='NO',
  atoms='N:1 O:1',
  thermo=(NASA([298.15, 1000.00],
[ 4.15036687E+00, -4.08890008E-03, 9.38071726E-06,
-7.50908901E-09, 2.11742798E-12, 9.77018679E+03,
 2.53971032E+00])),
  NASA([1000.00, 3000.00],
[ 2.79462839E+00, 2.12260586E-03, -1.11936971E-06,
 2.79521018E-10, -2.68625363E-14, 1.00019069E+04,
 8.88322674E+00])),
  transport=gas_transport(geom='linear',
    diam=3.339,
    well_depth=139.32,
    dipole=0.2,
    polar=1.76,
    rot_relax=4.0))
```

```
species(name='NO2',
  atoms='N:1 O:2',
  thermo=(NASA([298.15, 1000.00],
[ 3.39100918E+00, 2.62448348E-03, 5.09790306E-06,
-7.62120493E-09, 2.79960135E-12, 2.78130679E+03,
 8.57220275E+00])),
  NASA([1000.00, 3000.00],
```

```

[ 3.65239279E+00, 4.71632310E-03, -2.74591748E-06,
  7.45382834E-10, -7.63891108E-14, 2.57216137E+03,
  6.52683440E+00]],
transport=gas_transport(geom='nonlinear',
  diam=3.852,
  well_depth=333.59,
  dipole=0.4,
  rot_relax=1.0))

#-----
# Reaction data
#-----

# Reaction 1
three_body_reaction('H2 + M <=> H + H + M', [4.577e+19, -1.4, 104400.0],
  efficiencies='CH4:2.0 CO:1.9 CO2:3.8 H2:2.5 H2O:12.0')

# Reaction 2
reaction('O + H2 <=> OH + H', [3.800e+12, 0.0, 7948.0],
  options='duplicate')

# Reaction 3
reaction('O + H2 <=> OH + H', [5.531e+14, -0.021, 21049.2],
  options='duplicate')

# Reaction 4
reaction('H2 + OH <=> H + H2O', [8.468e+7, 1.455, 4406.0])

# Reaction 5
reaction('H + O2 + H <=> H2 + O2', [8.800e+22, -1.835, 800.0])

# Reaction 6
reaction('H + O2 + H <=> OH + OH', [4.000e+22, -1.835, 800.0])

# Reaction 7
reaction('H + O2 + O <=> OH + O2', [7.350e+22, -1.835, 800.0])

# Reaction 8
reaction('H + O2 + OH <=> H2O + O2', [2.560e+22, -1.835, 800.0])

# Reaction 9
three_body_reaction('O + O + M <=> O2 + M', [6.165e+15, -0.5, 0.0],
  efficiencies='CH4:2.0 CO:1.9 CO2:3.8 H2:2.5 H2O:12.0')

# Reaction 10
pdep_arrhenius('O2 + H <=> O + OH',
  [(1.00, 'atm'), 7.559e+14, 0.025, 15977.7],
  [(10.00, 'atm'), 2.65e+16, 0.023, 30724.0],
  [(40.00, 'atm'), 2.63e+17, 0.020, 42330.2])

# Reaction 11

```

```
falloff_reaction('H + OH (+ M) <=> H2O (+ M)',  
    kf=[2.500e+13, 0.234, -114.0],  
    kf0=[2.580e+22, -1.887, 512.8],  
    efficiencies='H2:1.5 H2O:13.0 N2:1.0 O2:1.0',  
    falloff=Troe(A=0.73, T3=1e-30, T1=1e+30, T2=1e+30))
```

```
# Reaction 12
```

```
reaction('OH + OH <=> H2O + O', [2.226e+05, 1.875, -1477.1])
```

```
# Reaction 13
```

```
three_body_reaction('O + H + M <=> OH + M', [4.714e+18, -1.0, 0.0],  
    efficiencies='CH4:2.0 CO:1.5 CO2:2.0 H2:2.5 H2O:12.0')
```

```
# Reaction 14
```

```
falloff_reaction('H2O2 (+ M) <=> OH + OH (+ M)',  
    kf=[2.000e+12, 0.9, 48749.0],  
    kf0=[2.353e+24, -2.293, 48743.4],  
    efficiencies='CO:2.8 CO2:1.06 H2:3.7 H2O:5.1 H2O2:5.2 N2:1.5 O2:0.79',  
    falloff=Troe(A=0.43, T3=1e-30, T1=1e+30))
```

```
# Reaction 15
```

```
reaction('H2O2 + H <=> H2O + OH', [2.410e+13, 0.0, 3970.0])
```

```
# Reaction 16
```

```
reaction('H2O2 + H <=> HO2 + H2', [5.020e+06, 2.07, 4300.0])
```

```
# Reaction 17
```

```
reaction('H2O2 + O <=> OH + HO2', [9.550e+06, 2.0, 3970.0])
```

```
# Reaction 18
```

```
reaction('H2O2 + OH <=> H2O + HO2', [1.740e+12, 0.0, 318.0],  
    options='duplicate')
```

```
# Reaction 19
```

```
reaction('H2O2 + OH <=> H2O + HO2', [7.590e+13, 0.0, 7269.0],  
    options='duplicate')
```

```
# Reaction 20
```

```
reaction('HO2 + H <=> H2 + O2', [3.259e+05, 2.055, -1896.6])
```

```
# Reaction 21
```

```
reaction('HO2 + H <=> OH + OH', [3.529e+14, -0.009, 382.6])
```

```
# Reaction 22
```

```
reaction('HO2 + O <=> OH + O2', [3.553e+12, -0.012, -0.02])
```

```
# Reaction 23
```

```
reaction('OH + HO2 <=> H2O + O2', [1.930e+20, -2.49, 584.2],  
    options='duplicate')
```

```
# Reaction 24
```

```
reaction('OH + HO2 <=> H2O + O2', [8.766e+7, 1.195, -1319.5],
        options='duplicate')

# Reaction 25
reaction('HO2 + HO2 <=> H2O2 + O2', [1.214e+10, 0.422, -1480.5],
        options='duplicate')

# Reaction 26
reaction('HO2 + HO2 <=> H2O2 + O2', [2.365e+16, -0.732, 20003.5],
        options='duplicate')

# Reaction 27
falloff_reaction('H + O2 (+ M) <=> HO2 (+ M)',
        kf=[4.660e+12, 0.44, 0.0],
        kf0=[7.521e+20, -1.140, -0.02],
        efficiencies='CH4:2.0 CO2:3.25 H2:1.35 H2O:16.6 N2:1.0 O2:0.9',
        falloff=Troe(A=0.5, T3=1.0, T1=10000000000.0))

# Reaction 28
falloff_reaction('CO + O (+ M) <=> CO2 (+ M)',
        kf=[1.362e+10, 0.0, 2384.0],
        kf0=[1.173e+24, -2.79, 4191.0],
        efficiencies='CO:1.75 CO2:3.6 H2:2.0 H2O:12.0')

# Reaction 29
pdep_arrhenius('CO + OH <=> CO2 + H',
        [(0.01315, 'atm'), 2.100e+05, 1.9, -1064.0],
        [(0.1315, 'atm'), 2.500e+05, 1.88, -1043.0],
        [(1.315, 'atm'), 8.700e+05, 1.73, -685.0],
        [(13.158, 'atm'), 5.812e+7, 1.271, 28.6],
        [(131.58, 'atm'), 2.300e+07, 1.35, 974.0])

# Reaction 30
reaction('CO + HO2 <=> CO2 + OH', [8.550e+03, 2.52, 15560.0])

# Reaction 31
reaction('CO + O2 <=> CO2 + O', [1.119e+12, 0.0, 47700.0])

# Reaction 32
falloff_reaction('CH3 + H (+ M) <=> CH4 (+ M)',
        kf=[6.470e+13, 0.185, -54.0],
        kf0=[4.910e+37, -5.815, 907.6],
        efficiencies='CH4:5.0 CO:2.3 CO2:4.0 H2:4.0 H2O:12.0 N2:1.5 O2:1.5',
        falloff=Troe(A=0.516194, T3=3637.8482, T1=1.0, T2=1e+30))

# Reaction 33
reaction('CH4 + H <=> CH3 + H2', [1.625e+03, 3.609, 8818.5])

# Reaction 34
reaction('CH4 + O <=> CH3 + OH', [5.172749e+6, 2.409, 9236.5])
```

Reaction 35

reaction('CH4 + OH <=> CH3 + H2O', [1.944e+8, 1.747, 3369.3])

Reaction 36

reaction('CH4 + HO2 <=> CH3 + H2O2', [3.122e-01, 2.975, 12865.3])

Reaction 37

reaction('CH3 + HO2 <=> CH4 + O2', [3.185e+02, 2.421, -3089.6])

Reaction 38

pdep_arrhenius('CH3 + O2 <=> CH2O + OH',
[(1.00, 'atm'), 0.0125, 4.125, 18761.8],
[(10.00, 'atm'), 2.882, 3.346, 15266.3],
[(40.00, 'atm'), 2.109, 3.644, 19400.7])

Reaction 39

reaction('CH3 + O <=> CH2O + H', [4.875e+13, 0.048, -150.9])

Reaction 40

pdep_arrhenius('CH3 + OH <=> CH2O + H2',
[(0.01, 'atm'), 3.502e+05, 1.441, -3244.0],
[(0.1, 'atm'), 8.854e+05, 1.327, -2975.0],
[(1.0, 'atm'), 1.650e+07, 0.973, -2010.0],
[(10.0, 'atm'), 2.943e+9, 0.285, 245.2],
[(100.0, 'atm'), 9.494e+18, -2.199, 9769.0])

Reaction 41

falloff_reaction('HCO + H (+ M) <=> CH2O (+ M)',
kf=[1.090e+12, 0.48, -260.0],
kf0=[1.350e+24, -2.57, 1425.0],
falloff=Troe(A=0.7824, T3=271.0, T1=2755.0, T2=6570.0))

Reaction 42

falloff_reaction('CO + H2 (+ M) <=> CH2O (+ M)',
kf=[4.300e+07, 1.5, 79600.0],
kf0=[5.070e+27, -3.42, 84348.0],
falloff=Troe(A=0.932, T3=197.0, T1=1540.0, T2=10300.0))

Reaction 43

reaction('CH2O + O2 <=> HCO + HO2', [1.760e+17, 0.017, 35587.6])

Reaction 44

reaction('CH2O + O <=> HCO + OH', [2.313e+09, 1.035, 1816.5])

Reaction 45

reaction('CH2O + H <=> HCO + H2', [4.069e+03, 2.717, 1963.4])

Reaction 46

reaction('CH2O + OH <=> HCO + H2O', [2.422e+11, 0.982, -503.3])

Reaction 47

reaction('CH2O + HO2 <=> HCO + H2O2', [2.632e-10, 4.342, 4465.8])

Reaction 48

reaction('CH2O + CH3 <=> HCO + CH4', [3.430e-05, 4.344, 3216.4])

Reaction 49

reaction('CH2O + OH => H + CO + H2O', [2.565e+11, 0.693, 9368.7])

Reaction 50

reaction('CH2O + H => H + CO + H2', [1.940e+07, 2.192, 11740.3])

Reaction 51

three_body_reaction('HCO + M <=> H + CO + M', [8.993e+11, 0.691, 14221.72],
efficiencies='CH4:2.0 CO:1.5 CO2:2.0 H2:2.0 H2O:6.0')

Reaction 52

reaction('HCO + O2 <=> CO + HO2', [7.567e+04, 0.765, -412.1383])

Reaction 53

reaction('HCO + O <=> CO + OH', [3.020e+13, 0.0, 0.0])

Reaction 54

reaction('HCO + H <=> CO + H2', [1.121e+12, 0.385, -144.4])

Reaction 55

reaction('HCO + OH <=> CO + H2O', [1.196e+13, 0.019, -0.013])

Reaction 56

reaction('HCO + CH3 <=> CO + CH4', [1.423e+12, -0.017, -0.014])

Reaction 57

reaction('HCO + HCO <=> CO + CH2O', [2.700e+13, 0.0, 0.0])

Reaction 58

reaction('HCO + O <=> CO2 + H', [3.000e+13, 0.0, 0.0])

Reaction 59

reaction('HCO + HO2 => CO2 + H + OH', [3.000e+13, 0.0, 0.0])

Reaction 60

reaction('HCO + HCO => H2 + CO + CO', [3.000e+12, 0.0, 0.0])

!!!! NOx !!!!!!!

Reaction 61

reaction('N + OH <=> NO + H', [7.896e+05, -0.0276, -0.013])

Reaction 62

reaction('N + O2 <=> NO + O', [3.84e+01, 1.182, 3022.0])

Reaction 63

reaction('N + NO <=> N2 + O', [1.29234E+14, 0.121, 0.015])

Reaction 64

reaction('NO + HO2 <=> NO2 + OH', [1.942e+13, 0.0045, -456.7])

Reaction 65

reaction('NO + O <=> NO2 ', [2.950e-10, 2.735, 1978.7])

Reaction 66

reaction('NO2 + O <=> NO + O2', [2.802e+08, 0.015, -190.1])

Reaction 67

reaction('NO2 + NO2 <=> NO + NO + O2', [6.050e+16, 0.026, 19800.0])

Reaction 68

reaction('CO + NO2 <=> NO + CO2', [4.264e+10, 0, 23131.7])

Reaction 69

reaction('CO2 + N <=> NO + CO', [2.594e+12, -0.007, 0.005])

Reaction 70

reaction('N2 + OH => NO + N + H', [1.037e+00, -0.015, 0.01])

Reaction 71

reaction('N2 + O => 2 N + O', [2.008e+02, 0.028, 0.02])

15sOp_NOx_2 Cantera File:

```
units(length='cm', time='s', quantity='mol', act_energy='cal/mol')
```

```
ideal_gas(name='gas',
  elements="C H N O",
  species="CH2O CH3 CH4 CO CO2 H H2 H2O H2O2
    HCO HO2 N2 O O2 OH N NO NO2",
  reactions='all',
  transport='Mix',
  initial_state=state(temperature=300.0, pressure=OneAtm))
```

```
#-----
# Species data
#-----
```

```
species(name='CH2O',
  atoms='C:1 H:2 O:1',
  thermo=(NASA([200.00, 1000.00],
    [ 4.79372312E+00, -9.90833322E-03, 3.73219990E-05,
      -3.79285237E-08, 1.31772641E-11, -1.43791953E+04,
      6.02798058E-01]),
    NASA([1000.00, 6000.00],
      [ 3.16952665E+00, 6.19320560E-03, -2.25056366E-06,
        3.65975660E-10, -2.20149458E-14, -1.45486831E+04,
        6.04207898E+00])),
  transport=gas_transport(geom='nonlinear',
    diam=3.59,
    well_depth=498.0,
    rot_relax=2.0),
  note='T5/11')
```

```
species(name='CH3',
  atoms='C:1 H:3',
  thermo=(NASA([200.00, 1000.00],
    [ 3.65717970E+00, 2.12659790E-03, 5.45838830E-06,
      -6.61810030E-09, 2.46570740E-12, 1.64227160E+04,
      1.67353540E+00]),
    NASA([1000.00, 6000.00],
      [ 2.97812060E+00, 5.79785200E-03, -1.97558000E-06,
        3.07297900E-10, -1.79174160E-14, 1.65095130E+04,
        4.72247990E+00])),
  transport=gas_transport(geom='linear',
    diam=3.8,
    well_depth=144.0),
  note='IU0702')
```

```
species(name='CH4',
  atoms='C:1 H:4',
  thermo=(NASA([200.00, 1000.00],
    [ 5.14911468E+00, -1.36622009E-02, 4.91453921E-05,
```

```
-4.84246767E-08, 1.66603441E-11, -1.02465983E+04,  
-4.63848842E+00]],  
NASA([1000.00, 6000.00],  
[ 1.65326226E+00, 1.00263099E-02, -3.31661238E-06,  
5.36483138E-10, -3.14696758E-14, -1.00095936E+04,  
9.90506283E+00])),  
transport=gas_transport(geom='nonlinear',  
diam=3.746,  
well_depth=141.4,  
polar=2.6,  
rot_relax=13.0),  
note='G8/99')
```

```
species(name='CO',  
atoms='C:1 O:1',  
thermo=(NASA([200.00, 1000.00],  
[ 3.57953350E+00, -6.10353690E-04, 1.01681430E-06,  
9.07005860E-10, -9.04424490E-13, -1.43440860E+04,  
3.50840930E+00])),  
NASA([1000.00, 6000.00],  
[ 3.04848590E+00, 1.35172810E-03, -4.85794050E-07,  
7.88536440E-11, -4.69807460E-15, -1.42661170E+04,  
6.01709770E+00])),  
transport=gas_transport(geom='linear',  
diam=3.65,  
well_depth=98.1,  
polar=1.95,  
rot_relax=1.8),  
note='RUS79')
```

```
species(name='CO2',  
atoms='C:1 O:2',  
thermo=(NASA([200.00, 1000.00],  
[ 2.35681300E+00, 8.98412990E-03, -7.12206320E-06,  
2.45730080E-09, -1.42885480E-13, -4.83719710E+04,  
9.90090350E+00])),  
NASA([1000.00, 6000.00],  
[ 4.63651110E+00, 2.74145690E-03, -9.95897590E-07,  
1.60386660E-10, -9.16198570E-15, -4.90249040E+04,  
-1.93489550E+00])),  
transport=gas_transport(geom='linear',  
diam=3.763,  
well_depth=244.0,  
polar=2.65,  
rot_relax=2.1),  
note='L7/88')
```

```
species(name='H',  
atoms='H:1',  
thermo=(NASA([200.00, 1000.00],  
[ 2.50000000E+00, 0.00000000E+00, 0.00000000E+00,
```

