

Details of previous work and significance of the scientific contribution

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My research interests lie in understanding the combustion characteristics of hydrocarbon fuels using an accurate description of their oxidation chemistry, which is important to make reliable predictions. Chemical kinetics is thus a central point in my research. An accurate kinetic description of the fuel oxidation is crucial in several applications. For instance, in Homogenous Charge Compression Ignition engines, controlling the ignition event is critical to achieve efficiency, which points to the need for an accurate description of the ignition kinetics of the fuel. Similarly, predicting the pollutants in engines need a detailed and accurate description of the NO_x and the soot formation pathways. Accurate chemical kinetics together with fluid mechanics and their interactions are needed to gain insights about important combustion processes.

As a part of my doctoral work, I developed a kinetic scheme to describe the oxidation of several hydrocarbons, which are relevant as components of transportation fuel surrogates [1–5]. The steps behind the development of a kinetic scheme are pictorially shown in Fig. 1. A chemical model contains (i) the reaction pathways by which the fuel gets converted to the products via different radicals and intermediates, with Arrhenius rate expressions for each reaction, (ii) thermodynamic data (ΔH_f , C_p , etc.) and (iii) transport data for the species taking part in the reactions. A kinetic mechanism, once assembled, is validated by comparing the results from the reaction scheme against experimental data obtained in certain 0D and 1D configurations with simplified fluid mechanics, where the kinetics could be studied in isolation from the fluid flow. Sensitive reactions are revisited and the underlying kinetics is updated, till the updated chemical mechanism reproduces the experimental results satisfactorily.

As a part of my current post-doctoral research, I am exploring the structure of flames that burn multi-component surrogate fuels using detailed simulations. In the following, a detailed discussion on my past research is provided. The discussions in these sections are also referred in my document on future work where appropriate.

1 Doctoral research

Typical transportation fuels are mixtures of several hundreds of compounds belonging to different hydrocarbon classes (see Fig. 2). Their composition varies from one source to another, and only average fuel properties are known at best. In order to understand the combustion characteristics of the real fuels, and to address the

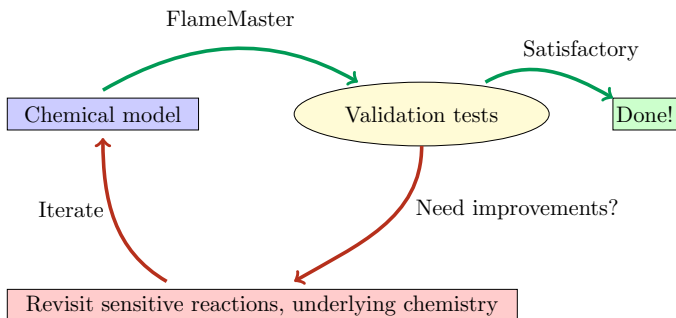


Figure 1: Schematic for chemical kinetic model development.

problem of combustion control, computational studies using a detailed kinetic model to represent the real fuel, serves as a highly useful tool. However, the complexity of the real fuels makes it infeasible to simulate their combustion characteristics directly, requiring a simplified fuel representation to circumvent this difficulty. Typically, the real fuels are modeled using a representative surrogate mixture, i.e. a well-defined mixture comprised of a few components chosen to mimic the desired physical and chemical properties of the real fuel under consideration.

Surrogates have been proposed for transportation fuels, including aviation fuels, and several kinetic modeling attempts for the proposed surrogates have also been made. However, (i) the fundamental kinetics of individual fuels, which make up the surrogate mixtures is not understood well, (ii) their combustion behavior at low through high temperatures has not been comprehensively validated, and this directly impacts the (iii) reliability of the multi-component reaction mechanism for a surrogate made up of these individual components. My doctoral research addresses these concerns.

In particular, my work focuses on the kinetics of few substituted aromatics, *n*-dodecane (a long chain *n*-alkane), and methycyclohexane (a cycloalkane), since these hydrocarbons are relevant as components of transportation fuel surrogates.

These molecules are chosen to represent their respective hydrocarbon classes in the real fuel. These fuels have been the object of several experimental and theoretical studies, and thus a chemical mechanism for their oxidation could be validated extensively and thereby reliable predictions for a mixture of these fuels could be made. A reaction mechanism that describes the oxidation of these hydrocarbons is constructed, following the Component Library Approach [4, 6], by which a library of the reaction pathways for the desired fuels are assembled in a systematic fashion.

A pictorial representation of the mechanism construction is shown in Fig. 3. As the first step, a detailed mechanism for the smaller hydrocarbons [7] (base model) is extended to describe the oxidation kinetics of few substituted aromatic species, which are important components of real fuel surrogates. Thereafter, a short mechanism is obtained for *n*-dodecane oxidation from a detailed reference reaction mechanism for this fuel, using mechanism reduction techniques. This short kinetic scheme is combined with the *base + aromatics* model developed earlier. Several reaction rate updates are introduced to the *n*-dodecane sub-mechanism to achieve an accurate description of the *n*-dodecane kinetics. The reaction pathways of methycyclohexane are also integrated into the *base + aromatics + dodecane* mechanism by following a similar procedure, i.e.

(i) combining a short mechanism for methycyclohexane with the *base + aromatics + dodecane* scheme and (ii) introducing improvements to the kinetic description of methycyclohexane oxidation in the combined model. The chemical model is validated comprehensively every time the oxidation pathways of a new component are incorporated into it.

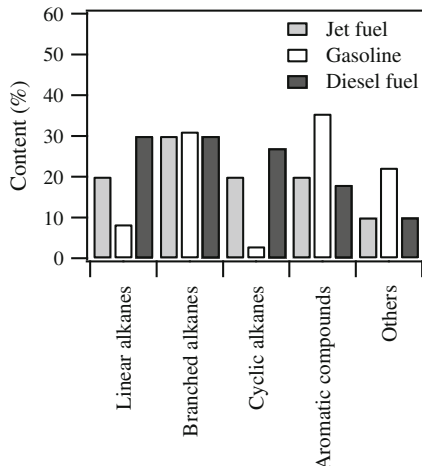


Figure 2: Hydrocarbon classes found in transportation fuels. Source: Clean Combustion, Springer (2013).

