



## Full Length Article

# High-fidelity combustion properties modeling of aviation kerosene with the aid of surrogate construction and its simplified chemical kinetics mechanism

Hossein S. Saraee<sup>\*</sup>, Kevin J. Hughes, Mohamed Pourkashanian

Department of Mechanical Engineering, Energy 2050, The University of Sheffield, Sheffield S3 7RD, United Kingdom

## ARTICLE INFO

## Keywords:

Jet fuel  
Combustion  
Reaction kinetics  
Surrogate  
Mechanism  
Aviation kerosene

## ABSTRACT

In spite of the great advances in surrogate development for conventional jet fuels, it is still a big challenge to allocate the appropriate components and proportion which accurately emulate the real fuel specifications. So, this study aims to investigate the development of a well-validated surrogate with a simplified chemical kinetics mechanism that delivers a good prediction ability for the key combustion parameters of aviation kerosene in a wide range of conditions for temperature, pressure and equivalence ratio. A surrogate consisting of 4 components including 30% (by mass) tetradecane, 30% iso-dodecane, 24% n-propylcyclohexane, and 16% toluene was developed based on the major components of the real fuel and the similar property targets to the target fuel. Then, a simplified compact mechanism was developed for the proposed surrogate. The model was used for the simulation of ignition delay, flame speed, and species concentration. In general, the results showed a good agreement compared to the experimental data, and a closer emulation of the empirical data for ignition delay and flame speed, in comparison to previously developed models for jet A. Considering the compact size and the predictive ability of the proposed surrogate, the model can be used as a tool for the combustion investigation of kerosene to improve engine designs, efficiency and reduce emissions.

## 1. Introduction

Combustion is one of the phenomena which has had significant effects in the development of civilization, from its beginnings for simple heating and cooking until now where it is integral to modern life. If it is harnessed well, it can be utilized as the useful energy extracted from the process of reacting substances (solid, liquid, or gaseous) with oxygen in the air that leads to an exothermic reaction. One of the devices that utilizes combustion phenomena is the turbine engine which nowadays is widely used as a main source for generating power. Shortly after the invention of this engine, kerosene became the main fuel source in this type of engine, especially in aircraft. In this regard, researchers are focused on the improvement of the combustion efficiency of conventional jet fuels and investigating promising alternative candidates. However, it is expensive and time-demanding to just investigate it empirically. So, computational combustion was utilized as a way of investigating combustion besides experimental works. Kinetic modeling is one of the significant aspects of computational combustion that has provided the opportunity of gaining a deeper understanding and

knowledge about the combustion phenomena in different media. It has a great role to improve the functionality of practical combustion applications, such as the engines of vehicles. With the aid of kinetic modeling, researchers can survey and analyze the fuel structure and the fundamental chemistry coupled with direct kinetic measurements of intermediate and products species, and the rate constants. The steps applied for a kinetic model to be utilized in practical applications include providing a detailed chemical kinetic model, applying a validation process, developing a reduced model, performing the CFD simulations, and improving the performance (see Fig. 1).

The complexity of real jet fuels structure made researchers to investigate the possibility of applying a surrogate which accurately emulates the real fuel specifications, as it is an economical time-saving way for jet fuel studies. Fuel modelling can provide an opportunity for academic and industrial investigators to rapidly conduct their intended scientific works over a broad range of conditions while releasing them from time-consuming and expensive changes in the design of a prototype. Traditional jet fuels comprise a combination of different classes of very many hydrocarbons, in the hundreds. The major classes include

<sup>\*</sup> Corresponding author.

E-mail address: [HSOUKHTSARAEI@SHEFFIELD.AC.UK](mailto:HSOUKHTSARAEI@SHEFFIELD.AC.UK) (H.S. Saraee).