```
0.00000000E+00, 0.00000000E+00, 2.54736600E+04,
-4.46682850E-01]),
NASA([1000.00, 6000.00],
[ 2.50000000E+00, 0.00000000E+00, 0.00000000E+00,
0.00000000E+00, 0.00000000E+00, 2.54736600E+04,
-4.46682850E-01])),
transport=gas_transport(geom='atom',
diam=1.53,
well_depth=541.672,
polar=0.666),
note='L6/94')

species(name='H2',
atoms='H:2',
thermo=(NASA([200.00, 1000.00],
[ 2.34433112E+00, 7.98052075E-03, -1.94781510E-05,
2.01572094E-08, -7.37611761E-12, -9.17935173E+02,
6.83010238E-01]),
NASA([1000.00, 6000.00],
[ 2.93286575E+00, 8.26608026E-04, -1.46402364E-07,
1.54100414E-11, -6.88804800E-16, -8.13065581E+02,
-1.02432865E+00])),
transport=gas_transport(geom='linear',
diam=2.19,
well_depth=304.69,
polar=0.775,
rot_relax=280.0),
note='TPIS78')

species(name='H2O',
atoms='H:2 O:1',
thermo=(NASA([200.00, 1000.00],
[ 4.19863520E+00, -2.03640170E-03, 6.52034160E-06,
-5.48792690E-09, 1.77196800E-12, -3.02937260E+04,
-8.49009010E-01]),
NASA([1000.00, 6000.00],
[ 2.67703890E+00, 2.97318160E-03, -7.73768890E-07,
9.44335140E-11, -4.26899910E-15, -2.98858940E+04,
6.88255000E+00])),
transport=gas_transport(geom='nonlinear',
diam=2.943,
well_depth=637.056,
dipole=1.851,
polar=1.407,
rot_relax=4.0),
note='L5/89')

species(name='H2O2',
atoms='H:2 O:2',
thermo=(NASA([200.00, 1000.00],
[ 4.31515149E+00, -8.47390622E-04, 1.76404323E-05,
```

```
-2.26762944E-08, 9.08950158E-12, -1.77067437E+04,  
3.27373319E+00]],  
NASA([1000.00, 6000.00],  
[ 4.57977305E+00, 4.05326003E-03, -1.29844730E-06,  
1.98211400E-10, -1.13968792E-14, -1.80071775E+04,  
6.64970694E-01])),  
transport=gas_transport(geom='nonlinear',  
diam=3.179,  
well_depth=1361.148,  
dipole=1.702,  
polar=2.239,  
rot_relax=3.8),  
note='T8/03')
```

```
species(name='HCO',  
atoms='C:1 H:1 O:1',  
thermo=(NASA([200.00, 1000.00],  
[ 4.23754610E+00, -3.32075257E-03, 1.40030264E-05,  
-1.34239995E-08, 4.37416208E-12, 3.87241185E+03,  
3.30834869E+00])),  
NASA([1000.00, 6000.00],  
[ 3.92001542E+00, 2.52279324E-03, -6.71004164E-07,  
1.05615948E-10, -7.43798261E-15, 3.65342928E+03,  
3.58077056E+00])),  
transport=gas_transport(geom='nonlinear',  
diam=3.59,  
well_depth=498.0),  
note='T5/03')
```

```
species(name='HO2',  
atoms='H:1 O:2',  
thermo=(NASA([200.00, 1000.00],  
[ 4.30179807E+00, -4.74912097E-03, 2.11582905E-05,  
-2.42763914E-08, 9.29225225E-12, 2.64018485E+02,  
3.71666220E+00])),  
NASA([1000.00, 5000.00],  
[ 4.17228741E+00, 1.88117627E-03, -3.46277286E-07,  
1.94657549E-11, 1.76256905E-16, 3.10206839E+01,  
2.95767672E+00])),  
transport=gas_transport(geom='nonlinear',  
diam=3.129,  
well_depth=963.003,  
dipole=2.146,  
polar=1.959,  
rot_relax=3.8),  
note='T1/09')
```

```
species(name='N2',  
atoms='N:2',  
thermo=(NASA([200.00, 1000.00],  
[ 3.53100528E+00, -1.23660988E-04, -5.02999433E-07,
```

```
2.43530612E-09, -1.40881235E-12, -1.04697628E+03,
2.96747038E+00)),
NASA([1000.00, 6000.00],
[ 2.95257637E+00, 1.39690040E-03, -4.92631603E-07,
7.86010195E-11, -4.60755204E-15, -9.23948688E+02,
5.87188762E+00])),
transport=gas_transport(geom='linear',
diam=3.61,
well_depth=97.839,
polar=1.756,
rot_relax=4.0),
note='G8/02')

species(name='O',
atoms='O:1',
thermo=(NASA([200.00, 1000.00],
[ 3.16826710E+00, -3.27931884E-03, 6.64306396E-06,
-6.12806624E-09, 2.11265971E-12, 2.91222592E+04,
2.05193346E+00]),
NASA([1000.00, 6000.00],
[ 2.54363697E+00, -2.73162486E-05, -4.19029520E-09,
4.95481845E-12, -4.79553694E-16, 2.92260120E+04,
4.92229457E+00])),
transport=gas_transport(geom='atom',
diam=2.485,
well_depth=235.686,
polar=0.744),
note='L1/90')

species(name='O2',
atoms='O:2',
thermo=(NASA([200.00, 1000.00],
[ 3.78245636E+00, -2.99673416E-03, 9.84730201E-06,
-9.68129509E-09, 3.24372837E-12, -1.06394356E+03,
3.65767573E+00]),
NASA([1000.00, 6000.00],
[ 3.66096065E+00, 6.56365811E-04, -1.41149627E-07,
2.05797935E-11, -1.29913436E-15, -1.21597718E+03,
3.41536279E+00])),
transport=gas_transport(geom='linear',
diam=3.069,
well_depth=676.424,
polar=1.487,
rot_relax=3.8),
note='RUS89')

species(name='OH',
atoms='H:1 O:1',
thermo=(NASA([200.00, 1000.00],
[ 3.99198424E+00, -2.40106655E-03, 4.61664033E-06,
-3.87916306E-09, 1.36319502E-12, 3.36889836E+03,
```

```
-1.03998477E-01]),  
NASA([1000.00, 6000.00],  
[ 2.83853033E+00, 1.10741289E-03, -2.94000209E-07,  
 4.20698729E-11, -2.42289890E-15, 3.69780808E+03,  
 5.84494652E+00])),  
transport=gas_transport(geom='linear',  
    diam=2.582,  
    well_depth=514.598,  
    dipole=1.635,  
    polar=1.077),  
note='IU3/03')
```

```
species(name='N',  
    atoms='N:1',  
    thermo=(NASA([200.00, 1000.00],  
        [ 2.49976643E+00, 5.02149594E-07, 1.93091211E-09,  
        -4.94632629E-12, 2.74089506E-15, 5.60760710E+04,  
        4.19499326E+00])),  
        NASA([1000.00, 6000.00],  
        [ 2.41604245E+00, 1.74663766E-04, -1.18864562E-07,  
        3.01850054E-11, -2.03260159E-15, 5.61051512E+04,  
        4.64905706E+00])),  
    transport=gas_transport(geom='atom',  
        diam=3.298,  
        well_depth=71.4),  
    note='ATcT3E')
```

```
species(name='NO',  
    atoms='N:1 O:1',  
    thermo=(NASA([298.15, 1000.00],  
        [ 4.15036687E+00, -4.08890008E-03, 9.38071726E-06,  
        -7.50908901E-09, 2.11742798E-12, 9.77018679E+03,  
        2.53971032E+00])),  
        NASA([1000.00, 3000.00],  
        [ 2.79462839E+00, 2.12260586E-03, -1.11936971E-06,  
        2.79521018E-10, -2.68625363E-14, 1.00019069E+04,  
        8.88322674E+00])),  
    transport=gas_transport(geom='linear',  
        diam=3.339,  
        well_depth=139.32,  
        dipole=0.2,  
        polar=1.76,  
        rot_relax=4.0))
```

```
species(name='NO2',  
    atoms='N:1 O:2',  
    thermo=(NASA([298.15, 1000.00],  
        [ 3.39100918E+00, 2.62448348E-03, 5.09790306E-06,  
        -7.62120493E-09, 2.79960135E-12, 2.78130679E+03,  
        8.57220275E+00])),  
        NASA([1000.00, 3000.00],
```

```
[ 3.65239279E+00, 4.71632310E-03, -2.74591748E-06,
  7.45382834E-10, -7.63891108E-14, 2.57216137E+03,
  6.52683440E+00])),
transport=gas_transport(geom='nonlinear',
  diam=3.852,
  well_depth=333.59,
  dipole=0.4,
  rot_relax=1.0))

#-----
# Reaction data
#-----

# Reaction 1
three_body_reaction('H2 + M <=> H + H + M', [4.577e+19, -1.4, 104400.0],
  efficiencies='CH4:2.0 CO:1.9 CO2:3.8 H2:2.5 H2O:12.0')

# Reaction 2
reaction('O + H2 <=> OH + H', [3.800e+12, 0.0, 7948.0],
  options='duplicate')

# Reaction 3
reaction('O + H2 <=> OH + H', [5.531e+14, -0.021, 21049.2],
  options='duplicate')

# Reaction 4
reaction('H2 + OH <=> H + H2O', [8.468e+7, 1.455, 4406.0])

# Reaction 5
reaction('H + O2 + H <=> H2 + O2', [8.800e+22, -1.835, 800.0])

# Reaction 6
reaction('H + O2 + H <=> OH + OH', [4.000e+22, -1.835, 800.0])

# Reaction 7
reaction('H + O2 + O <=> OH + O2', [7.350e+22, -1.835, 800.0])

# Reaction 8
reaction('H + O2 + OH <=> H2O + O2', [2.560e+22, -1.835, 800.0])

# Reaction 9
three_body_reaction('O + O + M <=> O2 + M', [6.165e+15, -0.5, 0.0],
  efficiencies='CH4:2.0 CO:1.9 CO2:3.8 H2:2.5 H2O:12.0')

# Reaction 10
pdep_arrhenius('O2 + H <=> O + OH',
  [(1.00, 'atm'), 7.559e+14, 0.025, 15977.7],
  [(10.00, 'atm'), 2.65e+16, 0.023, 30724.0],
  [(40.00, 'atm'), 2.63e+17, 0.020, 42330.2])

# Reaction 11
```

```
falloff_reaction('H + OH (+ M) <=> H2O (+ M)',  
    kf=[2.500e+13, 0.234, -114.0],  
    kf0=[2.580e+22, -1.887, 512.8],  
    efficiencies='H2:1.5 H2O:13.0 N2:1.0 O2:1.0',  
    falloff=Troe(A=0.73, T3=1e-30, T1=1e+30, T2=1e+30))
```

```
# Reaction 12
```

```
reaction('OH + OH <=> H2O + O', [2.226e+05, 1.875, -1477.1])
```

```
# Reaction 13
```

```
three_body_reaction('O + H + M <=> OH + M', [4.714e+18, -1.0, 0.0],  
    efficiencies='CH4:2.0 CO:1.5 CO2:2.0 H2:2.5 H2O:12.0')
```

```
# Reaction 14
```

```
falloff_reaction('H2O2 (+ M) <=> OH + OH (+ M)',  
    kf=[2.000e+12, 0.9, 48749.0],  
    kf0=[2.353e+24, -2.293, 48743.4],  
    efficiencies='CO:2.8 CO2:1.06 H2:3.7 H2O:5.1 H2O2:5.2 N2:1.5 O2:0.79',  
    falloff=Troe(A=0.43, T3=1e-30, T1=1e+30))
```

```
# Reaction 15
```

```
reaction('H2O2 + H <=> H2O + OH', [2.410e+13, 0.0, 3970.0])
```

```
# Reaction 16
```

```
reaction('H2O2 + H <=> HO2 + H2', [5.020e+06, 2.07, 4300.0])
```

```
# Reaction 17
```

```
reaction('H2O2 + O <=> OH + HO2', [9.550e+06, 2.0, 3970.0])
```

```
# Reaction 18
```

```
reaction('H2O2 + OH <=> H2O + HO2', [1.740e+12, 0.0, 318.0],  
    options='duplicate')
```

```
# Reaction 19
```

```
reaction('H2O2 + OH <=> H2O + HO2', [7.590e+13, 0.0, 7269.0],  
    options='duplicate')
```

```
# Reaction 20
```

```
reaction('HO2 + H <=> H2 + O2', [3.259e+05, 2.055, -1896.6])
```

```
# Reaction 21
```

```
reaction('HO2 + H <=> OH + OH', [3.529e+14, -0.009, 382.6])
```

```
# Reaction 22
```

```
reaction('HO2 + O <=> OH + O2', [3.553e+12, -0.012, -0.02])
```

```
# Reaction 23
```

```
reaction('OH + HO2 <=> H2O + O2', [1.930e+20, -2.49, 584.2],  
    options='duplicate')
```

```
# Reaction 24
```



```
reaction('OH + HO2 <=> H2O + O2', [8.766e+7, 1.195, -1319.5],
        options='duplicate')

# Reaction 25
reaction('HO2 + HO2 <=> H2O2 + O2', [1.214e+10, 0.422, -1480.5],
        options='duplicate')

# Reaction 26
reaction('HO2 + HO2 <=> H2O2 + O2', [2.365e+16, -0.732, 20003.5],
        options='duplicate')

# Reaction 27
falloff_reaction('H + O2 (+ M) <=> HO2 (+ M)',
        kf=[4.660e+12, 0.44, 0.0],
        kf0=[7.521e+20, -1.140, -0.02],
        efficiencies='CH4:2.0 CO2:3.25 H2:1.35 H2O:16.6 N2:1.0 O2:0.9',
        falloff=Troe(A=0.5, T3=1.0, T1=10000000000.0))

# Reaction 28
falloff_reaction('CO + O (+ M) <=> CO2 (+ M)',
        kf=[1.362e+10, 0.0, 2384.0],
        kf0=[1.173e+24, -2.79, 4191.0],
        efficiencies='CO:1.75 CO2:3.6 H2:2.0 H2O:12.0')

# Reaction 29
pdep_arrhenius('CO + OH <=> CO2 + H',
        [(0.01315, 'atm'), 2.100e+05, 1.9, -1064.0],
        [(0.1315, 'atm'), 2.500e+05, 1.88, -1043.0],
        [(1.315, 'atm'), 8.700e+05, 1.73, -685.0],
        [(13.158, 'atm'), 5.812e+7, 1.271, 28.6],
        [(131.58, 'atm'), 2.300e+07, 1.35, 974.0])

# Reaction 30
reaction('CO + HO2 <=> CO2 + OH', [8.550e+03, 2.52, 15560.0])

# Reaction 31
reaction('CO + O2 <=> CO2 + O', [1.119e+12, 0.0, 47700.0])

# Reaction 32
falloff_reaction('CH3 + H (+ M) <=> CH4 (+ M)',
        kf=[6.470e+13, 0.185, -54.0],
        kf0=[4.910e+37, -5.815, 907.6],
        efficiencies='CH4:5.0 CO:2.3 CO2:4.0 H2:4.0 H2O:12.0 N2:1.5 O2:1.5',
        falloff=Troe(A=0.516194, T3=3637.8482, T1=1.0, T2=1e+30))