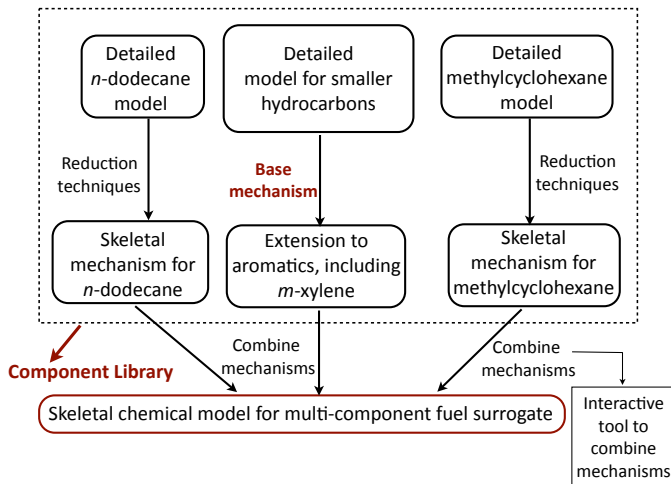


Figure 3: Schematic for a multi-component mechanism construction using the *component library approach*.

The resulting reaction scheme is well-suited to model the oxidation of all the hydrocarbons described by this kinetic scheme. A multi-component surrogate defined using these hydrocarbons as well as the chemical mechanism developed to describe its oxidation are used to make predictions about the combustion behavior of real fuels. Each of these steps are explained in greater detail below, with emphasis on the contributions.

1.1 Kinetics of substituted aromatics

Aromatic compounds are major constituents of real engine fuels: 25% by volume in gasoline, 33% in diesel, and 16% in jet fuels (JP-8, Jet A/A-1) [8]. They are used as anti-knock additives to enhance the octane number of the fuels, for they have high resistance to auto-ignition. Aromatic species also play a crucial role in the formation of soot as they enhance the formation of soot precursors such as Polycyclic Aromatic Hydrocarbons (PAHs). Therefore, understanding and accurately modeling the chemistry of aromatic compounds is essential in order to include them as components of surrogate fuels. A complete and *consistent* reaction scheme for the oxidation of a set of substituted aromatic species applicable at moderate to high temperatures is proposed.

Starting with a detailed mechanism for smaller hydrocarbons including *n*-heptane and iso-octane [7] (called the base mechanism), the oxidation pathways of few aromatic species, specifically toluene, ethylbenzene, styrene, 1-methylnaphthalene, and *m*-xylene have been added (see Fig. 4). The choice of the species considered in the current work was motivated by the necessity to model the oxidation of certain substituted aromatic species, which are crucial components of engine fuels. In addition, these species were chosen based on their relative importance in surrogate formulations. Toluene makes up 12% by weight in gasolines. Ethylbenzene and xylenes constitute roughly 7% with *m*-xylene being the dominant species (3.5%).

In steps of increasing complexity, toluene is the simplest alkane-substituted aromatic, ethylbenzene being the next simplest. Styrene, the simplest alkene-substituted aromatic species, is an important intermediate in ethylbenzene oxidation. Therefore, reaction pathways of styrene need to be understood in order to predict ethylbenzene oxidation characteristics accurately. Xylenes are the simplest aromatics with two alkane substituents. In addition, a bi-ringed substituted aromatic compound, specifically 1-methylnaphthalene, has been considered. PAHs are present to varying extents in modern distillation fuels and are important constituents of the surrogate fuel mixture. While their concentrations might remain low, they are characterized by large sooting tendencies which render them extremely important.

Ensuring consistency between the sub-mechanisms for the different aromatic species is crucial in the mechanism development for substituted aromatics, since their oxidation pathways are strongly coupled. For instance, the chemistry of xylene depends on the chemistry of toluene, which in turn depends on the chemistry of benzene. This chemical model has achieved a consistent framework to describe the oxidation of these aromatic fuels. Consistency here has three different meanings. First, the chemistry of all the fuels is described by one single kinetic mechanism. This means, for example, that the toluene part of the mechanism is used to describe the oxidation of toluene itself, but also as a sub-mechanism in the oxidation of larger species, such as xylene, ethylbenzene, and others. In addition, the chemistry for all aromatic fuel molecules is based on the same chemical mechanism for smaller hydrocarbons. Second, the rate constants used for reactions of a given class of chemical reactions are correlated. Whenever, in the absence of published data, rate constants have been determined by analogy to other reactions among smaller hydrocarbons (for instance, rate constants for reactions involving ethylbenzene are taken from those ethane and *n*-propane), the underlying rates used in the analogy are consistent throughout the mechanism. As an example, the rate of H-abstraction from a methyl group in toluene and in xylene are taken in analogy to the same reaction

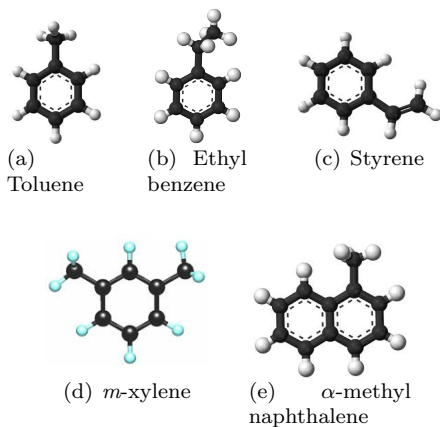


Figure 4: Set of substituted aromatics studied.

and are not independently adjusted. Third, none of the reaction rates has been fitted to match experimental data. All kinetic rate data are consistent with published literature.