<https://doi.org/10.1016/j.fuel.2024.131896>

Received 16 December 2023; Received in revised form 5 April 2024; Accepted 12 May 2024

Available online 17 May 2024

0016-2361/© 2024 The Author(s). Published by Elsevier Ltd. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

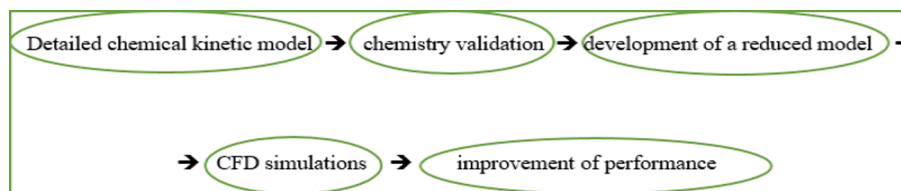


Fig. 1. The schematic of the steps applied for a kinetic model to be utilized in practical applications.

normal, iso, and cyclo alkanes and aromatics, and each of them have different impacts on the thermophysical and combustion properties of the fuel [1].

By using the surrogate approach and including a simplified version for its associated mechanism, researchers can mitigate the issues of using a big detailed mechanism such as the complexity, stiffness (how difficult an equation is to solve numerically), and the huge computational cost [2]. The number, type, and concentration of the surrogate components, and also the simplification process of the detailed mechanism (reduction of the species and reactions) are based on the numbers and types of the target combustion parameters. However, each of the processes, especially the mechanism simplification, need to be conducted with scrutiny in order to avoid significant loss of accuracy.

Surrogates and chemical kinetics mechanisms (simplified and complex) for aviation kerosene fuels have been developed by many researchers during recent decades, and have been reviewed from different aspects [3–5]. A majority of the early developed surrogates for jet fuels [6–10] consisted of one component including one alkane (mostly n-decane) or two components including an alkane and an aromatic. It was demonstrated that considering just one or two components representatives of one or two hydrocarbon classes of the target fuel for surrogates cannot adequately reproduce all of the combustion parameters, such as the ignition delay, and species profiles [4,11].

As one of the initial trials to develop a jet fuel surrogate containing more components and chemical groups which have significant percentage in the target fuel, Violi et al. [12] proposed a surrogate consisting of six components which showed a good ignition behaviour just at high temperatures [13]. A three components surrogate consisting of a normal and a cyclo alkane, and benzene developed by Dagaut et al. in 2006 [14], could deliver good simulation for the experiments in jet stirred reactors. The speciation in a jet stirred reactor were also simulated well by adding an alkene to Dagaut's proposed components and developing a detailed mechanism for the four components surrogate [15]. The works done by Dooley et al. in 2010 and 2012 [16,17] on the development of the 1st and 2nd generations of surrogates have had a great contribution to jet fuel surrogate development in recent years since they provided a number of the experiments that are being used as a base data by researchers who work on surrogate and mechanism development for jet fuels. The experiments and simulations have been conducted over a vast range of pressures, temperatures, and equivalence ratios for ignition delay, flame speed, and species profiles. The component selection for the surrogate development was based on the dominant hydrocarbon groups (n/iso/cyclo alkane, and an aromatic) which capture the cetane number (CN), hydrogen to carbon ratio (H/C), molecular weight (MW) and threshold sooting index (TSI) of the target jet fuel. A year later, Malewicki et al. [18] investigated the modelling capacity of the ignition characteristics and the mole fractions of the 2nd generation surrogate, and reported a good agreement with the experimental data in Dooley's work. In recent years, there has been more tendency to use n-dodecane and n-tetradecane (instead of n-decane) as the representative of n-alkane in jet fuel surrogates, since they have similar physical and chemical characteristics to aviation kerosene [19–21]. Yu et al. [20] developed a surrogate that includes 73 % n-dodecane, 14.7 % 1,3,5-trimethylcyclohexane and 12.3 % n-propylbenzene to surrogate RP-3 kerosene which just contained 138 species and 530 reactions. Liu et al. [21] experimentally and numerically investigated the combustion

behaviour of a surrogate jet fuel consisting of n-dodecane 66.2 %, n-propylbenzene 15.8 % and 1,3,5-trimethylcyclohexane 18.0 %, in mol, over a range of temperatures, fuel equivalence ratios, and pressures. In 2019, a surrogate for aviation kerosene with its simplified associated mechanism containing a combination of n-dodecane and n-tetradecane, and decalin was developed for engine application by Zhong and Peng [22]. There have been also advances in developing reduced kinetic mechanisms for surrogates through distinct approaches in recent years. Ranzi et al. [23], developed several skeletal and reduced mechanisms for typical surrogate mixtures of transportation hydrocarbon (and oxygenated) fuels including kerosene, through the lumped approach. The developed reduced mechanisms could partially capture the combustion parameters. Another interesting method to provide a reduced mechanism for a surrogate was an approach termed HYCHEM developed by Xu et al. [24]. They successfully developed a reaction kinetic model validated by experiments for jet and rocket fuels, which emulated the combustion behaviour of the target fuels at just high temperatures.