# Reaction 33
reaction('CH4 + H <=> CH3 + H2', [1.625e+03, 3.609, 8818.5])

# Reaction 34
reaction('CH4 + O <=> CH3 + OH', [5.172749e+6, 2.409, 9236.5])
```

Reaction 35

reaction('CH4 + OH <=> CH3 + H2O', [1.944e+8, 1.747, 3369.3])

Reaction 36

reaction('CH4 + HO2 <=> CH3 + H2O2', [3.122e-01, 2.975, 12865.3])

Reaction 37

reaction('CH3 + HO2 <=> CH4 + O2', [3.185e+02, 2.421, -3089.6])

Reaction 38

pdep_arrhenius('CH3 + O2 <=> CH2O + OH',
[(1.00, 'atm'), 0.0125, 4.125, 18761.8],
[(10.00, 'atm'), 2.882, 3.346, 15266.3],
[(40.00, 'atm'), 2.109, 3.644, 19400.7])

Reaction 39

reaction('CH3 + O <=> CH2O + H', [4.875e+13, 0.048, -150.9])

Reaction 40

pdep_arrhenius('CH3 + OH <=> CH2O + H2',
[(0.01, 'atm'), 3.502e+05, 1.441, -3244.0],
[(0.1, 'atm'), 8.854e+05, 1.327, -2975.0],
[(1.0, 'atm'), 1.650e+07, 0.973, -2010.0],
[(10.0, 'atm'), 2.943e+9, 0.285, 245.2],
[(100.0, 'atm'), 9.494e+18, -2.199, 9769.0])

Reaction 41

falloff_reaction('HCO + H (+ M) <=> CH2O (+ M)',
kf=[1.090e+12, 0.48, -260.0],
kf0=[1.350e+24, -2.57, 1425.0],
falloff=Troe(A=0.7824, T3=271.0, T1=2755.0, T2=6570.0))

Reaction 42

falloff_reaction('CO + H2 (+ M) <=> CH2O (+ M)',
kf=[4.300e+07, 1.5, 79600.0],
kf0=[5.070e+27, -3.42, 84348.0],
falloff=Troe(A=0.932, T3=197.0, T1=1540.0, T2=10300.0))

Reaction 43

reaction('CH2O + O2 <=> HCO + HO2', [1.760e+17, 0.017, 35587.6])

Reaction 44

reaction('CH2O + O <=> HCO + OH', [2.313e+09, 1.035, 1816.5])

Reaction 45

reaction('CH2O + H <=> HCO + H2', [4.069e+03, 2.717, 1963.4])

Reaction 46

reaction('CH2O + OH <=> HCO + H2O', [2.422e+11, 0.982, -503.3])

Reaction 47

reaction('CH2O + HO2 <=> HCO + H2O2', [2.632e-10, 4.342, 4465.8])

Reaction 48

reaction('CH2O + CH3 <=> HCO + CH4', [3.430e-05, 4.344, 3216.4])

Reaction 49

reaction('CH2O + OH => H + CO + H2O', [2.565e+11, 0.693, 9368.7])

Reaction 50

reaction('CH2O + H => H + CO + H2', [1.940e+07, 2.192, 11740.3])

Reaction 51

three_body_reaction('HCO + M <=> H + CO + M', [8.993e+11, 0.691, 14221.72],
efficiencies='CH4:2.0 CO:1.5 CO2:2.0 H2:2.0 H2O:6.0')

Reaction 52

reaction('HCO + O2 <=> CO + HO2', [7.567e+04, 0.765, -412.1383])

Reaction 53

reaction('HCO + O <=> CO + OH', [3.020e+13, 0.0, 0.0])

Reaction 54

reaction('HCO + H <=> CO + H2', [1.121e+12, 0.385, -144.4])

Reaction 55

reaction('HCO + OH <=> CO + H2O', [1.196e+13, 0.019, -0.013])

Reaction 56

reaction('HCO + CH3 <=> CO + CH4', [1.423e+12, -0.017, -0.014])

Reaction 57

reaction('HCO + HCO <=> CO + CH2O', [2.700e+13, 0.0, 0.0])

Reaction 58

reaction('HCO + O <=> CO2 + H', [3.000e+13, 0.0, 0.0])

Reaction 59

reaction('HCO + HO2 => CO2 + H + OH', [3.000e+13, 0.0, 0.0])

Reaction 60

reaction('HCO + HCO => H2 + CO + CO', [3.000e+12, 0.0, 0.0])

!!!! NOx !!!!!!!

Reaction 61

reaction('N + OH <=> NO + H', [1.400e+11, -0.009, -0.03])

Reaction 62

reaction('N + O2 <=> NO + O', [3.026e+09, 0.992, 3600.6])

Reaction 63

reaction('N + NO <=> N2 + O', [2.730e+14, 0.124, 0.006])

Reaction 64

reaction('NO + HO2 <=> NO2 + OH', [1.841e+11, 0.0148, -722.4])

Reaction 65

reaction('NO + O <=> NO2', [2.732e-01, 3.118, 1278.9])

Reaction 66

reaction('NO2 + O <=> NO + O2', [1.113e+07, 0.0179, -323.1])

Reaction 67

reaction('NO2 + NO2 <=> NO + NO + O2', [1.110e+10, 0.0276, 15261.9])

Reaction 68

reaction('CO + NO2 <=> NO + CO2', [5.770e+14, -0.012, 45010.2])

Reaction 69

reaction('CO2 + N <=> NO + CO', [2.980e+12, 0.023, 16973.9])

Reaction 70

reaction('N2 + OH => NO + N + H', [1.279e+01, 0.0233, 0.007])

Reaction 71

reaction('N2 + O => 2 N + O', [8.286e+00, 0.0015, -0.03])

Appendix G

Comparison of Optimisation Algorithms in Surrogate Formulator

To determine the most effective optimisation algorithm available in the SciPy library for finding the optimal surrogate formulation, several algorithms were evaluated, including:

1. Nelder-Mead: A simplex method as described in Section 7.3.2.2.
2. Sequential Least Squares Programming (SLSQP): A gradient-based algorithm that minimises a quadratic approximation of the objective error function. At each iteration, the algorithm solves a series of quadratic programming subproblems using a combination of gradient and Hessian information. The algorithm also incorporates a line search procedure at each step.
3. Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm: A quasi-Newton method that approximates the inverse of the Hessian matrix without computing it explicitly. At each iteration, the algorithm computes a search direction based on the current estimate of the Hessian matrix and the gradient of the function. It then takes a step along this direction, and updates the estimate of the Hessian matrix based on the change in the gradient and the change in the search direction.
4. L-BFGS-B: A variant of the BFGS algorithm that approximates the inverse Hessian matrix using only a limited amount of memory/information.
5. Conjugate Gradient (CG): A gradient-based method that does not solve the Hessian matrix explicitly. This method uses conjugate directions to search for the minima along a sequence of steps. At each step, the method finds a new conjugate direction that is orthogonal to all previous directions and moves along this direction to find the next minimum.

6. TNC: A combination of a truncated Newton method and a conjugate method. TNC iteratively minimises a quadratic approximation of the objective function. At each iteration, the method computes a search direction using the conjugate gradient method and takes a step along this direction. The step size is determined using a line search procedure.