The reactions of methylphenyl radical (toluene with a radical on the aromatic ring) are found to be important to describe the formation of benzene from the oxidation of toluene. Apart from the high temperature oxidation of ethylbenzene, reactions describing the moderate temperature oxidation of this fuel showing Negative Temperature Coefficient behavior are also incorporated in this mechanism. The decomposition pathways of benzyl and xylul (xylene with one H atom lost from its methyl group) radicals, decomposition of benzaldehyde, and oxygen addition to methylphenyl radicals are important pathways considered in the proposed mechanism.

The proposed chemical mechanism is validated against ignition delay times, species concentration profiles in shock tube experiments, plug flow reactor data, and laminar burning velocities. Ignition delay results are shown in Fig. 5 for toluene, ethylbenzene, and *m*-xylene. Detailed information on the mechanism development as well as the validation tests are available in Narayanaswamy *et al.* [1].

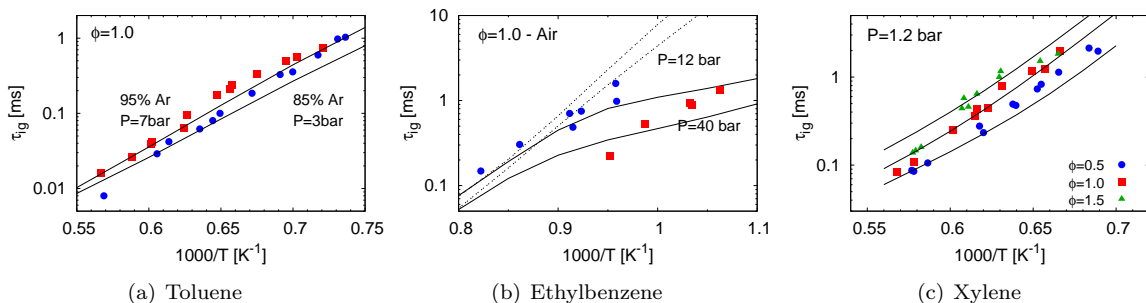


Figure 5: Ignition delay times of aromatics: symbols - experiments (a) Burcat *et al.* [9], (b) Shen *et al.* [10], and (c) Gail *et al.* [11]; solid lines - results from the *base + aromatics* mechanism; dashed lines in (b) - results without low temperature reactions of ethylbenzene. Discussions on these results are available in Narayanaswamy *et al.* [1].

This article [1] discussing the proposed aromatics mechanism has been well received in the combustion community with over 68 citations in less than 4 years since its publication. In some cases, individual rate constants for the aromatic species prescribed in this mechanism have been adopted in the kinetic models proposed thereafter. Further, the sub-mechanism for the aromatic species in the proposed kinetic scheme has been extracted and added to other existing kinetic models. In other cases, the kinetic scheme has been used as such in real engine simulations, and predictions of soot have been made. This article is also one of the top 25 most downloaded article in Combustion and Flame in the year 2010. In summary, this work has made a significant contribution to the kinetics of aromatic species through its impact.

1.2 Long chain *n*-alkane kinetics

Longer chain alkanes, such as *n*-decane, *n*-dodecane, and *n*-tetradecane, are potential candidates to represent the paraffin class in transportation fuel surrogates. Out of these normal alkanes, *n*-dodecane is interesting as a surrogate component [4, 12], and has been identified as a good compromise between a longer straight chain alkane, typical for transportation fuels, and a reasonable size of the molecule [13]. Following this, *n*-dodecane (see Fig. 6) is chosen here as the hydrocarbon to represent the *n*-alkane class in the real transportation fuels.

The relevance of *n*-dodecane as a component of real fuel surrogates has attracted a number of experimental studies in the last couple of years, thus widening the experimental database on *n*-dodecane oxidation. A vast majority of these experimental data were obtained very recently, and in some cases, the existing reaction mechanisms were not validated against all existing data, for example, species pro-

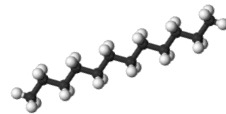


Figure 6: *n*-dodecane.

file measurements. There is therefore a rich experimental database, which has not been fully utilized for model evaluation and improvement.

The main achievement of the present work is that (i) this recent experimental knowledge has been leveraged to develop and extensively validate a model for low through high temperature oxidation of *n*-dodecane, (ii) the proposed reaction scheme retains a compact size, which is amenable to comprehensive kinetic analysis, and (iii) progress has been made towards a single chemical mechanism that can accurately describe the oxidation of a wide range of fuels, which are important surrogate components. The present model is built as an additional module on an existing well-validated model, whose base chemistry has been treated consistently [1, 7] (called as *base + aromatics* model), and thereby ensures kinetic compatibility between the various individual components included in the multi-component scheme by construction. Also, great care is taken to ensure that the oxidation of *n*-heptane, iso-octane, and aromatics, well described in the *base + aromatics* model [1], is little impacted by the introduction of the *n*-dodecane model.

In extending the previous reaction mechanism [1] to include the low through high temperature oxidation pathways of *n*-dodecane, it is desired to introduce only the necessary kinetics to ensure the compactness of the model. Therefore, in the present approach, mechanism reduction techniques developed previously by Pepiot and Pitsch [14, 15] are employed to first obtain a reduced reaction scheme applicable to low through high temperature oxidation of *n*-dodecane from a reference mechanism, which is then incorporated into the *base + aromatics* model (also seen from the left branch of Fig. 3). The recent detailed reaction scheme proposed by Sarathy *et al.* [16] is chosen as the reference mechanism for the present work. This kinetic scheme describes the low through high temperature chemistry of normal alkanes (including *n*-dodecane) and is constructed from elementary reactions, which is consistent with our base model and the aforementioned mechanism reduction approach.

A short mechanism for *n*-dodecane is obtained using reaction mechanism reduction techniques, which is then incorporated into the *base + aromatics* mechanism [1]. This combined model was found to be deficient in representing the ignition delay times and species profiles in shock tube experiments. In order to improve the kinetic description of *n*-dodecane oxidation at low through high temperatures, rate changes have been introduced to this combined model motivated by sensitivity studies and supported by recommendations from literature.