At first, there were two definitions for developing surrogates for a real target fuel; a physical surrogate in which surrogate components have similar physical properties like viscosity and density, and a chemical surrogate in which surrogate components have similar chemical properties, such as H/C ratio, chemical class composition, etc. However, in recent years, researchers have considered a combination of two types of the surrogate called a comprehensive surrogate, as it was found to be more useful to emulate the combustion parameters of a target fuel [25], both in chemical kinetic modelling and further, in 3D simulations and engine applications. Kim et al. [26] developed two surrogates, namely UM1 and UM2, for jet fuels by considering the capturing of both the physical and chemical properties of the target fuel. A jet fuel surrogate was proposed by Yu et al. in 2018 [27], to emulate real jet fuel properties including physical characteristics, gas-phase chemical properties and threshold sooting index, and captured a combination of both the physical and chemical target properties including 8 items.

In spite of the great advances in surrogate development for conventional jet fuels, it is still a big challenge to allocate the appropriate components and proportion which accurately emulate the real fuel specifications. There are only a few jet fuel surrogates which can simultaneously reproduce the physical and chemical properties of the target jet fuel and show a good emulation of the combustion characteristics. It is still a serious issue and it is necessary to develop jet fuel surrogates with a compact reduced mechanism applicable for further chemical kinetics investigations and some 3-D simulations such as equivalent reactor network analysis, while the surrogate's mechanism can demonstrate an good simulation behaviour for ignition, flame speed and species concentration together, and comprehensively is validated against experimental data. Therefore, developing a well-validated surrogate with a simplified mechanism having a good prediction ability for the combustion parameters of kerosene fuel, covering a wide range of conditions (temperatures, pressures and equivalence ratios), is the main goal for this study.

## 2. Development of the surrogate and its reaction kinetics mechanism

Surrogate development is the idea of the formulation of one or more

**Table 1**

The values of the combustion property targets for jet A POSF 4658.

| Fuel            | DCN  | MW(g/mol) | H/C ratio | Density<br>(kg m <sup>-3</sup> ) | Viscosity(cst) | Distillation Curve (figure) | Lower heating value (MJ/kg) |
|-----------------|------|-----------|-----------|----------------------------------|----------------|-----------------------------|-----------------------------|
| Jet-A POSF 4658 | 47.1 | 157.5     | 1.96      | 806                              | 5.2            | Kim et al. [26]             | 42.8                        |

simple fuel components which can emulate the thermophysical, thermochemical, and chemical kinetic properties of a more complex real fuel, in order to capture the intended fundamental experiments and predictive simulations. To reproduce the wide variety of properties of the target fuel, a surrogate should contain more and more components that leads to more detailed results and closer to the characteristics of the real fuel. However, the computational limitation of the current computing resources prevents researchers to consider many components for developing fuel surrogates. Indeed, In addition to the satisfaction of the physics and chemistry characteristics in the practical application viewpoint, a surrogate should be able to be coded and run smoothly on computers for simulation purposes. Development of the detailed mechanisms was a great step because they later were applied as the core mechanism for heavy fuels, such as diesel and jet hydrocarbon fuels [28]. In parallel to the development of new mechanisms for heavy species, the effort on the promotion of the core mechanisms is still on the agenda of many kinetics groups and researchers. In addition, some works are dedicated to providing more accurate rate constants through measurement methods or calculation by quantum chemistry [29]. How much the rates are more accurate, the model can provide a closer prediction of the combustion behaviour compared to the real target species. The combustion of heavy hydrocarbons contains a mixture of oxidation and decomposition reactions which constitutes smaller hydrocarbons in a hierarchical order until it reaches the provided core mechanism (usually a C<sub>0</sub>-C<sub>4</sub> mechanism).