For each optimisation algorithm, an entry from the library of surrogate components was selected. The algorithm was employed to determine the mole fractions that produced the lowest OEF (Equation 7.4). This was repeated for every entry. To ensure the reliability of the results, each optimisation algorithm was executed twenty times for each entry. The combustion property targets, along with the OEF values of the surrogate formulations with the lowest OEF from each optimisation algorithm, are presented in Table G.1. Compared to the other evaluated algorithms, the Nelder-Mead and L-BFGS-B methods generated considerably better surrogates, with the CG method proving to be the least effective for this purpose. Additionally, the Nelder-Mead method outperformed L-BFGS-B in terms of computational cost, completing the optimisation process approximately 5% faster. Therefore, the Nelder-Mead method was selected as the optimisation algorithm for the surrogate formulator developed in this study.

Table G.1. AXL combustion property targets and objective error function (OEF) of the best surrogate using each optimisation algorithm in the surrogate formulator algorithm.

	AXL	Nelder-Mead	SLSQP	BFGS	L-BFGS-B	CG	TNC
MW (g mol ⁻¹)	224.5	194.4	179.0	184.2	191.1	176.4	191.9
TSI	62.6	28.0	25.5	30.5	29.2	34.0	32.3
H/C	184	1.90	1.89	1.85	1.90	1.78	1.86
DCN	53.5	52.1	50.8	52.1	48.7	50.8	50.5
pCH ₃ (mol %)	18.2	18.2	13.8	13.2	19.7	8.7	16.5
pCH ₂ (mol %)	45.2	48.8	46.0	48.4	45.1	47.1	48.0
Total Ar (mol %)	11.5	11.5	12.7	14.2	11.5	18.2	16.0
OEF		0.239	0.297	0.312	0.244	0.392	0.300

Appendix H

Virtualised Detailed Model Validation

1. Constant UV: Ignition Delay Time

The Virtualised Detailed Model (429 nodes).has good replication of IDT, however the fidelity decreases notably at one atmosphere at lower temperatures. This can also be somewhat seen in the PSR plots that follow.

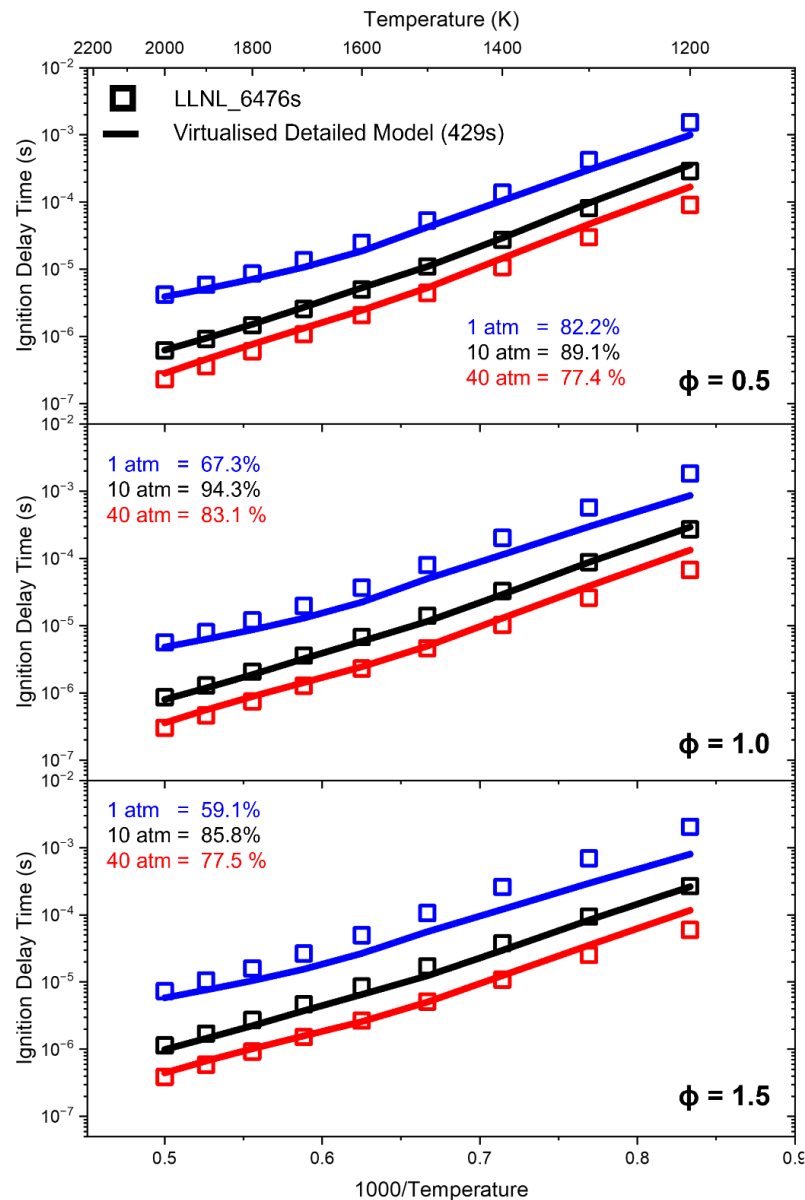


Figure H.1. Ignition delay time as a function of temperature for lean, stoichiometric, and rich AXL/air mixtures at 1, 10 and 40 atm using the LLNL_6476s detailed model (symbols) and Virtualised Detailed Model (lines).

2. Perfectly Stirred Reactor: Speciation

Mole fractions of CO are used as validation for Virtualised Detailed Model. The Virtualised Detailed Model has good replication across the performance conditions (Table 7.1). Representative temperature and equivalence ratio conditions are used here.

1200 K:

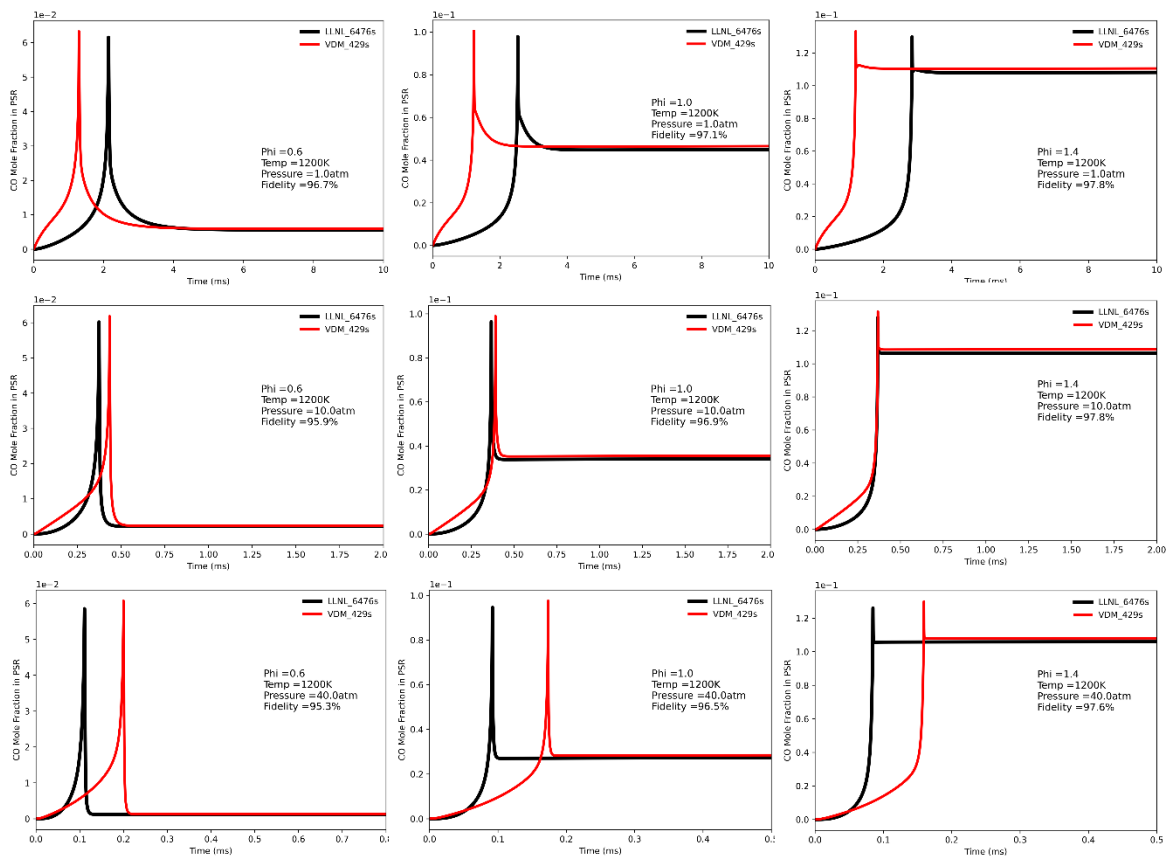


Figure H.2. CO mole fractions in PSR simulations at 1200 K using LLNL_6476s detailed model (black) and Virtualised Detailed Model (red). Equivalence ratios 0.6 (left), 1.0 (middle) and 1.4 (right). Virtualised Detailed Model has a good replication of detailed model CO mole fractions.

1600 K:

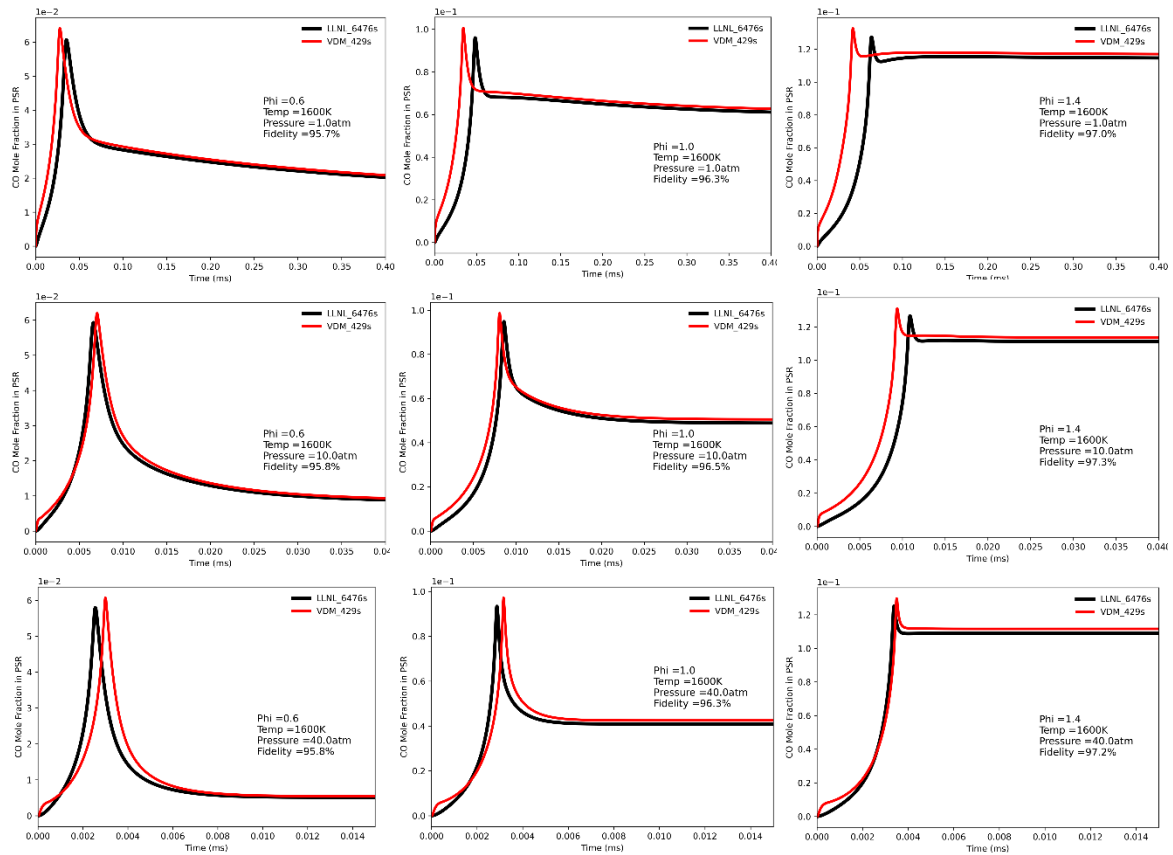


Figure H.3. CO mole fractions in PSR simulations at 1600 K using LLNL_6476s detailed model (black) and Virtualised Detailed Model (red). Equivalence ratios 0.6 (left), 1.0 (middle) and 1.4 (right). Virtualised Detailed Model has a good replication of detailed model CO mole fractions.

2000 K:

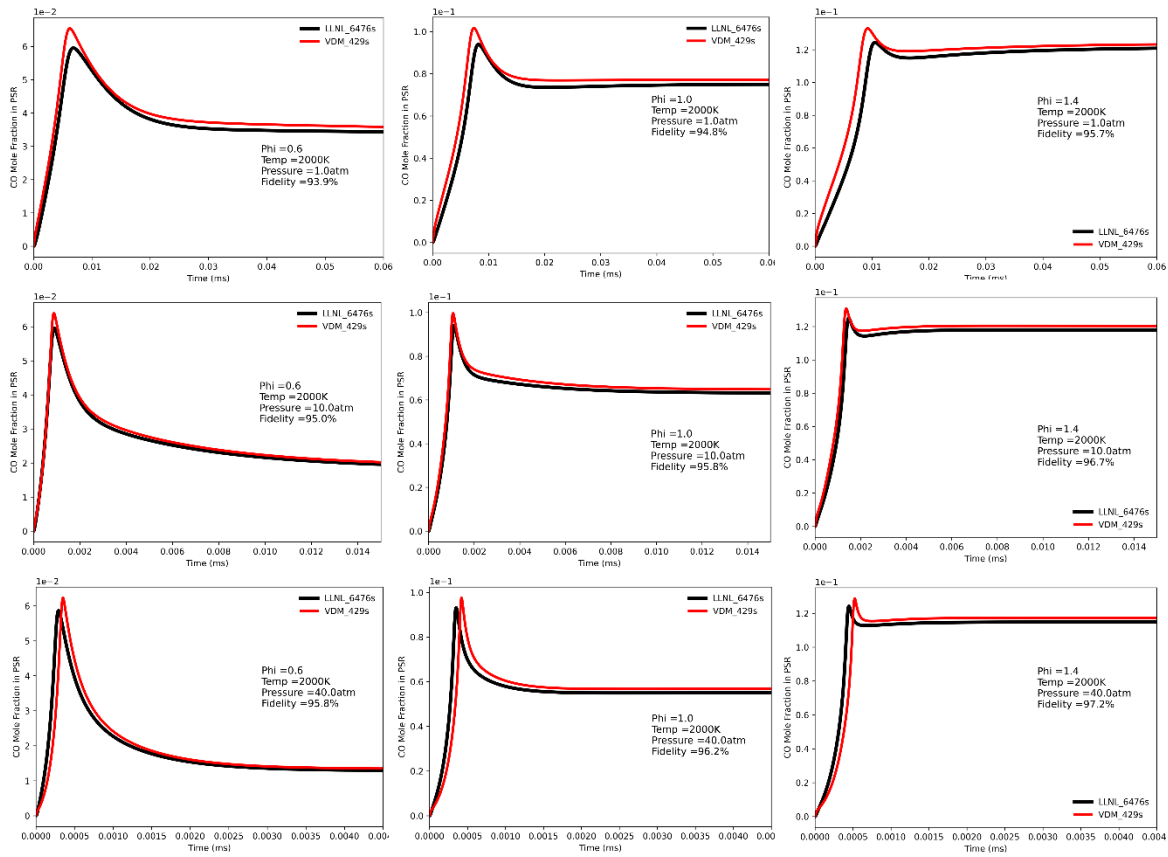


Figure H.4. CO mole fractions in PSR simulations at 2000 K using LLNL_6476s detailed model (black) and Virtualised Detailed Model (red). Equivalence ratios 0.6 (left), 1.0 (middle) and 1.4 (right). Virtualised Detailed Model has a good replication of detailed model CO mole fractions.

Appendix I

TCD_35sOp_HT Validation

1. Constant UV: Ignition Delay Time

The compact model has good replication of IDT across the performance conditions (Table 7.1).

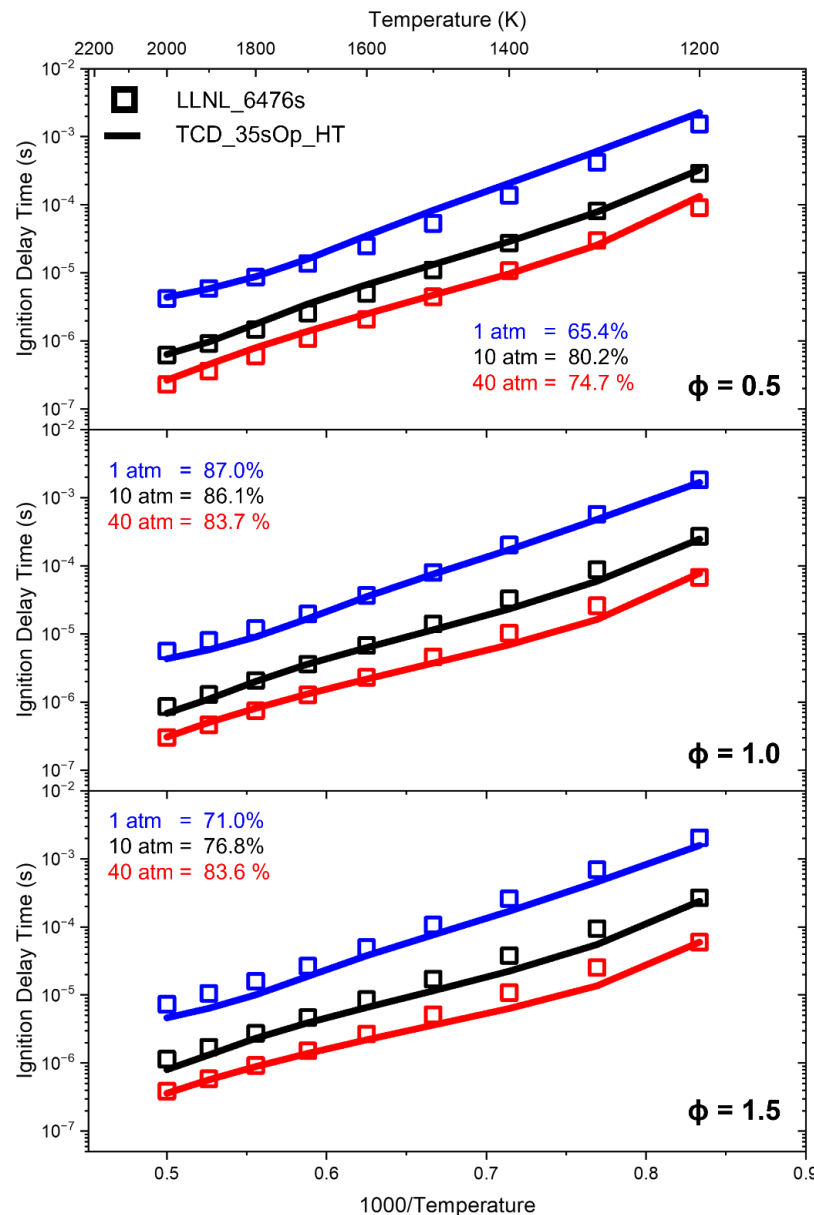


Figure I.1. Ignition delay time as a function of temperature for lean, stoichiometric, and rich AXL/air mixtures at 1, 10 and 40 atm using the LLNL_6476s detailed model (symbols) and TCD_35sOp_HT (lines).

2. Perfectly Stirred Reactor: Speciation

Mole fractions of CO are used as validation for TCD_35sOp_HT. The compact model has good replication across the performance conditions (Table 7.1). Representative temperature and equivalence ratio conditions are used here.

1200 K:

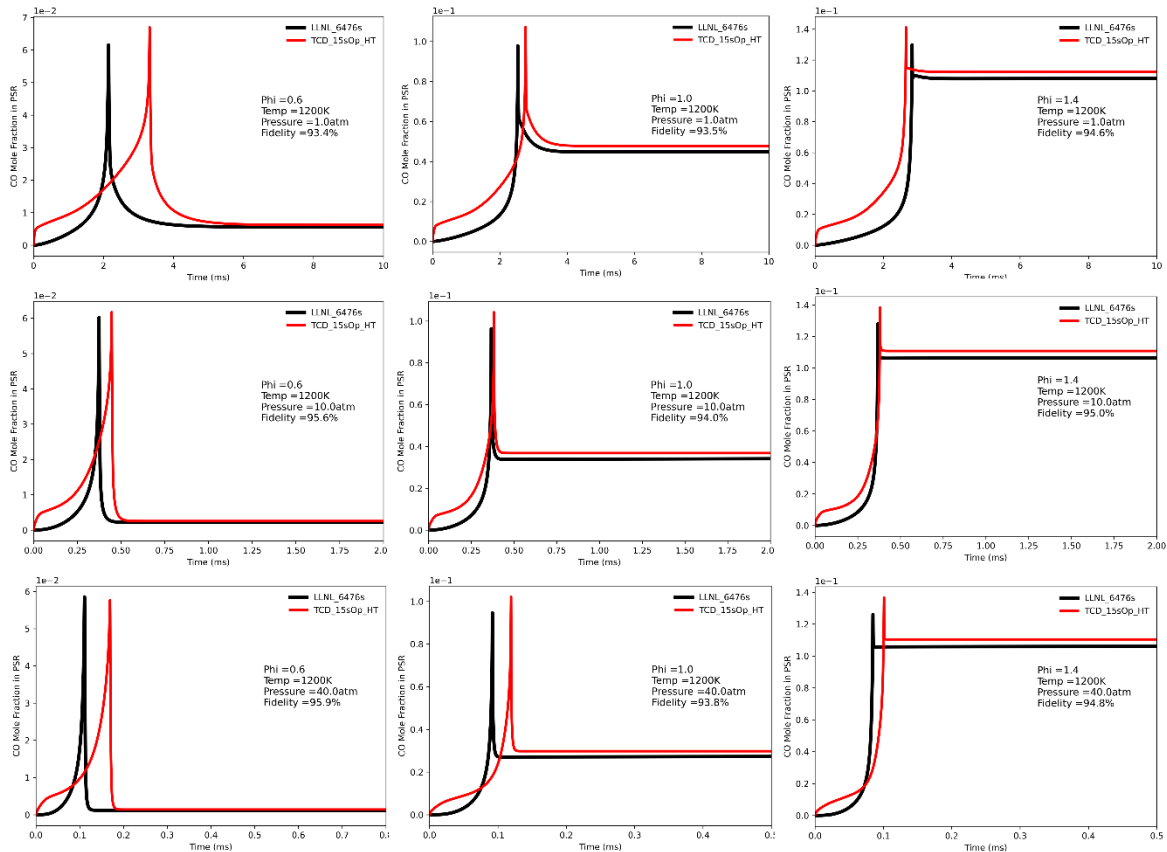


Figure I.2. CO mole fractions in PSR simulations at 1200 K using LLNL_6476s detailed model (black) and TCD_35sOp_HT (red). Equivalence ratios 0.6 (left), 1.0 (middle) and 1.4 (right). TCD_35sOp_HT has a good replication of detailed model CO mole fractions.

1600 K:

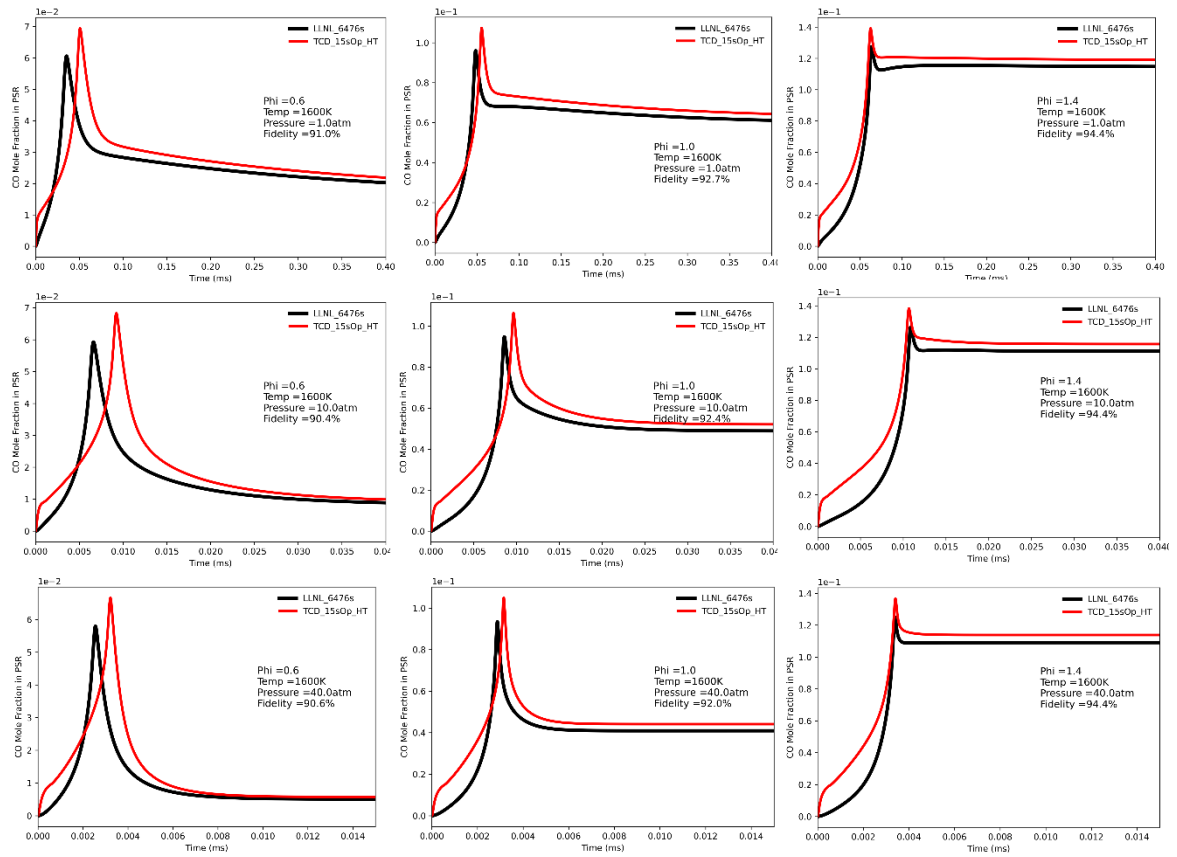


Figure I.3. CO mole fractions in PSR simulations at 1600 K using LLNL_6476s detailed model (black) and TCD_35sOp_HT (red). Equivalence ratios 0.6 (left), 1.0 (middle) and 1.4 (right). TCD_35sOp_HT has a good replication of detailed model CO mole fractions.

2000 K:

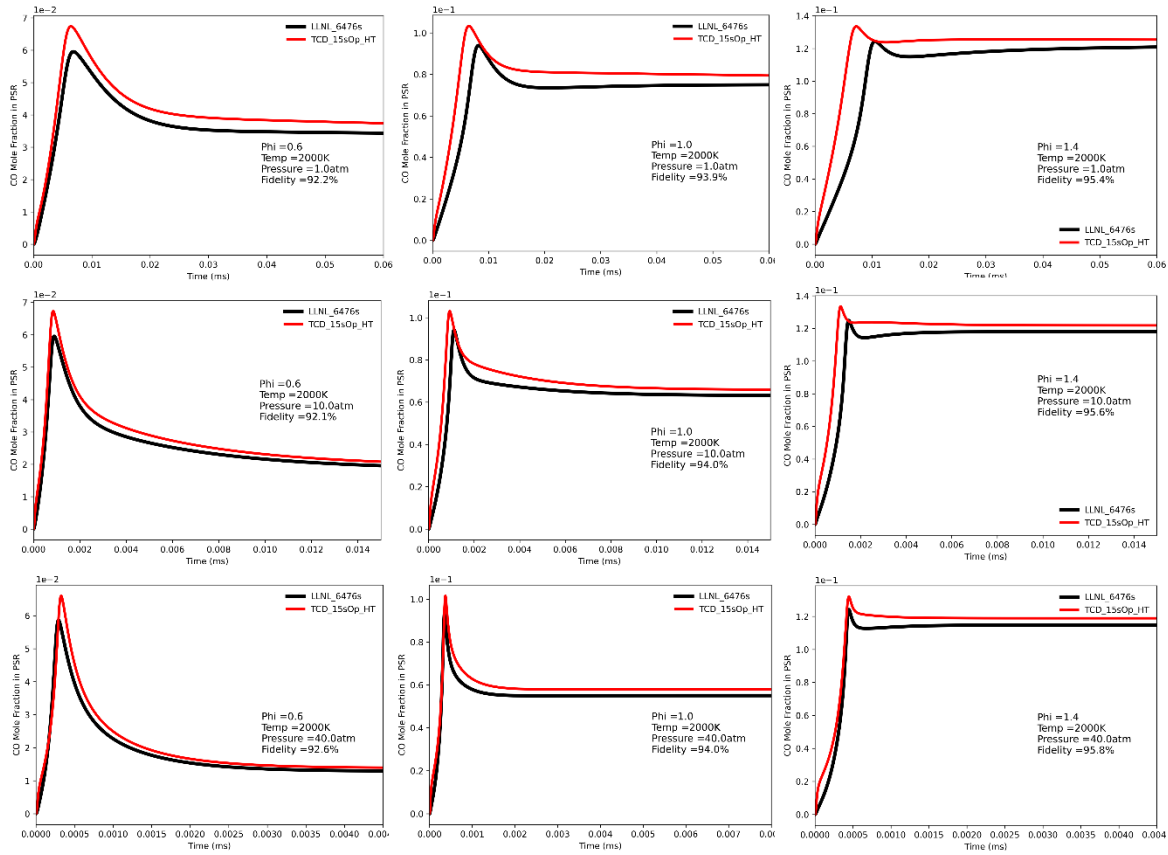


Figure I.4. CO mole fractions in PSR simulations at 2000 K using LLNL_6476s detailed model (black) and TCD_35sOp_HT (red). Equivalence ratios 0.6 (left), 1.0 (middle) and 1.4 (right). TCD_35sOp_HT has a good replication of detailed model CO mole fractions.

3. Freely Propagating Flame: Laminar Burning Velocity

The compact model has good replication of laminar burning velocity across the performance conditions (Table 7.1). The fidelity decreases at 1 atm.

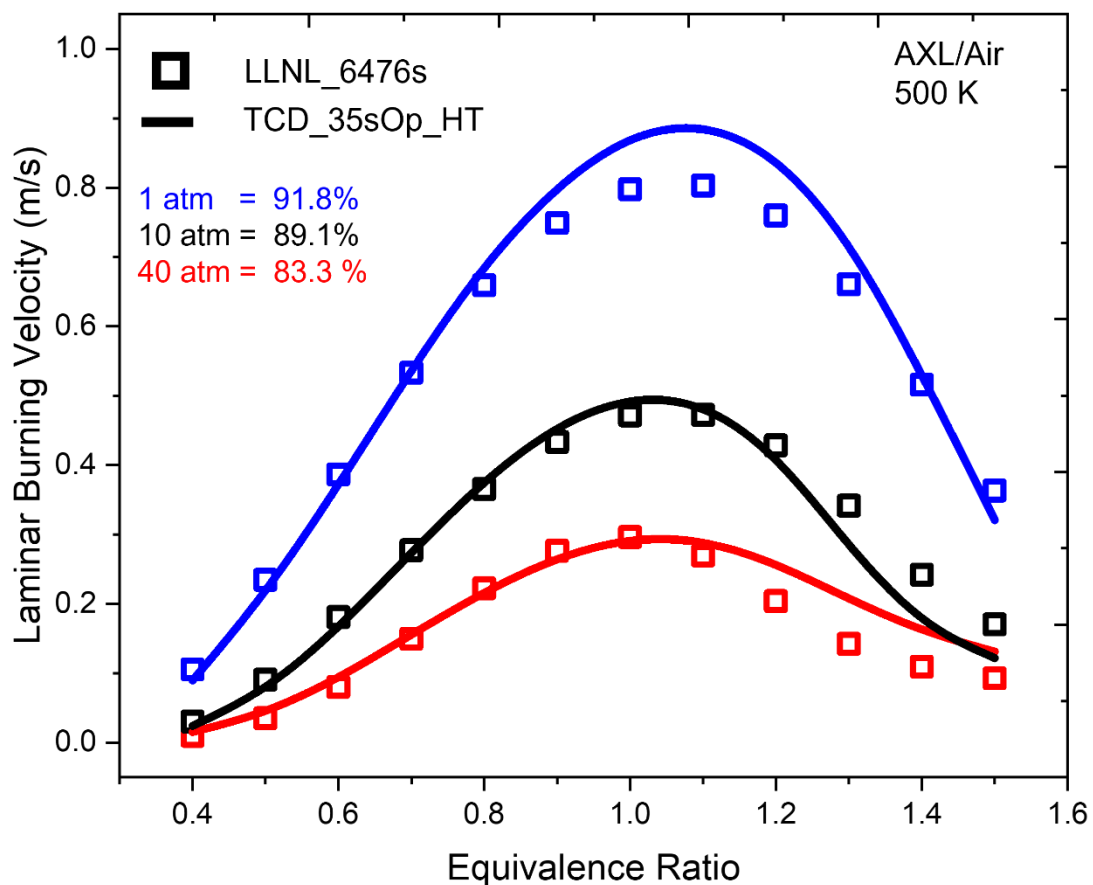


Figure I.5. Laminar burning velocity as a function of equivalence ratio at 1, 10 and 40 atm using the LLNL_6476s detailed model (symbols) and TCD_35sOp_HT (lines)

4. Freely Propagating Flame: Speciation

Mole fractions of CO are used as validation for TCD_35sOp_HT. The compact model has good replication across the performance conditions (Table 5.1). Representative temperature and equivalence ratio conditions are used here.

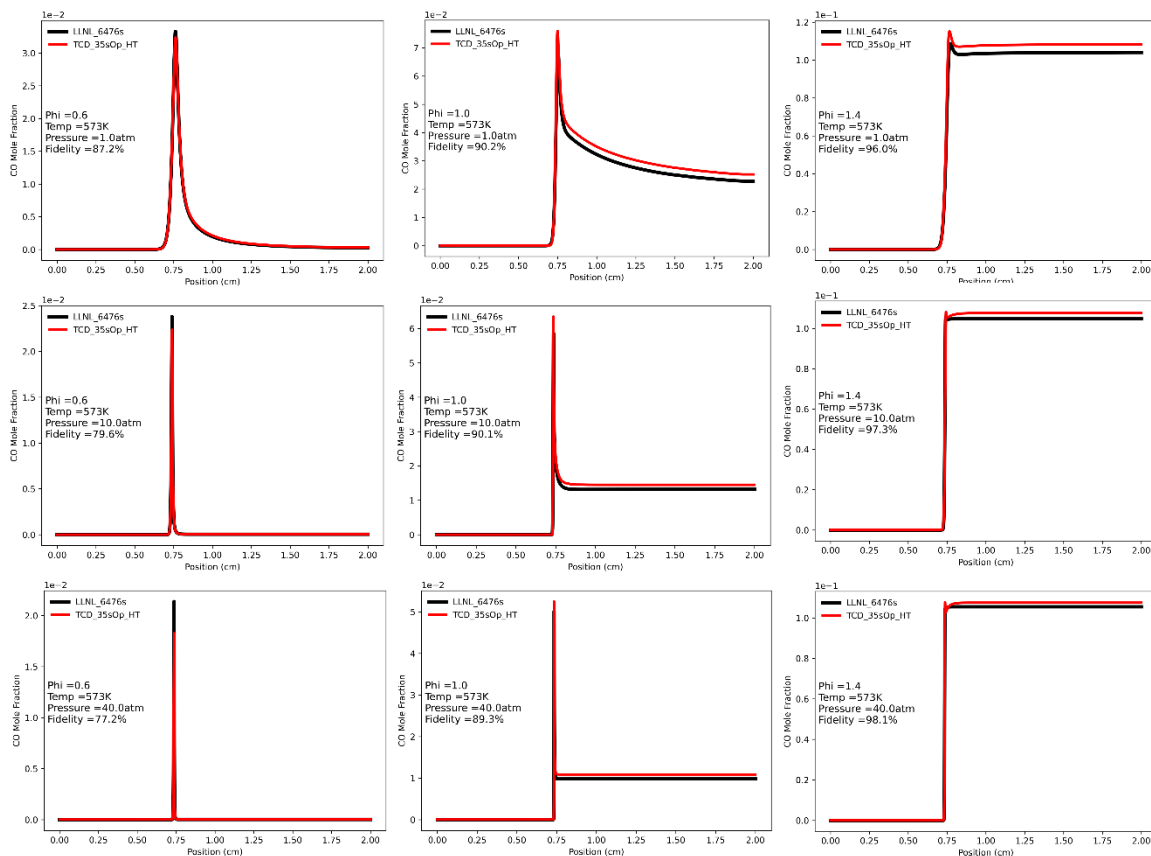


Figure I.6. CO mole fractions in freely propagating flame simulations at 573 K using LLNL_6476s detailed model (black) and TCD_35sOp_HT (red). Equivalence ratios 0.6 (left), 1.0 (middle) and 1.4 (right). NUIGMECH_15sOp has good replication of detailed model CO mole fractions at all conditions.

Appendix J

TCD_35sOp_HT Files

TCD_35sOp_HT Cantera File:

```
#-----  
# CTI file converted from solution object  
#-----  
  
units(length = "cm", time = "s", quantity = "mol", act_energy = "cal/mol")  
  
ideal_gas(name = "reduced_model_C3H4-A",  
  elements = "C H N O",  
  species = "" vAXL n-AXL n-AXLj i-AXL i-AXLj cy-AXL cy-AXLj Ar-AXL Ar-AXLj  
N2  
      H2 H O2 O H2O OH H2O2 HO2 CO CO2 CH3  
      CH2O HCO C2H4 C2H3 CH2CHO HCCO C3H6  
      C3H5-A C2H3CHO IC4H8 C4H8-1 C4H71-1  
      C4H71-4 C4H6 """,  
  reactions = "all",  
  initial_state = state(temperature = 300.0, pressure = 101325.0) )  
  
#-----  
# Species data  
#-----  
species(name = "vAXL",  
  atoms = "C:14, H:26",  
  thermo = (  
    NASA( [300.0, 1395.0], [-3.878600580e+00, 1.756486900e-01,  
      -1.284488850e-04, 5.257025940e-08,  
      -9.606138570e-12,  
      -3.080387030e+04, 6.033746160e+01] ),  
    NASA( [1395.0, 5000.0], [4.437667460e+01, 6.165724920e-02,  
      -2.108659070e-05, 3.273431010e-09,  
      -1.899013580e-13, -4.763423810e+04, -1.988149510e+02])),  
  transport = gas_transport(  
    geom = "nonlinear",  
    diam = 7.32,  
    well_depth = 878.89,  
    polar = 26.220000000000002,  
    rot_relax = 1.0)  
  )
```

```
species(name = "n-AXL",
  atoms = "C:7, H:13",
  thermo=(NASA([300.00, 1395.00],
    [-1.29241388E+00, 8.80209583E-02, -5.89244920E-05,
      2.21084517E-08, -3.82062585E-12, -2.57053655E+04,
      3.54340874E+01]),
    NASA([1395.00, 5000.00],
      [ 2.25012314E+01, 3.46122447E-02, -1.18043982E-05,
        1.82894500E-09, -1.05955678E-13, -3.42943478E+04,
        -9.33565656E+01])),
  transport=gas_transport(geom='nonlinear',
    diam=6.253,
    well_depth=459.6,
    rot_relax=1.0))
```

```
species(name = "n-AXLj",
  atoms = "C:7, H:12",
  thermo=(NASA([300.00, 1395.00],
    [-9.05065088E-01, 8.44203765E-02, -5.76612386E-05,
      2.22197633E-08, -3.93225174E-12, -9.86691856E+02,
      3.66040743E+01]),
    NASA([1395.00, 5000.00],
      [ 2.18654648E+01, 3.27099467E-02, -1.11707195E-05,
        1.73230780E-09, -1.00418683E-13, -9.15809161E+03,
        -8.64578314E+01])),
  transport=gas_transport(geom='nonlinear',
    diam=6.253,
    well_depth=459.6,
    rot_relax=1.0))
```

```
species(name = "i-AXL",
  atoms = "C:7, H:13",
  thermo = (
    NASA( [300.0, 1397.0], [-1.989529060e+00, 6.955863350e-02,
      -5.270053060e-05, 2.319291100e-08,
      -4.556671420e-12,
      -2.035525580e+04, 3.425834940e+01] ),
    NASA( [1397.0, 5000.0], [1.580241650e+01, 2.589624550e-02,
      -8.802112770e-06, 1.360510240e-09,
      -7.868047530e-14, -2.647616310e+04, -6.085495170e+01])),
  transport = gas_transport(
    geom = "nonlinear",
    diam = 5.548,
    well_depth = 382.1,
    polar = 0.0,
    rot_relax = 1.0))
```

```
species(name = "i-AXLj",
  atoms = "C:7, H:12",
  thermo = (
```

```
NASA( [300.0, 1397.0], [-1.989529060e+00, 6.955863350e-02,  
-5.270053060e-05, 2.319291100e-08,  
-4.556671420e-12,-2.035525580e+04, 3.425834940e+01] ),  
NASA( [1397.0, 5000.0], [1.580241650e+01, 2.589624550e-02,  
-8.802112770e-06, 1.360510240e-09,  
-7.868047530e-14,-2.647616310e+04,-6.085495170e+01] )),  
transport = gas_transport(  
  geom = "nonlinear",  
  diam = 5.548,  
  well_depth = 382.1,  
  polar = 0.0,  
  rot_relax = 1.0))  
  
species(name = "cy-AXL",  
  atoms = "C:7, H:13",  
  thermo = (  
    NASA( [300.0, 1391.0], [-8.572309280e+00, 1.041575590e-01,  
-7.802079050e-05, 3.213749350e-08,  
-5.859717260e-12,-1.994014610e+04, 6.206999380e+01] ),  
    NASA( [1391.0, 5000.0], [2.147853430e+01, 3.322159170e-02,  
-1.148619340e-05, 1.796389330e-09,  
-1.047618640e-13,-3.040176560e+04,-9.929376650e+01] )),  
  transport = gas_transport(  
    geom = "nonlinear",  
    diam = 10.31,  
    well_depth = 531.322,  
    polar = 0.0,  
    rot_relax = 1.0))  
  
species(name = "cy-AXLj",  
  atoms = "C:7, H:12",  
  thermo = (  
    NASA( [300.0, 1397.0], [-1.989529060e+00, 6.955863350e-02,  
-5.270053060e-05, 2.319291100e-08,  
-4.556671420e-12,-2.035525580e+04, 3.425834940e+01] ),  
    NASA( [1397.0, 5000.0], [1.580241650e+01, 2.589624550e-02,  
-8.802112770e-06, 1.360510240e-09,  
-7.868047530e-14,-2.647616310e+04,-6.085495170e+01] )),  
  transport = gas_transport(  
    geom = "nonlinear",  
    diam = 5.548,  
    well_depth = 382.1,  
    polar = 0.0,  
    rot_relax = 1.0))  
  
species(name = "Ar-AXL",  
  atoms = "C:7, H:13",  
  thermo = (  
    NASA( [200.0, 1000.0], [-2.433953330e+00, 5.526653820e-02,  
-1.430125030e-05,
```

```
-1.342114180e-08, 6.316477000e-12,  
4.433347510e+03, 3.664319860e+01] ),  
NASA( [1000.0, 6000.0], [1.294003400e+01, 2.669128700e-02,  
-9.683850500e-06, 1.573862900e-09,  
-9.466360100e-14,-6.586705410e+02,-4.668554200e+01] )),  
transport = gas_transport(  
    geom = "nonlinear",  
    diam = 5.68,  
    well_depth = 495.30000000000007,  
    polar = 12.300000000000002,  
    rot_relax = 1.0,  
    dipole= 0.4300001227206934))
```

```
species(name = "Ar-AXLj",  
atoms = "C:7, H:12",  
thermo = (  
    NASA( [200.0, 1000.0], [-2.433953330e+00, 5.526653820e-02,  
-1.430125030e-05,  
-1.342114180e-08, 6.316477000e-12,  
4.433347510e+03, 3.664319860e+01] ),  
    NASA( [1000.0, 6000.0], [1.294003400e+01, 2.669128700e-02,  
-9.683850500e-06, 1.573862900e-09,  
-9.466360100e-14,-6.586705410e+02,-4.668554200e+01] )),  
transport = gas_transport(  
    geom = "nonlinear",  
    diam = 5.68,  
    well_depth = 495.30000000000007,  
    polar = 12.300000000000002,  
    rot_relax = 1.0,  
    dipole= 0.4300001227206934))
```

```
species(name = "N2",  
atoms = "N:2",  
thermo = (  
    NASA( [200.0, 1000.0], [3.587600400e+00, -6.025471250e-04,  
8.983313280e-07, 7.549216010e-10,  
-7.074675720e-13,-1.051964560e+03, 2.738940360e+00] ),  
    NASA( [1000.0, 6000.0], [2.952576370e+00, 1.396900400e-03,  
-4.926316030e-07, 7.860101950e-11,  
-4.607552040e-15,-9.245018380e+02, 5.871290100e+00] )),  
transport = gas_transport(  
    geom = "linear",  
    diam = 3.621,  
    well_depth = 97.53,  
    polar = 1.76,  
    rot_relax = 4.0))
```

```
species(name = "H2",  
atoms = "H:2",
```

```
thermo = (  
  NASA( [200.0, 1000.0], [2.721136140e+00, 4.792141710e-03,  
    -1.014822220e-05, 8.969367160e-09,  
    -2.706630130e-12, -9.511467110e+02, -8.385212940e-01] ),  
  NASA( [1000.0, 6000.0], [2.932865750e+00, 8.266080260e-04,  
    -1.464023640e-07, 1.541004140e-11,  
    -6.888048000e-16, -8.167484190e+02, -1.028306820e+00] )),  
transport = gas_transport(  
  geom = "linear",  
  diam = 2.9200000000000004,  
  well_depth = 38.0,  
  polar = 0.7900000000000001,  
  rot_relax = 280.0))  
  
species(name = "H",  
  atoms = "H:1",  
  thermo = (  
    NASA( [200.0, 1000.0], [2.500000000e+00, -2.969035190e-15,  
      8.236085410e-18, -9.309089260e-21,  
      3.606033040e-24, 2.547366000e+04, -4.466828500e-01] ),  
    NASA( [1000.0, 6000.0], [2.500000000e+00, 0.000000000e+00,  
      0.000000000e+00, 0.000000000e+00,  
      0.000000000e+00, 2.547366000e+04, -4.466828500e-01] )),  
  transport = gas_transport(  
    geom = "atom",  
    diam = 2.05,  
    well_depth = 145.0,  
    polar = 0.0,  
    rot_relax = 0.0))  
  
species(name = "O2",  
  atoms = "O:2",  
  thermo = (  
    NASA( [200.0, 1000.0], [3.654933020e+00, -1.917680640e-03,  
      6.689743760e-06, -5.894957100e-09,  
      1.663418450e-12, -1.052703670e+03, 4.172612600e+00] ),  
    NASA( [1000.0, 6000.0], [3.660960650e+00, 6.563658110e-04,  
      -1.411496270e-07, 2.057979350e-11,  
      -1.299134360e-15, -1.214730770e+03, 3.416709190e+00] )),  
  transport = gas_transport(  
    geom = "linear",  
    diam = 3.458,  
    well_depth = 107.4,  
    polar = 1.6,  
    rot_relax = 3.8))  
  
species(name = "O",  
  atoms = "O:1",  
  thermo = (  
    NASA( [200.0, 1000.0], [3.106527750e+00, -2.756904210e-03,  
      5.114358810e-06, -4.294942630e-09,
```

```
1.347565970e-12, 2.912770090e+04, 2.301235780e+00] ),
NASA( [1000.0, 6000.0], [2.543636970e+00, -2.731624860e-05,
-4.190295200e-09, 4.954818450e-12,
-4.795536940e-16, 2.922661550e+04, 4.922946370e+00] )),
transport = gas_transport(
  geom = "atom",
  diam = 2.7500000000000004,
  well_depth = 80.0,
  polar = 0.0,
  rot_relax = 0.0))

species(name = "H2O",
  atoms = "H:2, O:1",
  thermo = (
    NASA( [200.0, 1000.0], [4.239470850e+00, -2.381937210e-03,
7.531457410e-06, -6.700390480e-09,
2.278015550e-12, -3.029732530e+04, -1.013902610e+00] ),
    NASA( [1000.0, 6000.0], [2.677038900e+00, 2.973181600e-03,
-7.737688900e-07, 9.443351400e-11,
-4.268999100e-15, -2.988629310e+04, 6.882119110e+00] )),
  transport = gas_transport(
    geom = "nonlinear",
    diam = 2.6050000000000004,
    well_depth = 572.4,
    polar = 0.0,
    rot_relax = 4.0,
    dipole= 1.8440005262719967))

species(name = "OH",
  atoms = "H:1, O:1",
  thermo = (
    NASA( [200.0, 1000.0], [3.984540360e+00, -2.338079350e-03,
4.432325390e-06, -3.658144720e-09,
1.270948310e-12, 3.369554460e+03, -7.394023780e-02] ),
    NASA( [1000.0, 6000.0], [2.838530330e+00, 1.107412890e-03,
-2.940002090e-07, 4.206987290e-11,
-2.422898900e-15, 3.697880830e+03, 5.845025070e+00] )),
  transport = gas_transport(
    geom = "linear",
    diam = 2.7500000000000004,
    well_depth = 80.0,
    polar = 0.0,
    rot_relax = 0.0))

species(name = "H2O2",
  atoms = "H:2, O:2",
  thermo = (
    NASA( [200.0, 1000.0], [3.828191160e+00, 3.273080420e-03,
5.582988110e-06, -8.217793020e-09,
3.054933630e-12, -1.766382310e+04, 5.240069800e+00] ),
    NASA( [1000.0, 6000.0], [4.579773050e+00, 4.053260030e-03,
```