The H_2/O_2 chemistry of the underlying base model has been updated based on the recent Burke *et al.* [17] reaction mechanism. The activation energies of the decomposition reactions of peroxy hydroperoxy radical (one of the main species in the low temperature oxidation chemistry) forming ketohydroperoxide and OH in the *n*-dodecane sub-mechanism have also been updated using recommendations from theoretical studies. The rate of H-abstraction from *n*-dodecane by HO_2 has also been updated. Further, the reactions of alkenes and alkenyl radicals in the *n*-dodecane sub-mechanism have been assigned new rate constants, based on recommendations from recent theoretical and experimental studies. These are explained in greater detail in the article based on this work [2]. Identifying the reaction pathways that needed to be updated as well as assigning revised rate constants for these reactions are important contributions of this work.

The resulting revised mechanism has been comprehensively validated for *n*-dodecane oxidation against various experimental data sets. The validation test cases included ignition delays, species time histories, and major species concentration profiles measured in shock tubes, laminar burning velocity measurements, and major species profiles in a pressurized flow reactor configuration. The improved predictions for ignition delays obtained using the updated reaction mechanism (solid lines) is shown in Fig. 7(a). Results for species profiles in a shock tube as well laminar flame speeds are also shown in Fig. 7. Exhaustive validation test results and discussions are presented in Narayanaswamy *et al.* [2]. The ability of the present reaction mechanism in predicting different targets is promising.

Similarity in ignition delays and laminar flame speeds among normal alkanes was invoked to assess the kinetic model, thereby complementing the existing experimental data. For instance, in Fig. 7(c), the laminar flame speed data for $\text{C}_5\text{--C}_8$ *n*-alkanes at higher pressures have been used to evaluate the ability of the present model to predict laminar flame speeds at elevated pressures and lower pre-heat temperatures, by exploiting the fuel similarity exhibited by *n*-alkanes. In addition, correlations are used to bring together data obtained by different groups to common conditions, and thus evaluate the performance of the proposed mechanism.

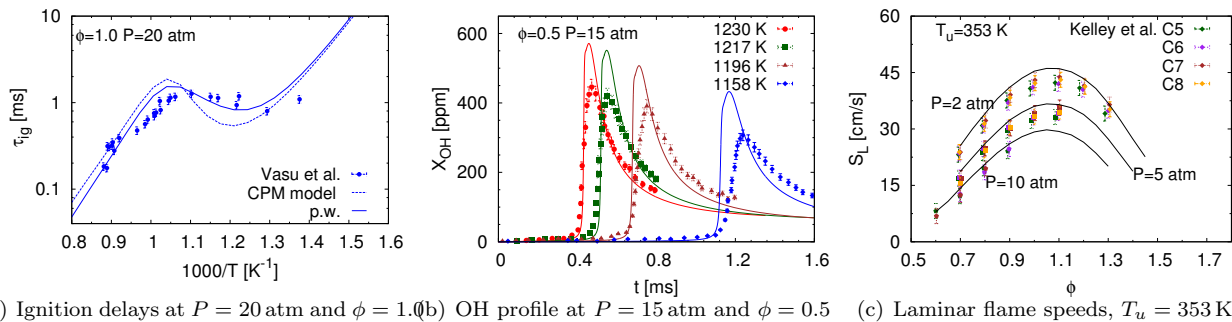


Figure 7: Results for *n*-dodecane oxidation; symbols - experiments: (a) and (b) Vasu *et al.* [18], (c) Kelley *et al.* [19]; solid lines - results computed using the proposed *base + aromatics + dodecane* mechanism; dashed lines in (a) correspond to the results obtained using the mechanism prior to the reaction rate updates (CPM model) introduced in the present work. Discussions on these results are available in Narayanaswamy *et al.* [2].

This analysis of the results in conjunction with existing experimental data in Narayanaswamy *et al.* [2] stands out as an important contribution of this work.

It is worth re-emphasizing that the present work has undertaken for the first time an extensive validation for *n*-dodecane oxidation chemistry by comparing against a wide range of experimental data that have become available in the last couple of years. The ability of the present model to adequately describe the ignition behavior for low through high temperatures is also noteworthy. The key contribution of this work is that the proposed reaction mechanism can describe the kinetics of *n*-dodecane, as well as that of *n*-heptane, iso-octane, and substituted aromatics considered in our previous works [1, 7], which are important components of transportation fuel surrogates. Further, a reaction mechanism applicable only at high temperatures is also derived and provided in Narayanaswamy *et al.* [2]. The full mechanism as well as the one valid at high temperatures have been used in simulations (for instance, Ref. [20]), since *n*-dodecane is of great interest to the engine industry.

1.3 Cycloalkane kinetics

Substituted cyclic alkanes, such as methyl, ethyl, *n*-propyl cyclohexane, and bicyclic alkanes, such as tetralin, are potential candidates to represent the cycloalkane class of compounds in transportation fuel surrogates. Out of these, methylcyclohexane (see Fig. 8) is chosen as the naphthene representative for this work, because it is the simplest substituted cyclic alkane that can be modeled reliably: the global ignition and flame propagation characteristics of methylcyclohexane have been examined in several experimental studies, and some of the key chemical reaction pathways encountered during its oxidation have also been the object of theoretical and experimental kinetic rate constant determinations.

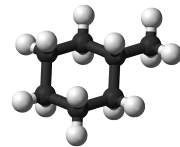


Figure 8: Methylcyclohexane

Similar to the increasing interest in *n*-dodecane due to its relevance as a transportation fuel surrogate, the experimental database on methylcyclohexane kinetics has also widened in recent times. Since existing reaction mechanisms were not validated against all available experimental data, there is a rich experimental database that has yet to be fully utilized for model evaluation and improvement.