To formulate and develop a surrogate, it is usually necessary to apply a series of steps such as defining the combustion property targets, choosing the number and type of surrogate components, selecting a powerful standard simulator software, providing reaction mechanism files, and performing simulation runs of some of the combustion parameters. The results of these can then be compared with the experimental data for validation that leads to the modification on reaction rates or other parameters if required, and to develop a skeletal and/or reduced mechanism.

The first step to develop a surrogate is defining the intended target properties for a surrogate formulation. The projected usage of the surrogate fuel defines the property targets in the process of formulating a surrogate fuel. However, considering too many property targets makes it hard to meet all the property targets. On the other hand, selecting too few property targets does not manifest the properties of the target fuel. The consideration for the targets number should cover just those property targets which indicate the main physicochemical properties of the target real fuel.

In the past, researchers considered just a narrow range of combustion property targets (CPTs) which only includes two or three chemical parameters such as chemical composition, molecular weight, and cetane number. However, nowadays, the range has been broadened up to 8 parameters which covers both combustion properties and those physical properties which affect the combustion of jet fuel such as viscosity, density, and distillation [16,26]. In this study, the considered candidate components are those which met the important seven targets of the main combustion property targets (CPTs) of jet fuel and were used more by researchers for the surrogate formulation. The targets include H/C ratio, molecular weight, lower heating value, cetane number, viscosity, distillation, and density. The values can be seen in Table 1.

To choose components of the surrogate, some prerequisites were adopted in this study, based on the previous publication [26] and the goals of this research. Firstly, the selection is conducted based on the major component/components of the real fuel, or a representative of the

average properties of the major components of the real fuel in terms of hydrocarbon class and molecular size. Secondly, the candidates should have similar property targets (listed above) to the target fuel. Thirdly, reliable and accurate mechanisms should exist for them and also be accessible. To give weight to each component of the surrogate and the number of components in the kerosene surrogate, a recently published gas chromatography–mass spectrometry (GC/MS) report [30] and the report by Edward [31] were used which provided data about the number and type of the dominant chemical groups that constitute the real fuel. Based on the data, the kerosene fuel (jet A) has four major chemical groups including normal alkanes, iso-alkanes, naphthene, and aromatics. As these four hydrocarbon classes have quite different chemical and physical characteristics, the proposed surrogate must include at least four components to cover the impact of each class on the emulation of the target fuel characteristics. To select the components related to the mentioned groups, those which make up the highest proportions in the group were considered. For instance, the percentage of n-dodecane and n-tetradecane are the major contributors for n-alkane in the GC report, and also meet the 4 prerequisites mentioned before. The candidates should also be in the range of the typical molecular size distribution of the target fuel (C7 ~ C14) based on the GC report [30,31]. Since it was recommended that using normal alkanes larger than n-dodecane such as n-tetradecane, with a higher MW and boiling points, might be useful to achieve a better agreement with the Jet-A properties [19], it is taken into account in this study.

Previously, researchers usually selected one or two important components of the major groups, due to the limitations on the ability of the models and available tools in the chemical kinetics and also for providing a small mechanism having a low number of species and reactions which is suitable for 3D engine simulation. However, in recent years, surrogates have developed from a range of 3 to 7 components covering all the individual chemical groups, because of the advances in kinetic modelling and related tools and software [32]. It should be noted that how many groups we include in our formulation could be more, the simulation behaviour of the surrogate can be closer to that of the real fuel, although the provided mechanism would be big. Thus, the surrogate formulation proposed in this research was defined based on choosing the components from 4 major groups, based on the availability of a reliable and accurate sub-mechanism, their weight, and the similarity of their chemical formula to each major group in the GC/MS report. The final consideration for developing the proposed surrogate was keeping the total number of carbon and hydrogen close to the target jet A fuel (roughly 11 carbons and 22 hydrogens).