```
-1.298447300e-06, 1.982114000e-10,  
-1.139687920e-14,  
-1.800241800e+04, 6.701119310e-01] )),  
transport = gas_transport(  
    geom = "nonlinear",  
    diam = 3.458,  
    well_depth = 107.4,  
    polar = 0.0,  
    rot_relax = 3.8))  
  
species(name = "HO2",  
    atoms = "H:1, O:2",  
    thermo = (  
        NASA( [200.0, 1000.0], [3.877615000e+00, -1.159847110e-03,  
            1.065525160e-05, -1.168183220e-08,  
            4.035641140e-12, 3.014059170e+02, 5.429505420e+00] ),  
        NASA( [1000.0, 5000.0], [4.172287410e+00, 1.881176270e-03,  
            -3.462772860e-07, 1.946575490e-11,  
            1.762569050e-16, 3.516659350e+01, 2.962155150e+00] )),  
    transport = gas_transport(  
        geom = "nonlinear",  
        diam = 3.458,  
        well_depth = 107.4,  
        polar = 0.0,  
        rot_relax = 1.0))  
  
species(name = "CO",  
    atoms = "C:1, O:1",  
    thermo = (  
        NASA( [200.0, 1000.0], [3.625396780e+00, -9.984311890e-04,  
            2.152418340e-06, -4.547367910e-10,  
            -3.360716210e-13, -1.434812840e+04, 3.323214240e+00] ),  
        NASA( [1000.0, 6000.0], [3.048485900e+00, 1.351728100e-03,  
            -4.857940500e-07, 7.885364400e-11,  
            -4.698074600e-15, -1.426656540e+04, 6.016613460e+00] )),  
    transport = gas_transport(  
        geom = "linear",  
        diam = 3.65,  
        well_depth = 98.1,  
        polar = 1.9500000000000002,  
        rot_relax = 1.8))  
  
species(name = "CO2",  
    atoms = "C:1, O:2",  
    thermo = (  
        NASA( [200.0, 1000.0], [2.134170410e+00, 1.086804560e-02,  
            -1.263483210e-05, 9.067852460e-09,  
            -2.901941240e-12, -4.835234740e+04, 1.079993010e+01] ),  
        NASA( [1000.0, 6000.0], [4.636511100e+00, 2.741456900e-03,  
            -9.958975900e-07, 1.603866600e-10,  
            -9.161985700e-15, -4.902272800e+04, -1.932545110e+00] )),
```

```
transport = gas_transport(  
    geom = "linear",  
    diam = 3.763,  
    well_depth = 244.0,  
    polar = 2.6500000000000004,  
    rot_relax = 2.1))
```

```
species(name = "CH3",  
    atoms = "C:1, H:3",  
    thermo = (  
        NASA( [200.0, 1000.0], [3.428879980e+00, 4.058382190e-03,  
            -1.944554200e-07, 1.604206440e-10,  
            -3.634543110e-13, 1.644283830e+04, 2.595405370e+00] ),  
        NASA( [1000.0, 6000.0], [2.978120600e+00, 5.797852000e-03,  
            -1.975580000e-06, 3.072979000e-10,  
            -1.791741600e-14, 1.651174430e+04, 4.724890040e+00] )),  
    transport = gas_transport(  
        geom = "linear",  
        diam = 3.8,  
        well_depth = 144.0,  
        polar = 0.0,  
        rot_relax = 0.0))
```

```
species(name = "CH2O",  
    atoms = "C:1, H:2, O:1",  
    thermo = (  
        NASA( [200.0, 1000.0], [4.178126060e+00, -4.699387720e-03,  
            2.207942890e-05, -1.965062710e-08,  
            5.548589190e-12, -1.432493670e+04, 3.088567330e+00] ),  
        NASA( [1000.0, 6000.0], [3.169526650e+00, 6.193205600e-03,  
            -2.250563660e-06, 3.659756600e-10,  
            -2.201494580e-14, -1.454266630e+04, 6.048578310e+00] )),  
    transport = gas_transport(  
        geom = "nonlinear",  
        diam = 3.59,  
        well_depth = 498.00000000000006,  
        polar = 0.0,  
        rot_relax = 2.0))
```

```
species(name = "HCO",  
    atoms = "C:1, H:1, O:1",  
    thermo = (  
        NASA( [200.0, 1000.0], [3.953242930e+00, -9.150884650e-04,  
            6.963500860e-06, -4.982659010e-09,  
            8.509861510e-13, 3.897470290e+03, 4.456359510e+00] ),  
        NASA( [1000.0, 6000.0], [3.920015420e+00, 2.522793240e-03,  
            -6.710041640e-07, 1.056159480e-10,  
            -7.437982610e-15, 3.656208040e+03, 3.583772170e+00] )),  
    transport = gas_transport(  
        geom = "nonlinear",  
        diam = 3.59,
```



```
        well_depth = 498.00000000000006,  
        polar = 0.0,  
        rot_relax = 0.0))  
  
species(name = "C2H4",  
        atoms = "C:2, H:4",  
        thermo = (  
            NASA( [300.0, 1392.0], [3.662488530e-01, 1.919979100e-02,  
                -1.190214500e-05, 4.477403390e-09,  
                -8.462580550e-13, 5.455261950e+03, 1.906660850e+01] ),  
            NASA( [1392.0, 5000.0], [5.070612890e+00, 9.111407680e-03,  
                -3.105066920e-06, 4.807338510e-10,  
                -2.783213960e-14, 3.667437430e+03, -6.640670300e+00] )),  
        transport = gas_transport(  
            geom = "nonlinear",  
            diam = 3.496,  
            well_depth = 238.4,  
            polar = 0.0,  
            rot_relax = 1.5)  
        )  
  
species(name = "C2H3",  
        atoms = "C:2, H:3",  
        thermo = (  
            NASA( [300.0, 1400.0], [1.157186360e+00, 1.644976570e-02,  
                -1.284294400e-05, 5.987501570e-09,  
                -1.233851740e-12, 3.475331960e+04, 1.737709920e+01] ),  
            NASA( [1400.0, 5000.0], [4.996754150e+00, 6.558382710e-03,  
                -2.209219090e-06, 3.393002720e-10,  
                -1.953169260e-14, 3.346351790e+04, -3.010729200e+00] )),  
        transport = gas_transport(  
            geom = "nonlinear",  
            diam = 3.7210000000000005,  
            well_depth = 265.3,  
            polar = 0.0,  
            rot_relax = 1.0))  
  
species(name = "CH2CHO",  
        atoms = "C:2, H:3, O:1",  
        thermo = (  
            NASA( [200.0, 1000.0], [1.734933910e+00, 1.908003860e-02,  
                -1.007348200e-05, 4.452316190e-10,  
                8.066148950e-13, 2.563813310e+02, 1.664529740e+01] ),  
            NASA( [1000.0, 6000.0], [6.539283380e+00, 7.802386290e-03,  
                -2.764136120e-06, 4.420989060e-10,  
                -2.629542900e-14, -1.178225370e+03, -8.709721780e+00] )),  
        transport = gas_transport(  
            geom = "nonlinear",  
            diam = 3.97,  
            well_depth = 436.0,  
            polar = 0.0,
```

```
rot_relax = 2.0))
```

```
species(name = "HCCO",  
  atoms = "C:2, H:1, O:1",  
  thermo = (  
    NASA( [200.0, 1000.0], [2.022173970e+00, 2.088434830e-02,  
      -3.226954660e-05, 2.620252080e-08,  
      -8.317660290e-12, 2.015050730e+04,  
      1.310690310e+01] ),  
    NASA( [1000.0, 6000.0], [5.914793330e+00, 3.714087300e-03,  
      -1.301370100e-06, 2.064733450e-10,  
      -1.214767590e-14, 1.935820230e+04, -5.507215160e+00] )),  
  transport = gas_transport(  
    geom = "nonlinear",  
    diam = 2.5,  
    well_depth = 150.0,  
    polar = 0.0,  
    rot_relax = 1.0))
```

```
species(name = "C3H6",  
  atoms = "C:3, H:6",  
  thermo = (  
    NASA( [300.0, 1387.0], [5.780899730e-01, 2.869414370e-02,  
      -1.628751010e-05, 5.263381460e-09,  
      -8.798234690e-13, 1.162285950e+03,  
      2.080310600e+01] ),  
    NASA( [1387.0, 5000.0], [7.969046580e+00, 1.378118010e-02,  
      -4.697826040e-06, 7.275791480e-10,  
      -4.213689200e-14, -1.715916180e+03, -1.987417220e+01] )),  
  transport = gas_transport(  
    geom = "nonlinear",  
    diam = 4.14,  
    well_depth = 307.8,  
    polar = 0.0,  
    rot_relax = 1.0))
```

```
species(name = "C3H5-A",  
  atoms = "C:3, H:5",  
  thermo = (  
    NASA( [300.0, 1373.0], [4.478890520e-01, 2.795075440e-02,  
      -1.694900360e-05, 5.543788830e-09,  
      -8.957190690e-13, 1.925655540e+04, 2.130536210e+01] ),  
    NASA( [1373.0, 5000.0], [8.839262440e+00, 1.084895200e-02,  
      -3.768079870e-06, 5.912172370e-10,  
      -3.455957030e-14, 1.604240920e+04, -2.475553130e+01] )),  
  transport = gas_transport(  
    geom = "nonlinear",  
    diam = 4.22,  
    well_depth = 316.0,  
    polar = 0.0,  
    rot_relax = 1.0))
```

```
species(name = "C2H3CHO",
  atoms = "C:3, H:4, O:1",
  thermo = (
    NASA( [300.0, 1398.0], [6.327568710e-01, 3.247041510e-02,
      -2.462990630e-05, 9.945469390e-09,
      -1.709961880e-12, -9.374696340e+03, 2.145333600e+01] ),
    NASA( [1398.0, 5000.0], [9.991553940e+00, 9.823480010e-03,
      -3.312030880e-06, 5.095244220e-10,
      -2.938218900e-14, -1.252719660e+04, -2.851301250e+01] )),
  transport = gas_transport(
    geom = "nonlinear",
    diam = 4.9580000000000001,
    well_depth = 428.8,
    polar = 0.0,
    rot_relax = 1.0,
    dipole= 2.900000827651188))
```

```
species(name = "IC4H8",
  atoms = "C:4, H:8",
  thermo = (
    NASA( [300.0, 1392.0], [-1.581775940e-01, 4.331827660e-02,
      -2.848272170e-05, 1.081437460e-08,
      -1.943371030e-12, -3.700290170e+03, 2.446989670e+01] ),
    NASA( [1392.0, 5000.0], [1.114440280e+01, 1.816092650e-02,
      -6.177911160e-06, 9.554818710e-10,
      -5.528260920e-14, -7.833603770e+03, -3.684271050e+01] )),
  transport = gas_transport(
    geom = "nonlinear",
    diam = 5.089,
    well_depth = 344.5,
    polar = 0.0,
    rot_relax = 1.0,
    dipole= 0.5000001426984807))
```

```
species(name = "C4H8-1",
  atoms = "C:4, H:8",
  thermo = (
    NASA( [300.0, 1388.0], [-3.617792920e-02, 4.152918200e-02,
      -2.511059900e-05, 8.504876110e-09,
      -1.402589680e-12, -1.634319890e+03, 2.564719880e+01] ),
    NASA( [1388.0, 5000.0], [1.101892950e+01, 1.827141770e-02,
      -6.218019070e-06, 9.620386110e-10,
      -5.567913410e-14, -5.803933180e+03, -3.478676260e+01] )),
  transport = gas_transport(
    geom = "nonlinear",
    diam = 4.65,
    well_depth = 355.0,
    polar = 0.0,
    rot_relax = 1.0))
```

```
species(name = "C4H71-1",
  atoms = "C:4, H:7",
  thermo = (
    NASA( [300.0, 1390.0], [7.172644600e-01, 3.898884440e-02,
      -2.630920070e-05, 1.012518640e-08,
      -1.805781980e-12, 2.766766320e+04, 2.273532000e+01] ),
    NASA( [1390.0, 5000.0], [1.105317500e+01, 1.556687820e-02,
      -5.258530440e-06, 8.096270950e-10,
      -4.670154770e-14, 2.395108170e+04, -3.314806040e+01] )),
  transport = gas_transport(
    geom = "nonlinear",
    diam = 4.65,
    well_depth = 355.0,
    polar = 0.0,
    rot_relax = 1.0))
```

```
species(name = "C4H71-4",
  atoms = "C:4, H:7",
  thermo = (
    NASA( [300.0, 1389.0], [3.410960740e-01, 3.803790160e-02,
      -2.403670660e-05, 8.734478950e-09,
      -1.538577670e-12, 2.308394970e+04, 2.615490300e+01] ),
    NASA( [1389.0, 5000.0], [1.038750840e+01, 1.636772640e-02,
      -5.584160360e-06, 8.653887360e-10,
      -5.014153850e-14, 1.933425730e+04, -2.860074240e+01] )),
  transport = gas_transport(
    geom = "nonlinear",
    diam = 4.65,
    well_depth = 355.0,
    polar = 0.0,
    rot_relax = 1.0))
```

```
species(name = "C4H6",
  atoms = "C:4, H:6",
  thermo = (
    NASA( [100.0, 946.05], [2.805965280e+00, 1.025878900e-02,
      6.172476590e-05, -9.016254660e-08,
      3.591092300e-11, 1.165849840e+04, 1.206224230e+01] ),
    NASA( [946.05, 5000.0], [1.246946230e+01, 1.005523380e-02,
      -2.411977460e-06, 4.570555490e-10,
      -3.931424040e-14, 8.010740870e+03, -4.363797870e+01] )),
  transport = gas_transport(
    geom = "nonlinear",
    diam = 4.7200000000000001,
    well_depth = 357.0,
    polar = 0.0,
    rot_relax = 1.0))
```

```
#-----
# Reactions
```

#-----

Reaction 1

reaction("vAXL => 2 n-AXL", [2.5700E+32, -4.1539, 41424.53])

Reaction 2

reaction("vAXL + 2 O => 2 OH + 2 n-AXLj", [6.8245e+06, 2.498, 2838.0])

Reaction 3

reaction("vAXL + 2 H => 2 H2 + 2 n-AXLj", [5.7913e+06, 2.518, 4339.6])

Reaction 4

reaction("vAXL + 2 OH => 2 H2O + 2 n-AXLj", [6.9752e+10, 0.974, 51.0])

Reaction 5

reaction("vAXL + 2 HO2 => 2 H2O2 + 2 n-AXLj", [6.0733e+02, 3.49, 13479.3])

Reaction 6

reaction("vAXL + 2 O2 => 2 HO2 + 2 n-AXLj", [1.6492e+15, 0.081, 52803.4])

Reaction 7

reaction("n-AXL => C4H71-1 + 0.75 C4H8-1", [2.3695E+06, -0.0024, 4821.6])

Reaction 8

reaction("n-AXL => C3H5-A + 1.333 C3H6", [2.2051E+12, 0.0127, 101526.3])

Reaction 9

reaction("n-AXL => C2H3 + 2.5 C2H4", [2.4425e+07, 0.0, 31379.3])

Reaction 10

reaction("n-AXL => C3H5-A + C4H8-1", [1.0248e+01, 0.0, 4109.2])

Reaction 11

reaction("n-AXL => C2H3 + 1.667 C3H6", [3.740810e+12, 0.0, 75482.7])

Reaction 12

reaction("H + n-AXL => C4H6 + 0.75 C4H8-1 + H2", [3.5983e+18, 0.0, 6545.1])

Reaction 13

reaction("H + n-AXL => 2 C3H5-A + 0.333 C3H6 + H2", [7.5715e+13, 0.0, 78176.0])

Reaction 14

reaction("H + n-AXL => 2 C2H3 + 1.5 C2H4 + H2", [2.4814e+14, 0.0, 31280.3])

Reaction 15

reaction("H + n-AXL => 2 C3H5-A + 0.25 C4H8-1 + H2", [1.1053e+14, 0.0, 43261.7])

Reaction 16

reaction("H + n-AXL => 2 C2H3 + C3H6 + H2", [1.5718e+11, 0.0, 59956.4])

Reaction 17

```
reaction( "n-AXLj => C4H6 + 0.75 C4H8-1", [1.6687e+14, 0.0, 3376.5])