The achievement of the present work is that (i) this recent experimental knowledge has been leveraged to develop and extensively validate a model for low through high temperature oxidation of methylcyclohexane, (ii) the proposed reaction scheme retains a compact size, as a kinetic scheme with a reasonably small number of species (say < 500) permits certain calculations, such as calculation of laminar flame speeds, detailed species profiles in flames, sensitivity analysis, and integration in CFD simulations (for example, using tabulation methods), which become very tedious with larger reaction mechanisms, and (iii) a single

chemical mechanism is arrived at that can accurately describe the oxidation of a wide range of fuels, which are important surrogate components. The present model is built as an additional module on a consistent well-validated model developed in stages [1, 2, 7], and thereby ensures kinetic compatibility between the various individual components included in the multi-component scheme by construction.

Similar to the incorporation of the *n*-dodecane reaction pathways, to ensure the compactness of the reaction scheme, only the kinetics essential to describe the low through high temperature oxidation pathways of methylcyclohexane are introduced into the *base + aromatics + dodecane* model [2]. Mechanism reduction techniques developed previously by Pepiot and Pitsch [14, 15] are employed to first obtain a reduced reaction scheme applicable to low through high temperature oxidation of methylcyclohexane, which is then combined with the *base+aromatics+dodecane* model (see right branch of Fig. 3). Since the chemical mechanisms being combined are small in size, the risk of introducing truncated paths or involuntarily duplicating reaction pathways in the combined mechanism is best circumvented by this approach.

In the present work, the detailed reaction scheme proposed by Pitz *et al.* [21] is chosen as the reference mechanism to obtain a short mechanism for methylcyclohexane. This kinetic scheme describes the entire low through high temperature chemistry of methylcyclohexane and is constructed from elementary reactions, which makes it preferable for the aforementioned mechanism reduction approach.

A short mechanism for methylcyclohexane is obtained starting with the reference Pitz *et al.* mechanism using reaction mechanism reduction techniques, which is then incorporated into the *base + aromatics + dodecane* mechanism [2]. This combined model was found to be deficient in representing the ignition delay times and species profiles in shock tube experiments. In order to improve the kinetic description of methylcyclohexane oxidation at low through high temperatures, a number of rate changes have been introduced to this combined model motivated by sensitivity studies and reaction flux analysis. The rate constants of the sensitive reactions have been checked and updated wherever possible, irrespective of whether the update leads to an improvement of the ignition delay and the species profiles predictions or a deterioration. The rate constant changes are also guided by reaction flux analysis performed using the combined model. The updates are primarily based on recent rate recommendations from theoretical and experimental work available in the literature. An additional pathway important at moderate to low temperatures is also introduced.

The modifications to the reaction mechanism dealt with (i) ring opening pathways of methylcyclohexane to form biradicals, (ii) ring opening of methylcyclohexyl radicals, (iii) decomposition of γ -QOOH radicals, (iv) H-abstraction from cyclohexylmethyl by oxygen molecule, (v) ketohydroperoxide decomposition, (vi) H-abstraction from methylcyclohexane by H, OH, and HO₂, (vii) decomposition of alkenyl radicals, and (viii) formation of benzene and toluene during the oxidation of methylcyclohexane. The schematic of formation of toluene from methylcyclohexyl radical is shown in Fig. 9 and is important for representing toluene concentrations in methylcyclohexane flames (see Fig. 10(e)). The concerted elimination pathway involving direct elimination of HO₂ from the peroxy radicals, which is important at moderate and low temperatures has been newly added to this mechanism. The improved kinetic description of methylcyclohexane oxidation is a highlight of the proposed kinetic mechanism.

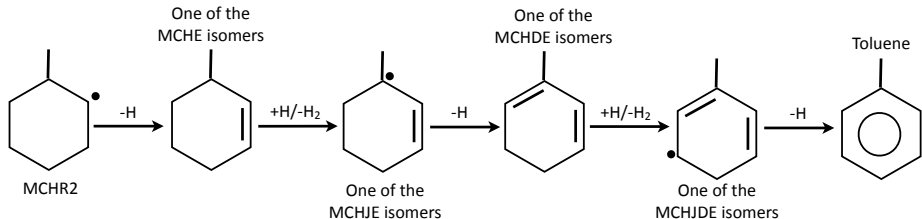


Figure 9: Formation of toluene via successive loss of H atoms from methylcyclohexyl radicals. Only a representative pathway starting with 2-methylcyclohexyl radical (MCHR2) is shown here. Full species names: (i) MCHE - methylcyclohexene, (ii) MCHJE - methylcyclohexenyl radical, (iii) MCHDE - methylcyclohexadiene, (iv) MCHJDE - methylcyclohexadienyl radical.

The resulting revised mechanism was comprehensively validated for methylcyclohexane oxidation against a large number of experimental data sets. The kinetic validation test cases include ignition delays, species time histories measured in shock tubes, laminar burning velocity measurements, detailed species measurements in premixed flames, and major species profiles in a plug flow reactor configuration. Some of these results are shown in Fig. 10. Detailed discussion of these results are provided in Narayanaswamy *et al.* [3].

It is worth re-emphasizing the use of several, very recent data sets for kinetic model validation in the present work. The ability of the proposed reaction scheme to adequately describe the ignition behavior for low through high temperatures is also noteworthy. Further, the pathways for the formation of aromatics from methylcyclohexane oxidation are well represented by this model. Also, the base mechanism on which the methylcyclohexane kinetics is built, allows a detailed description of the aromatic chemistry [1]. Together, this makes the present kinetic scheme well suited for assessing the formation of pollutants in engines.

One other key contribution of this work is that the proposed reaction mechanism can describe the kinetics of methylcyclohexane, as well as that of *n*-heptane, iso-octane, substituted aromatics, and *n*-dodecane, considered in the *base + aromatics + dodecane* mechanism [1, 2, 7], which are important components of transportation fuel surrogates. In addition, the proposed reaction mechanism also retains a compact size, 370 species and 2694 reactions counting forward and reverse reactions separately, which makes kinetic analysis feasible using this model. This size of the reaction mechanism is suitable to be coupled in LES simulations employing flamelet models with tabulation [22], which expands the usability of the kinetic scheme to real-time simulations. Further, a reaction mechanism applicable only at high temperatures is also derived and provided in Narayanaswamy *et al.* [3], which will be useful in simulations studying the high temperature combustion behavior of methylcyclohexane.