# Reaction 18
reaction( "n-AXLj => 2 C3H5-A + 0.333 C3H6", [4.0880E+10, 0.0169, 74735.9])

# Reaction 19
reaction( "n-AXLj => 2 C2H3 + 1.5 C2H4", [2.6137e+15, 0.0, 89662.3])

# Reaction 20
reaction( "n-AXLj => 2 C3H5-A + 0.25 C4H8-1", [1.4400e+17, 0.0, 31240.6])

# Reaction 21
reaction( "n-AXLj => 2 C2H3 + C3H6", [8.7500e+18, 0.0, 55896.6])

# Reaction 22
reaction( "vAXL => 2 i-AXL", [1.6300E+27, -2.4238, 42923.8])

# Reaction 23
reaction( "vAXL + 2 O => 2 OH + 2 i-AXLj", [2.8217e+04, 3.067, 1819.9])

# Reaction 24
reaction( "vAXL + 2 H => 2 H2 + 2 i-AXLj", [2.7078e+12, 1.133, 13257.0])

# Reaction 25
reaction( "vAXL + 2 OH => 2 H2O + 2 i-AXLj", [2.3752e+06, 2.316, -724.0])

# Reaction 26
reaction( "vAXL + 2 HO2 => 2 H2O2 + 2 i-AXLj", [5.6153e+01, 3.735, 14363.5])

# Reaction 27
reaction( "vAXL + 2 O2 => 2 HO2 + 2 i-AXLj", [7.0704e+13, 0.133, 51157.1])

# Reaction 28
reaction( "i-AXL => C4H71-1 + 0.75 IC4H8", [1.7794e+12, 0.0, 91226.8])

# Reaction 29
reaction( "i-AXL => C3H5-A + 1.333 C3H6", [9.4706e+15, 0.0, 85543.1])

# Reaction 30
reaction( "i-AXL => C2H3 + 2.5 C2H4", [3.9310E+12, 0.0288, 43698.6])

# Reaction 31
reaction( "i-AXL => C3H5-A + IC4H8", [3.7843e+03, 0.0, 2089.2])

# Reaction 32
reaction( "i-AXL => C2H3 + 1.667 C3H6", [1.9211e+14, 0.0, 94732.1])

# Reaction 33
reaction( "H + i-AXL => C4H6 + H2 + 0.75 IC4H8", [8.7189e+18, 0.0, 17873.0])

# Reaction 34
```

reaction("H + i-AXL => 2 C3H5-A + 0.333 C3H6 + H2", [2.9802E+12, 0.018, 59779.7])

Reaction 35

reaction("H + i-AXL => 2 C2H3 + 1.5 C2H4 + H2", [5.0239E+05, 0.0093, 12958.8])

Reaction 36

reaction("H + i-AXL => 2 C3H5-A + H2 + 0.25 IC4H8", [5.1300e+24, 0.0, 82552.7])

Reaction 37

reaction("H + i-AXL => 2 C2H3 + C3H6 + H2", [4.0835e+14, 0.0, 46965.0])

Reaction 38

reaction("i-AXLj => C4H6 + 0.75 IC4H8", [6.3406e+12, 0.0, 97504.7])

Reaction 39

reaction("i-AXLj => 2 C3H5-A + 0.333 C3H6", [4.0209e+12, 0.0, 23239.8])

Reaction 40

reaction("i-AXLj => 2 C2H3 + 1.5 C2H4", [5.3486e+07, 0.0, 65184.6])

Reaction 41

reaction("i-AXLj => 2 C3H5-A + 0.25 IC4H8", [2.9939e+08, 0.0, 13417.1])

Reaction 42

reaction("i-AXLj => 2 C2H3 + C3H6", [1.5084e+04, 0.0, 17991.8])

Reaction 43

reaction("vAXL => 2 cy-AXL", [1.6455e+15, -0.063, 80861.4])

Reaction 44

reaction("vAXL + 2 O => 2 OH + 2 cy-AXLj", [3.0185e+06, 2.518, 2594.1])

Reaction 45

reaction("vAXL + 2 H => 2 H2 + 2 cy-AXLj", [5.4238e+06, 2.5, 4176.3])

Reaction 46

reaction("vAXL + 2 OH => 2 H2O + 2 cy-AXLj", [1.3499e+07, 2.025, -588.0])

Reaction 47

reaction("vAXL + 2 HO2 => 2 H2O2 + 2 cy-AXLj", [3.0306e+02, 3.492, 13344.9])

Reaction 48

reaction("vAXL + 2 O2 => 2 HO2 + 2 cy-AXLj", [1.0324e+14, 0.068, 49387.1])

Reaction 49

reaction("cy-AXL => C4H71-1 + 0.75 C4H8-1", [1.0258e+11, 0.0, 47400.7])

Reaction 50

reaction("cy-AXL => C3H5-A + 1.333 C3H6", [3.5600e+16, 0.0, 58530.5])

Reaction 51

```
reaction( "cy-AXL => C2H3 + 2.5 C2H4", [5.5932e+11, 0.0, 58015.6])

# Reaction 52
reaction( "cy-AXL => C3H5-A + C4H8-1", [9.0539e+14, 0.0, 18506.7])

# Reaction 53
reaction( "cy-AXL => C2H3 + 1.667 C3H6", [3.2017e+06, 0.0, 27874.0])

# Reaction 54
reaction( "H + cy-AXL => C4H6 + 0.75 C4H8-1 + H2", [2.1800e+26, 0.0, 87563.1])

# Reaction 55
reaction( "H + cy-AXL => 2 C3H5-A + 0.333 C3H6 + H2", [1.1136e+18, 0.0, 93900.4])

# Reaction 56
reaction( "H + cy-AXL => 2 C2H3 + 1.5 C2H4 + H2", [8.3400e+21, 0.0, 87979.0])

# Reaction 57
reaction( "H + cy-AXL => 2 C3H5-A + 0.25 C4H8-1 + H2", [7.3850e+12, 0.0, 60748.5])

# Reaction 58
reaction( "H + cy-AXL => 2 C2H3 + C3H6 + H2", [9.4174e+13, 0.0, 74928.2])

# Reaction 59
reaction( "cy-AXLj => C4H6 + 0.75 C4H8-1", [5.6292e+11, 0.0, 58590.0])

# Reaction 60
reaction( "cy-AXLj => 2 C3H5-A + 0.333 C3H6", [2.7264e+11, 0.0, 75165.8])

# Reaction 61
reaction( "cy-AXLj => 2 C2H3 + 1.5 C2H4", [3.3717e+11, 0.0, 35161.8])

# Reaction 62
reaction( "cy-AXLj => 2 C3H5-A + 0.25 C4H8-1", [1.5600e+17, 0.0, 56431.3])

# Reaction 63
reaction( "cy-AXLj => 2 C2H3 + C3H6", [6.9321e+06, 0.0, 30884.2])

# Reaction 64
reaction( "vAXL => 2 Ar-AXL", [3.1100E+16, 0.0836, 98126.2])

# Reaction 65
reaction( "vAXL + 2 O => 2 Ar-AXLj + 2 OH", [1.9689e+04, 3.057, 1525.1])

# Reaction 66
reaction( "vAXL + 2 H => 2 Ar-AXLj + 2 H2", [9.3200e+03, 3.167, 2976.6])

# Reaction 67
reaction( "vAXL + 2 OH => 2 Ar-AXLj + 2 H2O", [1.3465e+06, 2.394, -741.7])

# Reaction 68
```


reaction("vAXL + 2 HO2 => 2 Ar-AXLj + 2 H2O2", [9.0569e+07, 1.989, 19907.5])

Reaction 69

reaction("vAXL + 2 O2 => 2 Ar-AXLj + 2 HO2", [1.0349e+14, 0.815, 53183.3])

Reaction 70

reaction("Ar-AXL => C4H71-1 + 0.75 C4H8-1", [5.6811e+10, 0.0, 87186.8])

Reaction 71

reaction("Ar-AXL => C3H5-A + 1.333 C3H6", [4.8813e+07, 0.0, 65501.5])

Reaction 72

reaction("Ar-AXL => C2H3 + 2.5 C2H4", [6.0959e+04, 0.0, 32884.4])

Reaction 73

reaction("Ar-AXL => C3H5-A + C4H8-1", [1.5100e+20, 0.0, 77542.3])

Reaction 74

reaction("Ar-AXL => C2H3 + 1.667 C3H6", [2.1000E+17, -0.0149, 42235.5])

Reaction 75

reaction("Ar-AXL + H => C4H6 + 0.75 C4H8-1 + H2", [1.3649e+16, 0.0, 93326.1])

Reaction 76

reaction("Ar-AXL + H => 2 C3H5-A + 0.333 C3H6 + H2", [1.8475e+16, 0.0, 29181.0])

Reaction 77

reaction("Ar-AXL + H => 2 C2H3 + 1.5 C2H4 + H2", [1.1600e+20, 0.0, 59936.6])

Reaction 78

reaction("Ar-AXL + H => 2 C3H5-A + 0.25 C4H8-1 + H2", [3.0254e+15, 0.0, 48351.3])

Reaction 79

reaction("Ar-AXL + H => 2 C2H3 + C3H6 + H2", [3.8121e+14, 0.0, 92930.0])

Reaction 80

reaction("Ar-AXLj => C4H6 + 0.75 C4H8-1", [7.6700e+21, 0.0, 99762.4])

Reaction 81

reaction("Ar-AXLj => 2 C3H5-A + 0.333 C3H6", [4.8773e+04, 0.0, 25834.2])

Reaction 82

reaction("Ar-AXLj => 2 C2H3 + 1.5 C2H4", [1.2861e+04, 0.0, 33042.8])

Reaction 83

reaction("Ar-AXLj => 2 C3H5-A + 0.25 C4H8-1", [3.0300e+17, 0.0, 48569.1])

Reaction 84

reaction("Ar-AXLj => 2 C2H3 + C3H6", [2.7015e+10, 0.0, 53143.8])

Reaction 85

```
three_body_reaction( "H2 + M <=> 2 H + M", [4.5770e+19, -1.4, 104400.0],  
    efficiencies = "CO:1.9 CO2:3.8 H2:2.5 H2O:12.0")
```

```
# Reaction 86
```

```
reaction( "H2 + O <=> H + OH", [5.0800e+04, 2.67, 6292.0])
```

```
# Reaction 87
```

```
reaction( "H2 + OH <=> H + H2O", [4.3800e+13, 0.0, 6990.0])
```

```
# Reaction 88
```

```
three_body_reaction( "2 O + M <=> O2 + M", [6.1650e+15, -0.5, 0.0],  
    efficiencies = "CO:1.9 CO2:3.8 H2:2.5 H2O:12.0")
```

```
# Reaction 89
```

```
reaction( "H + O2 <=> O + OH", [1.0400e+14, 0.0, 15286.0])
```

```
# Reaction 90
```

```
three_body_reaction( "H + OH + M <=> H2O + M", [3.5000e+22, -2.0, 0.0],  
    efficiencies = "H2:0.73 H2O:3.65")
```

```
# Reaction 91
```

```
reaction( "H2O + O <=> 2 OH", [6.7000e+07, 1.704, 14986.8])
```

```
# Reaction 92
```

```
three_body_reaction( "H + O + M <=> OH + M", [4.7140e+18, -1.0, 0.0],  
    efficiencies = "CO:1.5 CO2:2.0 H2:2.5 H2O:12.0")
```

```
# Reaction 93
```

```
falloff_reaction( "H2O2 (+M) <=> 2 OH (+M)",  
    kf = [2.0000E+12, 0.9, 48749.0],  
    kf0 = [2.4900E+24, -2.3, 48749.0],  
    falloff = Troe(A = 0.43, T3 = 1e-30, T1 = 1.00e+30),  
    efficiencies = "CO:2.8 CO2:1.6 H2:3.7 H2O:7.65 H2O2:7.7 N2:1.5 O2:1.2")
```

```
# Reaction 94
```

```
reaction( "H + H2O2 <=> H2O + OH", [2.4100e+13, 0.0, 3970.0])
```

```
# Reaction 95
```

```
reaction( "H + H2O2 <=> H2 + HO2", [2.1500e+10, 1.0, 6000.0])
```

```
# Reaction 96
```

```
reaction( "H2O2 + O <=> HO2 + OH", [9.5500e+06, 2.0, 3970.0])
```

```
# Reaction 97
```

```
reaction( "H2O2 + OH <=> H2O + HO2", [1.7400e+12, 0.0, 318.0],  
    options = "duplicate")
```

```
# Reaction 98
```

```
reaction( "H2O2 + OH <=> H2O + HO2", [7.5900e+13, 0.0, 7269.0],  
    options = "duplicate")
```

```
# Reaction 99
reaction( "H + HO2 <=> 2 OH", [7.0790e+13, 0.0, 295.0])

# Reaction 100
reaction( "H + HO2 <=> H2 + O2", [1.1402e+10, 1.083, 553.8])

# Reaction 101
reaction( "HO2 + O <=> O2 + OH", [3.2500e+13, 0.0, 0.0])

# Reaction 102
reaction( "HO2 + OH <=> H2O + O2", [7.0000e+12, 0.0, -1093.0],
  options = "duplicate")

# Reaction 103
reaction( "HO2 + OH <=> H2O + O2", [4.5000e+14, 0.0, 10929.6],
  options = "duplicate")

# Reaction 104
reaction( "2 HO2 <=> H2O2 + O2", [1.0000e+14, 0.0, 11040.9],
  options = "duplicate")

# Reaction 105
reaction( "2 HO2 <=> H2O2 + O2", [1.9000e+11, 0.0, -1408.9],
  options = "duplicate")

# Reaction 106
falloff_reaction( "H + O2 (+M) <=> HO2 (+M)",
  kf = [4.6500E+12, 0.44, 0.0],
  kf0 = [1.7370E+19, -1.23, 0.0],
  falloff = Troe(A = 0.67, T3 = 1e-30, T1 = 1.00e+30, T2 = 1e+30),
  efficiencies = "CO:1.9 CO2:3.8 H2:1.3 H2O:10.0")

# Reaction 107
falloff_reaction( "CO + O (+M) <=> CO2 (+M)",
  kf = [1.3620E+10, 0.0, 2384.0],
  kf0 = [1.1730E+24, -2.79, 4191.0],
  efficiencies = "CO:1.75 CO2:3.6 H2:2.0 H2O:12.0")

# Reaction 108
reaction( "CO + OH <=> CO2 + H", [7.0150e+04, 2.053, -355.7],
  options = "duplicate")

# Reaction 109
reaction( "CO + OH <=> CO2 + H", [5.7570e+12, -0.664, 331.8],
  options = "duplicate")

# Reaction 110
reaction( "CO + HO2 <=> CO2 + OH", [1.5700e+05, 2.18, 17940.0])

# Reaction 111
reaction( "CO + O2 <=> CO2 + O", [1.110e+12, 0.0, 47700.0])
```

```
# Reaction 112
reaction("CH3 + O2 <=> CH2O + OH", [2.64100e+00, 3.283, 8105.0])

# Reaction 113
reaction("CH3 + O <=> CH2O + H", [5.5400e+13, 0.05, -136.0])

# Reaction 114
pdep_arrhenius("CH3 + OH <=> CH2O + H2",
  [(0.01000, "atm"), 3.5020e+05, 1.441, -3244.0],
  [(0.10000, "atm"), 8.8540e+05, 1.327, -2975.0],
  [(0.99999, "atm"), 1.6500e+07, 0.973, -2010.0],
  [(9.99999, "atm"), 5.3740e+09, 0.287, 280.0],
  [(99.9999, "atm"), 9.4940e+18, -2.199, 9769.0])

# Reaction 115
falloff_reaction("H + HCO (+M) <=> CH2O (+M)",
  kf = [1.0900E+12, 0.48, -260.0],
  kf0 = [1.3500E+24, -2.57, 1425.0],
  falloff = Troe(A = 0.7824, T3 = 271.0, T1 = 2755.0, T2 = 6570.0),
  efficiencies = "CO:1.5 CO2:2.0 H2:2.0 H2O:6.0")

# Reaction 116
falloff_reaction("CO + H2 (+M) <=> CH2O (+M)",
  kf = [4.3000E+07, 1.5, 79600.0],
  kf0 = [5.0700E+27, -3.42, 84348.0],
  falloff = Troe(A = 0.932, T3 = 197.0, T1 = 1540.0, T2 = 10300.0),
  efficiencies = "CO:1.5 CO2:2.0 H2:2.0 H2O:6.0")

# Reaction 117
reaction("CH2O + O2 <=> HCO + HO2", [8.0700e+15, 0.0, 53420.0])

# Reaction 118
reaction("CH2O + O <=> HCO + OH", [6.2600e+09, 1.15, 2260.0])

# Reaction 119
reaction("CH2O + H <=> H2 + HCO", [5.7400e+07, 1.9, 2740.0])

# Reaction 120
reaction("CH2O + OH <=> H2O + HCO", [7.8200e+07, 1.63, -1055.0])

# Reaction 121
reaction("CH2O + HO2 <=> H2O2 + HCO", [1.8800e+04, 2.7, 11520.0])

# Reaction 122
three_body_reaction("HCO + M <=> CO + H + M", [7.2054E+11, 0.585, 13695.5],
  efficiencies = "CO:1.5 CO2:2.0 H2:2.0 H2O:6.0")

# Reaction 123
reaction("HCO + O2 <=> CO + HO2", [7.5800e+12, 0.0, 410.0])
```

```
# Reaction 124
reaction( "HCO + O <=> CO + OH", [3.0200e+13, 0.0, 0.0])

# Reaction 125
reaction( "H + HCO <=> CO + H2", [7.340000e+13, 0.0, 0.0])

# Reaction 126
reaction( "HCO + OH <=> CO + H2O", [3.0110e+13, 0.0, 0.0])

# Reaction 127
reaction( "2 HCO <=> CH2O + CO", [1.8000e+13, 0.0, 0.0])

# Reaction 128
reaction( "HCO + O <=> CO2 + H", [3.0000e+13, 0.0, 0.0])

# Reaction 129
reaction( "HCO + HO2 => CO2 + H + OH", [3.0000e+13, 0.0, 0.0])

# Reaction 130
reaction( "2 HCO => 2 CO + H2", [3.0000e+12, 0.0, 0.0])

# Reaction 131
falloff_reaction( "C2H3 + H (+M) <=> C2H4 (+M)",
    kf = [6.0800E+12, 0.27, 280.0],
    kf0 = [1.4000E+30, -3.86, 3320.0],
    falloff = Troe(A = 0.782, T3 = 207.5, T1 = 2663.0, T2 = 6095.0),
    efficiencies = "CO:1.5 CO2:2.0 H2:2.0 H2O:6.0")