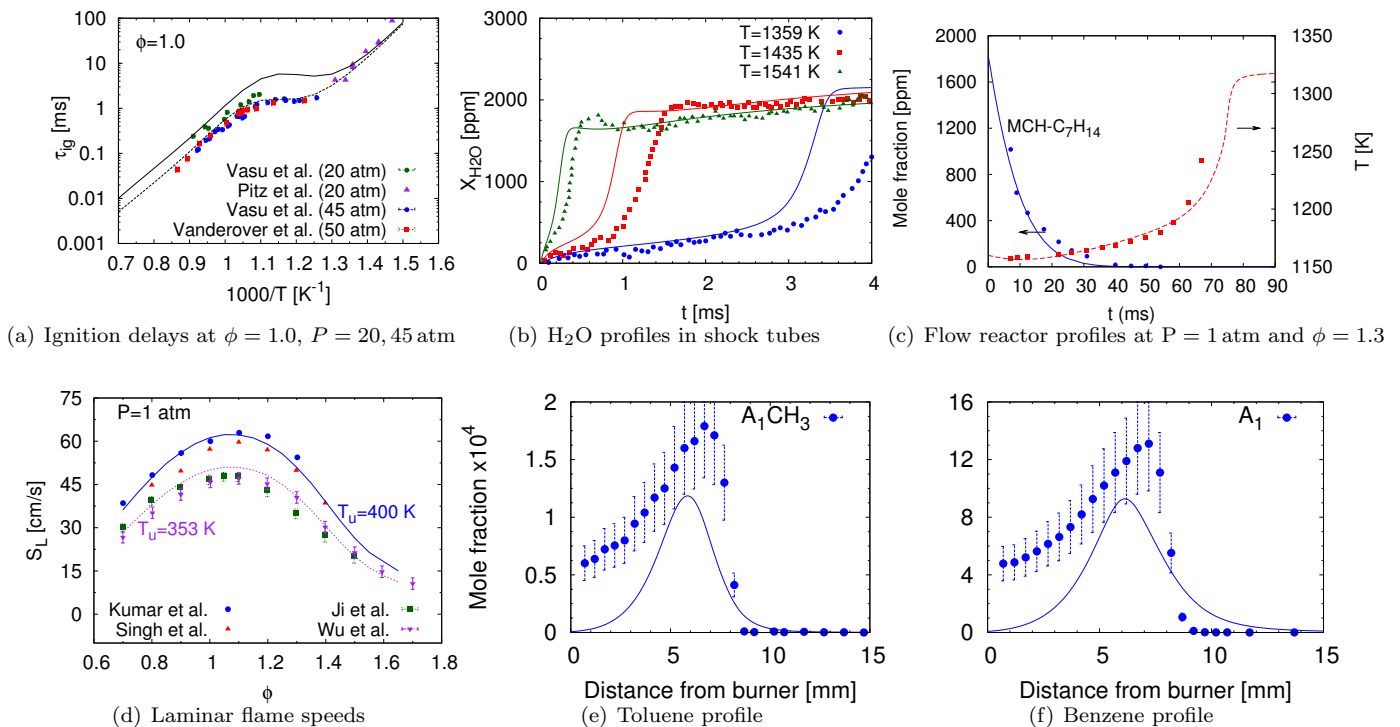


Figure 10: Results for methylcyclohexane oxidation; symbols - experiments (a) Vasu *et al.* [23], Pitz *et al.* [21], and Vanderover *et al.* [24] (b) Hong *et al.* [25], (c) Zeppieri *et al.* [26], (d) Kumar and Sung [27], Singh *et al.* [28], Ji *et al.* [29], and Wu *et al.* [30], (e) and (f) - Aromatics in a low pressure methylcyclohexane flame at $P = 30$ torr and $\phi = 1.75$ from Wang *et al.* [31]. Discussions on these results are available in Narayanaswamy *et al.* [3].

1.4 Surrogates for real fuels

The reaction mechanism thus developed in stages [1–3] well-represents the individual hydrocarbon oxidation and is ideally suited to be used to describe the oxidation of a multi-component surrogate for a real fuel made up of these fuel components. A surrogate is defined to consist of 30% *n*-dodecane (in gas phase mole fractions), 48% methylcyclohexane, and the rest *m*-xylene to mimic the heating value, sooting index, cetane number, and H/C ratio properties of the average jet fuel. The surrogate along with the reaction mechanism to describe its oxidation is validated by comparing against experimental data for the real jet fuel. In Fig. 11, the model well represents the ignition delays at low through high temperatures, CO₂ profile in a variable flow reactor, as well as the laminar flame speeds. Some of these results have been discussed in an earlier work [4] and additional validation tests will be discussed in an upcoming article [5].

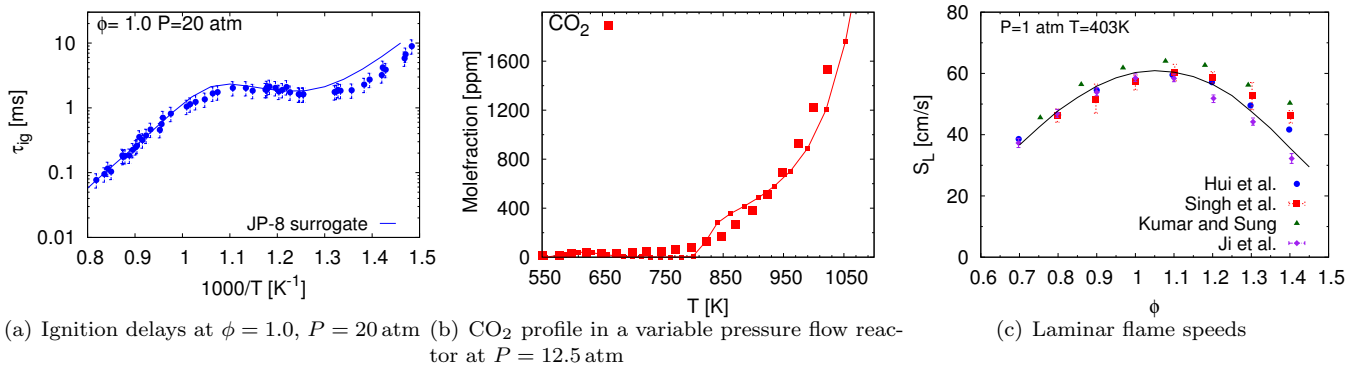


Figure 11: Results for the jet fuel surrogate; symbols - experiments (a) Wang and Oehlschlaeger [32], (b) Dooley *et al.* [33], (c) Ji *et al.* [34], Kumar *et al.* [35], Hui *et al.* [36], Singh *et al.* [37]. Some of these results have been discussed in an earlier work [4] and additional validation tests will be discussed in an upcoming article [5].

2 Post-doctoral research

As a part of my post-doctoral research, I am exploring reactive flow simulations. Triple flames are found in jet flames and play an important role in the stabilization and thereby lift-off height of lifted jet flames. These are special types of edge flames, which have a lean premixed flame branch, a rich premixed flame branch, and a diffusion flame in between. A 2D laminar triple flame burning *n*-heptane is studied. The temperature field in the computational domain is shown in Fig. 12.

As a continuation of this work, 2D laminar triple flames burning jet fuel are simulated using finite rate chemistry and detailed transport of species. The jet fuel is represented by using the surrogate mixture defined in section 1.4, comprised of *n*-dodecane, methylcyclohexane, and *m*-xylene. The chemical kinetics of this multi-component surrogate are described using the reaction mechanism derived above [1–3, 5]. The structure of the simulated triple flames is explored by examining the reactivity of the different hydrocarbons in the multi-component fuel and the radical profiles. The heat release profiles of the lean and rich branches of the triple flame are compared to their unstretched 1D counterparts to identify similarities. The simulations are repeated for different fuel mixtures in order to investigate the effect of the surrogate fuel composition on the combustion process. The results of this analysis will be presented at an upcoming conference meeting.

A discussion on my future research plans is provided in a separate document.

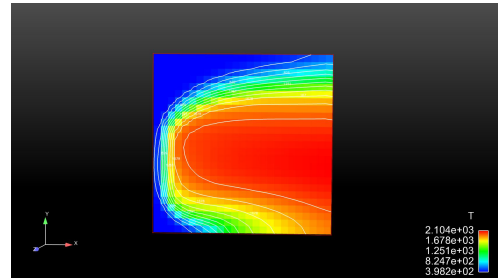


Figure 12: Temperature field in an *n*-heptane triple flame.

References

- [1] K. Narayanaswamy, G. Blanquart, and H. Pitsch. A consistent chemical mechanism for the oxidation of substituted aromatic species. *Combust. Flame*, 157 (10):1879–1898, 2010.
- [2] K. Narayanaswamy, P. Pepiot, and H. Pitsch. A chemical mechanism for low to high temperature oxidation of *n*-dodecane as a component of transportation fuel surrogates. *Combust. Flame*, 161(4):866–884, 2014.
- [3] K. Narayanaswamy, H. Pitsch, and P. Pepiot. A chemical mechanism for low to high temperature oxidation of methylcyclohexane as a component of transportation fuel surrogates. *Combust. Flame (under review)*, 2014.
- [4] K. Narayanaswamy, P. Pepiot, and H. Pitsch. Jet fuels and Fischer-tropsch fuels: Surrogate definition and chemical kinetic modeling. In *U.S National Combustion Meeting*, 2013.
- [5] K. Narayanaswamy, H. Pitsch, and P. Pepiot. Jet fuel and fischer-tropsch fuels - surrogate definition and chemical kinetic modeling. *In preparation*.
- [6] P. Pepiot-Desjardins. *Automatic strategies to model transportation fuel surrogates*. PhD thesis, Stanford University, Department of Mechanical Engineering, 2008.
- [7] G. Blanquart, P. Pepiot-Desjardins, and H. Pitsch. Chemical mechanism for high temperature combustion of engine relevant fuels with emphasis on soot precursors. *Combust. Flame*, 156:588–607, 2009.
- [8] Northrop Grumman Petroleum Product survey reports. Technical report, 2005. updated annually.
- [9] A. Burcat, C. Snyder, and T. Brabbs. Ignition delay times of benzene and toluene with oxygen in argon mixtures. *Tech. Rep. NASA*, TM-87312, 1986.
- [10] H-P. S. Shen and M. A. Oehlschlaeger. The autoignition of C_8H_{10} aromatics at moderate temperatures and elevated pressures. *Combust. Flame*, 156:1053–1062, 2009.
- [11] S. Gail. *Etude cinétique de l’oxydation de composés aromatiques en relation avec la composition du gazole et de l’essence: Approche expérimentale et modélisation cinétique détaillée*. PhD thesis, University of Orléans, 2003.
- [12] A. Violi, S Yan, E. G. Eddings, A. F. Sarofim, S. Granata, T. Faravelli, and E. Ranzi. Experimental formulation and kinetic model for JP-8 surrogate mixtures. *Combust. Sci. Tech.*, 174(11-12):399–417, 2002.
- [13] M. Colket, T. Edwards, S. Williams, N. P. Cernansky, D. L. Miller, F. Egolfopoulos, P. Lindstedt, K. Seshadri, F. L. Dryer, C. K. Law, D. Friend, D. B. Lenhert, H. Pitsch, A. Sarofim, M. Smooke, and W. Tsang. Development of an experimental database and kinetic models for surrogate jet fuels. In *45th AIAA Aerospace Sciences Meeting and Exhibit*, pages 2007–770, 2007.
- [14] P. Pepiot-Desjardins and H. Pitsch. An efficient error propagation based reduction method for large chemical kinetic mechanisms. *Combust. Flame*, 154:67–81, 2008.
- [15] P. Pepiot-Desjardins and H. Pitsch. An automatic chemical lumping method for the reduction of large chemical kinetic mechanisms. *Combust. Theory. Mod.*, 12 (6):1089–1108, 2008.
- [16] S. M. Sarathy, C. K. Westbrook, M. Mehl, W. J. Pitz, C. Togbe, P. Dagaut, H. Wang, M. A. Oehlschlaeger, U. Niemann, and K. Seshadri. Comprehensive chemical kinetic modeling of the oxidation of 2-methylalkanes from C_7 to C_{20} . *Combust. Flame*, 158(12):2338–2357, 2011.
- [17] Michael P Burke, Marcos Chaos, Yiguang Ju, Frederick L Dryer, and Stephen J Klippenstein. Comprehensive H_2/O_2 kinetic model for high-pressure combustion. *Int. J. Chem. Kinet.*, 44(7):444–474, July 2012.
- [18] S. S. Vasu, D. F. Davidson, Z. Hong, V. Vasudevan, and R. K. Hanson. *n*-Dodecane oxidation at high-pressures: Measurements of ignition delay times and OH concentration time-histories. *Proc. Combust. Inst.*, 32 (1):173–180, 2009.
- [19] A. P. Kelley, A. J. Smallbone, D. L. Zhu, and C. K. Law. Laminar flame speeds of C_5 to C_8 *n*-alkanes at elevated pressures: Experimental determination, fuel similarity, and stretch sensitivity. *Proc. Combust. Inst.*, 33:963–970, 2011.