# Reaction 132
reaction( "C2H4 + O2 <=> C2H3 + HO2", [4.2200e+13, 0.0, 57623.1])

# Reaction 133
reaction( "C2H4 + H <=> C2H3 + H2", [5.4200e+14, 0.0, 14900.0])

# Reaction 134
reaction( "C2H4 + OH <=> C2H3 + H2O", [2.2300e+04, 2.745, 2215.5])

# Reaction 135
reaction( "C2H4 + O <=> CH3 + HCO", [7.4530e+06, 1.88, 183.0])

# Reaction 136
reaction( "C2H4 + O <=> CH2CHO + H", [6.0980e+06, 1.88, 183.0])

# Reaction 137
pdep_arrhenius( "C2H4 + OH <=> CH2O + CH3",
    [(0.010, "atm"), 5.3500e+00, 2.92, -1732.7],
    [(0.025, "atm"), 3.1900e+01, 2.71, -1172.3],
    [(0.100, "atm"), 5.5500e+02, 2.36, -180.8],
    [(0.999, "atm"), 1.7800e+05, 1.68, 2060.5],
    [(9.999, "atm"), 2.3700e+09, 0.56, 6006.7],
    [(99.99, "atm"), 2.7600e+13, -0.5, 11455.1])
```

Reaction 138

reaction("C2H3 + O2 <=> CH2CHO + O", [7.3400e+09, 0.72, 778.0])

Reaction 139

reaction("C2H3 + O2 <=> CH2O + HCO", [7.1800E+35, -6.837747, 15402.9])

Reaction 140

reaction("C2H3 + O2 => CH2O + CO + H", [1.4977E+13, -1.036864, 1801.6])

Reaction 141

pdep_arrhenius("C2H3 + O2 <=> CH3 + CO2",
[(0.0100, "atm"), 6.2700e+13, -1.16, 406.0],
[(0.1000, "atm"), 6.2400e+13, -1.16, 401.0],
[(0.3159, "atm"), 6.1200e+13, -1.16, 397.0],
[(0.9999, "atm"), 5.3200e+13, -1.14, 447.0],
[(3.1600, "atm"), 1.4500e+14, -1.26, 988.0],
[(9.9999, "atm"), 5.0200e+13, -1.11, 1409.0],
[(31.599, "atm"), 3.8400e+18, -2.44, 5408.0],
[(99.999, "atm"), 9.2100e+08, 0.25, 855.0])

Reaction 142

falloff_reaction("CH2CHO (+M) <=> CH3 + CO (+M)",
kf = [2.9300E+12, 0.29, 40300.0],
kf0 = [9.5200E+33, -5.07, 41300.0],
falloff = Troe(A = 7.13e-17, T3 = 1150.0, T1 = 4990000000.0, T2 = 1790000000.0))

Reaction 143

pdep_arrhenius("CH2CHO + O2 <=> CH2O + CO + OH",
[(0.010, "atm"), 2.6800e+17, -1.84, 6530.0],
[(0.100, "atm"), 1.5200e+20, -2.58, 8980.0],
[(0.999, "atm"), 1.6500e+19, -2.22, 10340.0],
[(9.999, "atm"), 8.9530e+13, -0.6, 10120.0])

Reaction 144

reaction("HCCO + OH => 2 CO + H2", [1.0000e+14, 0.0, 0.0])

Reaction 145

reaction("HCCO + O => 2 CO + H", [8.0000e+13, 0.0, 0.0])

Reaction 146

reaction("HCCO + O2 => 2 CO + OH", [1.9100e+11, -0.02, 1020.0])

Reaction 147

reaction("HCCO + O2 => CO + CO2 + H", [4.7800e+12, -0.142, 1150.0])

Reaction 148

```
pdep_arrhenius( "C2H3 + CH3 <=> C3H5-A + H",  
  [(0.01000, "atm"), 4.1200e+29, -4.95, 7996.0],  
  [(0.01000, "atm"), 5.7300e+15, -0.77, 1196.0],  
  [(0.10000, "atm"), 4.8600e+30, -5.03, 11287.0],  
  [(0.10000, "atm"), 2.0600e+13, -0.07, 1429.0],  
  [(0.99999, "atm"), 5.3000e+29, -4.57, 14443.0],  
  [(0.99999, "atm"), 4.4800e+10, 0.6, 1422.0],  
  [(9.99999, "atm"), 1.3200e+30, -4.54, 19255.0],  
  [(9.99999, "atm"), 4.1000e+06, 1.71, 1057.0],  
  [(99.9999, "atm"), 5.1600e+28, -4.03, 23821.0],  
  [(99.9999, "atm"), 1.3700e-01, 3.91, -354.0])
```

Reaction 149

```
pdep_arrhenius( "C3H6 <=> C2H3 + CH3",  
  [(0.0100, "atm"), 1.8800e+78, -18.72, 129850.0],  
  [(0.0100, "atm"), 1.6900e+59, -13.61, 113290.0],  
  [(0.1000, "atm"), 8.7400e+76, -17.89, 131540.0],  
  [(0.1000, "atm"), 2.0000e+60, -13.66, 114890.0],  
  [(0.9999, "atm"), 5.8000e+75, -17.17, 134430.0],  
  [(0.9999, "atm"), 6.7000e+54, -11.79, 113840.0],  
  [(9.9999, "atm"), 8.1200e+71, -15.75, 135960.0],  
  [(9.99999, "atm"), 1.0600e+47, -9.27, 111510.0],  
  [(99.9999, "atm"), 2.1500e+64, -13.37, 134540.0],  
  [(99.9999, "atm"), 7.2900e+38, -6.7, 108740.0])
```

Reaction 150

```
pdep_arrhenius( "C3H6 <=> C3H5-A + H",  
  [(0.0100, "atm"), 9.1600e+74, -17.61, 120370.0],  
  [(0.0100, "atm"), 2.9800e+54, -12.32, 101200.0],  
  [(0.1000, "atm"), 1.7300e+70, -16.01, 119510.0],  
  [(0.1000, "atm"), 1.3800e+43, -8.87, 96365.0],  
  [(0.9999, "atm"), 1.0800e+71, -15.91, 124860.0],  
  [(0.9999, "atm"), 6.2800e+42, -8.51, 98004.0],  
  [(9.9999, "atm"), 6.4000e+65, -14.219, 124980.0],  
  [(9.9999, "atm"), 4.7300e+35, -6.26, 95644.0],  
  [(99.999, "atm"), 8.0500e+56, -11.52, 121820.0],  
  [(99.999, "atm"), 4.3500e+28, -4.06, 93114.0])
```

Reaction 151

```
reaction( "C3H6 + H <=> C3H5-A + H2", [3.6440e+05, 2.455, 4361.2])
```

Reaction 152

```
reaction( "C3H6 + O2 <=> C3H5-A + HO2", [5.9600e+19, -1.67, 46192.1])
```

Reaction 153

```
reaction( "C3H6 + O <=> C3H5-A + OH", [9.6497E+00, 0.611, 7248.5])
```

Reaction 154

```
reaction( "C3H6 + OH <=> C3H5-A + H2O", [4.4600e+06, 2.072, 1050.8])
```

Reaction 155

```
reaction( "C3H6 + HO2 <=> C3H5-A + H2O2", [3.0700e-02, 4.403, 13547.2])
```

```
# Reaction 156
```

```
pdep_arrhenius( "C3H6 + H <=> C2H4 + CH3",  
  [(0.00130, "atm"), 1.5400e+09, 1.35, 2542.0],  
  [(0.03999, "atm"), 7.8800e+10, 0.87, 3599.6],  
  [(0.99999, "atm"), 2.6700e+12, 0.47, 5431.1],  
  [(9.99999, "atm"), 9.2500e+22, -2.6, 12898.0],  
  [(99.9999, "atm"), 1.3200e+23, -2.42, 16500.0],  
  options = "duplicate")
```

```
# Reaction 157
```

```
pdep_arrhenius( "C3H6 + H <=> C2H4 + CH3",  
  [(0.00130, "atm"), 1.0000e-10, 0.0, 0.0],  
  [(0.03999, "atm"), 1.0000e-10, 0.0, 0.0],  
  [(0.99999, "atm"), 1.0000e-10, 0.0, 0.0],  
  [(9.99999, "atm"), 1.2400e+05, 2.52, 3679.1],  
  [(99.9999, "atm"), 2.5100e+03, 2.91, 3980.9],  
  options = "duplicate")
```

```
# Reaction 158
```

```
reaction( "C3H5-A + HCO <=> C3H6 + CO", [6.0000e+13, 0.0, 0.0])
```

```
# Reaction 159
```

```
reaction( "C3H5-A + O <=> C2H3CHO + H", [6.0000e+13, 0.0, 0.0])
```

```
# Reaction 160
```

```
pdep_arrhenius( "C3H5-A + OH => C2H3CHO + 2 H",  
  [(0.1000, "atm"), 5.3000e+37, -6.71, 29306.0],  
  [(0.9999, "atm"), 4.2000e+32, -5.16, 30126.0],  
  [(9.9999, "atm"), 1.6000e+20, -1.56, 26330.0])
```

```
# Reaction 161
```

```
pdep_arrhenius( "C3H5-A + O2 <=> C2H3CHO + OH",  
  [(0.9999, "atm"), 1.8200e+13, -0.41, 22859.0],  
  [(9.9999, "atm"), 2.4700e+13, -0.45, 23017.0])
```

```
# Reaction 162
```

```
pdep_arrhenius( "C3H5-A + HO2 <=> C2H3CHO + H2O",  
  [(0.0100, "atm"), 1.0900e+00, 3.01, -3421.1],  
  [(0.1000, "atm"), 6.3500e+01, 2.5, -2341.4],  
  [(0.9999, "atm"), 6.0500e+05, 1.39, 595.1],  
  [(9.9999, "atm"), 3.1000e+05, 1.59, 2677.6],  
  [(99.999, "atm"), 5.0700e-05, 4.59, 927.5])
```

```
# Reaction 163
```

```
pdep_arrhenius( "C2H3 + CH2O <=> C2H3CHO + H",  
  [(0.0010, "atm"), 2.6000e+04, 2.26, 1510.3],  
  [(0.0100, "atm"), 5.1300e+04, 2.17, 1675.5],  
  [(0.1000, "atm"), 3.9900e+05, 1.91, 2218.3],  
  [(0.9999, "atm"), 1.7500e+07, 1.45, 3428.0],
```



```
[(9.9999, "atm"), 1.3500e+09, 0.933, 5173.0],  
[(99.999, "atm"), 2.2400e+11, 0.357, 8001.3],  
[(999.99, "atm"), 6.0100e+05, 2.09, 7895.6])
```

Reaction 164

```
pdep_arrhenius( "C2H3 + CH2O <=> C2H4 + HCO",  
  [(0.0010, "atm"), 1.1100e+07, 1.09, 1807.2],  
  [(0.0100, "atm"), 2.4700e+07, 0.993, 1994.9],  
  [(0.1000, "atm"), 2.4700e+08, 0.704, 2596.2],  
  [(0.9999, "atm"), 1.4200e+10, 0.209, 3934.2],  
  [(9.9999, "atm"), 3.4500e+13, -0.726, 6944.3],  
  [(99.999, "atm"), 3.3100e+14, -0.866, 10965.7],  
  [(999.99, "atm"), 1.6500e+01, 3.17, 9399.8])
```

Reaction 165

```
reaction( "C2H3 + HCO <=> C2H3CHO", [1.8100e+13, 0.0, 0.0])
```

Reaction 166

```
pdep_arrhenius( "H + IC4H8 <=> C3H6 + CH3",  
  [(0.00130, "atm"), 5.1300e+08, 1.35, 2542.0],  
  [(0.00130, "atm"), 7.7000e+02, 1.35, 2542.0],  
  [(0.03999, "atm"), 2.6300e+10, 0.87, 3600.0],  
  [(0.03999, "atm"), 3.9400e+04, 0.87, 3600.0],  
  [(0.99999, "atm"), 8.9000e+11, 0.47, 5431.0],  
  [(0.99999, "atm"), 1.3400e+06, 0.47, 5431.0],  
  [(9.99999, "atm"), 3.0800e+22, -2.6, 12898.0],  
  [(9.99999, "atm"), 4.1300e+04, 2.52, 3679.0],  
  [(99.9999, "atm"), 4.4000e+22, -2.42, 16500.0],  
  [(99.9999, "atm"), 8.3700e+02, 2.91, 3981.0])
```

Reaction 167

```
falloff_reaction( "C3H5-A + CH3 (+M) <=> C4H8-1 (+M)",  
  kf = [1.0000E+14, -0.32, -262.0],  
  kf0 = [3.9100E+60, -12.81, 6250.0],  
  falloff = Troe(A = 0.104, T3 = 1606.0, T1 = 60000.0, T2 = 6118.0),  
  efficiencies = "CO:1.5 CO2:2.0 H2:2.0 H2O:6.0")
```

Reaction 168

```
pdep_arrhenius( "C4H71-1 + H <=> C4H8-1",  
  [(0.01000, "atm"), 5.8200e+56, -14.28, 16407.0],  
  [(0.01000, "atm"), 1.9500e+45, -11.4, 6309.0],  
  [(0.10000, "atm"), 1.2400e+62, -15.22, 19112.0],  
  [(0.10000, "atm"), 2.6500e+48, -11.75, 7584.0],  
  [(0.99999, "atm"), 3.7700e+60, -14.24, 20603.0],  
  [(0.99999, "atm"), 4.2800e+42, -9.54, 6789.0],  
  [(9.99999, "atm"), 9.1000e+56, -12.74, 22284.0],  
  [(9.99999, "atm"), 4.4400e+34, -6.79, 5170.0],  
  [(99.9999, "atm"), 6.3900e+49, -10.35, 21902.0],  
  [(99.9999, "atm"), 5.1100e+26, -4.13, 3313.0])
```

Reaction 169

```
pdep_arrhenius( "C4H8-1 <=> C4H71-4 + H",
  [(0.01000, "atm"), 3.8800e+101, -26.74, 136707.0],
  [(0.10000, "atm"), 7.9000e+108, -28.45, 142837.0],
  [(0.99999, "atm"), 1.3500e+116, -30.07, 150954.0],
  [(2.00000, "atm"), 6.7000e+116, -30.14, 152681.0],
  [(4.99999, "atm"), 1.4400e+116, -29.78, 153956.0],
  [(9.99999, "atm"), 2.7100e+114, -29.17, 154079.0],
  [(19.9999, "atm"), 5.9000e+111, -28.31, 153502.0],
  [(50.0000, "atm"), 1.4800e+107, -26.88, 151838.0])

# Reaction 170
reaction( "C4H8-1 + OH <=> C4H71-4 + H2O", [8.6000e+06, 2.03, 2623.1])

# Reaction 171
reaction( "C4H8-1 + OH <=> C4H71-1 + H2O", [6.9300e+06, 1.92, 4962.0])

# Reaction 172
reaction( "C4H8-1 + HO2 <=> C4H71-4 + H2O2", [4.0800e+01, 3.59, 17160.0])

# Reaction 173
reaction( "C4H8-1 + HO2 <=> C4H71-1 + H2O2", [9.5700e+02, 3.06, 20798.6])

# Reaction 174
reaction( "C4H8-1 + H <=> C4H71-4 + H2", [3.8400e+04, 2.87, 6611.0])

# Reaction 175
reaction( "C4H8-1 + H <=> C4H71-1 + H2", [2.6300e+04, 2.83, 12050.0],
  options = "duplicate")

# Reaction 176
reaction( "C4H8-1 + H <=> C4H71-1 + H2", [2.2300e+04, 2.85, 11710.0],
  options = "duplicate")

# Reaction 177
reaction( "C4H8-1 + O <=> C4H71-1 + OH", [1.2000e+11, 0.7, 8959.1])

# Reaction 178
reaction( "C4H8-1 + O <=> C4H71-4 + OH", [1.1300e+14, 0.0, 7850.0])

# Reaction 179
reaction( "C4H8-1 + O2 <=> C4H71-1 + HO2", [2.0000e+13, 0.0, 62270.0])

# Reaction 180
reaction( "C4H8-1 + O2 <=> C4H71-4 + HO2", [6.0000e+13, 0.0, 52340.0])

# Reaction 181
reaction( "C4H71-4 <=> C2H3 + C2H4", [2.8400e+10, 0.99, 38998.8])

# Reaction 182
reaction( "C4H71-4 <=> C4H6 + H", [1.3200e+05, 2.28, 33245.856])
```

Reaction 183

reaction("C4H71-4 + O2 <=> C4H6 + HO2", [1.0000e+11, 0.0, 0.0])

Reaction 184

pdep_arrhenius("C4H8-1 + H <=> C3H6 + CH3",
[(0.0010, "atm"), 7.8300e+09, 1.17, 1442.0],
[(0.0100, "atm"), 3.3900e+10, 1.0, 1895.0],
[(0.1000, "atm"), 3.7000e+13, 0.14, 4127.0],
[(0.9999, "atm"), 4.5700e+19, -1.54, 9061.0],
[(9.9999, "atm"), 8.5700e+23, -2.66, 14140.0],
[(99.999, "atm"), 1.3200e+20, -1.46, 15383.0],
options = "duplicate")

Reaction 185

pdep_arrhenius("C4H8-1 + H <=> C3H6 + CH3",
[(0.0010, "atm"), 1.800e+06, 1.76, 5900.0],
[(0.0100, "atm"), 3.4600e+06, 1.68, 6100.0],
[(0.1000, "atm"), 4.0200e+08, 1.1, 7574.0],
[(0.9999, "atm"), 1.2100e+16, -0.99, 13175.0],
[(9.9999, "atm"), 7.1400e+27, -4.23, 23319.0],
[(99.999, "atm"), 1.0000e+33, -5.49, 31922.0],
options = "duplicate")

Reaction 186

pdep_arrhenius("C4H6 + H <=> C2H3 + C2H4",
[(0.9999 "atm"), 1.4600e+30, -4.34, 21647.0],
[(9.999, "atm"), 5.4500e+30, -4.51, 21877.0])

Reaction 187

reaction("C4H6 + OH <=> C2H3CHO + CH3", [1.3700e+12, 0.0, -1040.0])

Reaction 188

reaction("C4H6 + OH <=> C3H5-A + CH2O", [1.3700e+12, 0.0, -1040.0])

Reaction 189

reaction("2 C2H3 <=> C4H6",[4.4300E+38, -9.500978, 15169.461])