- [20] S. Ayyapureddi, U. Egüz, C. Bekdemir, B. Somers, P. de Goey, and B. Albrecht. Modeling of conventional and early diesel injection combustion characteristics using fgm approach. Technical report, SAE Technical Paper, 2013.
- [21] W. J. Pitz, C. V. Naik, T. N. Mhaolduin, C. K. Westbrook, H. J. Curran, J. P. Orme, and J. M. Simmie. Modeling and experimental investigation of methylcyclohexane ignition in a rapid compression machine. *Proc. Combust. Inst.*, 31 (1):267–275, 2007.
- [22] M. E. Mueller and H. Pitsch. Large eddy simulation of soot evolution in an aircraft combustor. *Phys. Fluids*, 25(110812):1–21, 2013.
- [23] S. S. Vasu, D. F. Davidson, Z. Hong, V. Vasudevan, and R. K. Hanson. Shock tube study of methylcyclohexane ignition over a wide range of pressure and temperature. *Energy & Fuels*, 23:175–185, 2009.
- [24] J. Vanderover and M. A. Oehlschlaeger. Ignition time measurements for methylcyclohexane-and ethylcyclohexane-air mixtures at elevated pressures. *Int. J. Chem. Kinet.*, 41(2):82–91, 2009.
- [25] Z. Hong, K. Y. Lam, D. F. Davidson, and R. K. Hanson. A comparative study of the oxidation characteristics of cyclohexane, methylcyclohexane, and *n*-butylcyclohexane at high temperatures. *Combust. Flame.*, 158:1456–1468, 2011.
- [26] S. Zeppieri, K. Brezinsky, and I. Glassman. Pyrolysis studies of Methylcyclohexane and Oxidation studies of Methylcyclohexane and Methylcyclohexane/Toluene blends. *Combust. Flame*, 108:266–286, 2009.
- [27] K. Kumar and C.-J. Sung. Flame propagation and extinction characteristics of neat surrogate fuel components. *Energy & Fuels*, 24(7):3840–3849, 2010.
- [28] D. Singh, T. Nishiie, and L. Qiao. Laminar flame speeds and markstein lengths of *n*-Decane/Air, *n*-Decane/O₂/He and MCH/Air flames. In *Central States Meeting*, 2010.
- [29] C. Ji, E. Dames, B. Sirjean, H. Wang, and F. N. Egolfopoulos. An experimental and modeling study of the propagation of cyclohexane and mono-alkylated cyclohexane flames. *Proc. Combust. Inst.*, 33:971–978, 2011.
- [30] F. Wu, A. P. Kelley, and C. K. Law. Laminar flame speeds of cyclohexane and mono-alkylated cyclohexanes at elevated pressures. *Combust. Flame.*, 159 (4):1417–1425, 2012.
- [31] Z. Wang, L. Ye, W. Yuan, L. Zhang, Y. Wang, Z. Cheng, F. Zhang, and F. Qi. Experimental and kinetic modeling study on methylcyclohexane pyrolysis and combustion. *Combust. Flame.*, 161(1):84–100, 2014.
- [32] H. Wang and M. A. Oehlschlaeger. Autoignition studies of conventional and Fischer-Tropsch jet fuels. *Fuel*, 98:249–258, 2012.
- [33] S. Dooley, S. H. Won, M. Chaos, J. Heyne, Y. Ju, F. L. Dryer, K. Kumar, C.-J. Sung, H. Wang, M. A. Oehlschlaeger, R. J. Santoro, and T. A. Litzinger. A jet fuel surrogate formulated by real fuel properties. *Combust. Flame*, 157(12):2333–2339, 2010.
- [34] C. Ji, Y. L. Wang, and F. N. Egolfopoulos. Flame studies of conventional and alternative jet fuels. *J. Prop. Power*, 27(4):856, 2011.
- [35] K. Kumar, C.-J. Sung, and X. Hui. Laminar flame speeds and extinction limits of conventional and alternative jet fuels. *Fuel*, 90(3):1004–1011, 2011.
- [36] X. Hui, K. Kumar, C.-J. Sung, T. Edwards, and D. Gardner. Experimental studies on the combustion characteristics of alternative jet fuels. *Fuel*, 98:176–182, 2012.
- [37] D. Singh, T. Nishiie, and L. Qiao. Experimental and kinetic modeling study of the combustion of *n*-decane, Jet-A, and S-8 in laminar premixed flames. *Combust. Sci. Tech.*, 183(10):1002–1026, 2011.