Based on researchers' previous investigations [4,16,19–22,25–27,33] and especially from the works of Kim et al. [19] who provided a collection of possible candidates from their results and previous works, a number of component representatives of the above-mentioned hydrocarbon classes were chosen from the candidates' pool to develop a simplified mechanism for each components and study their functions in Chemkin-Pro. Finally, a surrogate including 30 % (by mass) tetradecane, 30 % iso-dodecane, 24 % n-propylcyclohexane, and 16 % toluene was selected for this study. Iso-dodecane [34] and n-propylcyclohexane [35] mechanisms used in this study are in-house mechanisms developed by the author of this study, tetradecane and toluene mechanisms were selected from the published works in the literature [36,37]. The associated mechanism of the surrogate was completed by coupling a well-validated core mechanism [37] to the provided sub-mechanisms. It is noteworthy that these components also include some of the Chemical Functional Groups (CFGs) matching CFGs of the targeted fuel [CH<sub>3</sub>,

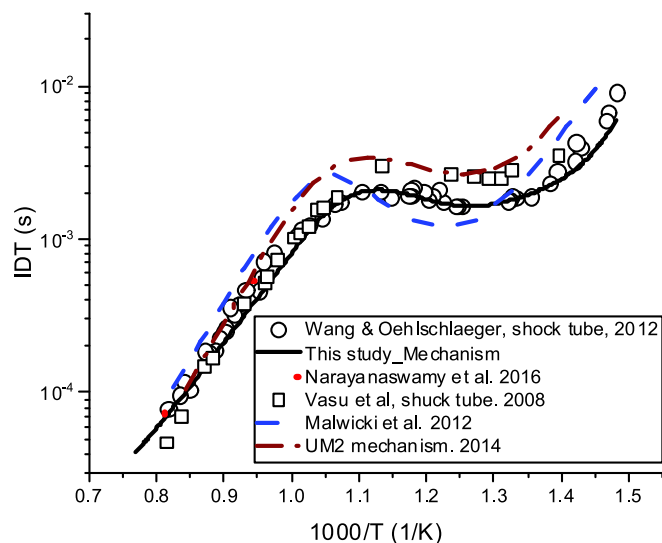


Fig. 2. IDT results of the developed mechanism of this study, against the mechanisms in the literature [18,26,37] and the experimental data at  $P = 20$  bar for stoichiometric condition [13,39].

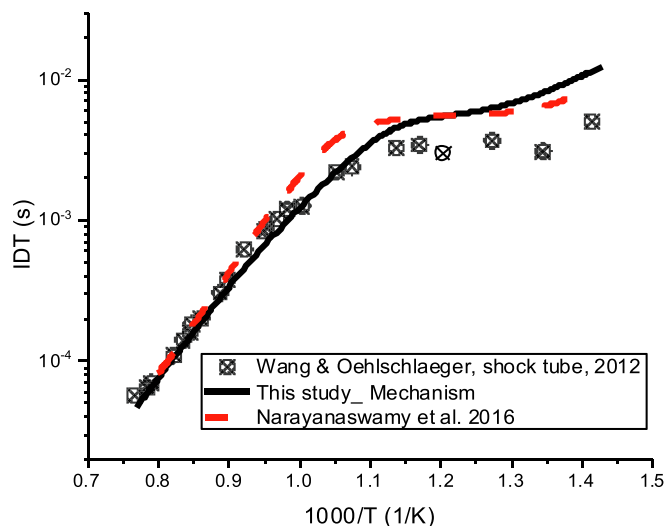


Fig. 3. IDT results of the developed mechanism of this study, against the mechanisms in the literature [37] and the experimental data at  $P = 20$  bar for lean condition ( $\Phi = 0.5$ ) [39].

$\text{CH}_2$ ,  $\text{CH}$ ,  $\text{C}$ ,  $\text{ACH}$  and  $\text{ACCH}_3$ ], that has been proven to help the surrogate closely emulates the combustion properties such as ignition delay time, laminar flame speed, oxidation product concentration [38].

The decoupling methodology which utilizes coupling a detailed  $\text{C}_0$ - $\text{C}_n$  mechanism as the core to simplified sub-mechanisms is applied to provide a compact mechanism for the proposed surrogate, as this methodology is an effective approach to build a compact mechanism for heavy hydrocarbons [34–36]. A well-developed simplified sub-mechanism of a heavy hydrocarbon considerably reduces the number of species and reactions in the final model by only considering the representative species required for the prediction of the intended combustion parameter of the heavy hydrocarbon. Because of the dominating role of small species in predicting the laminar flame speed of heavy hydrocarbons and the necessity of a detailed description of those species in emissions prediction, and the simplified nature of the core mechanism in comparison with other available detailed mechanisms, this core model has been applied in this investigation. While the prediction ability

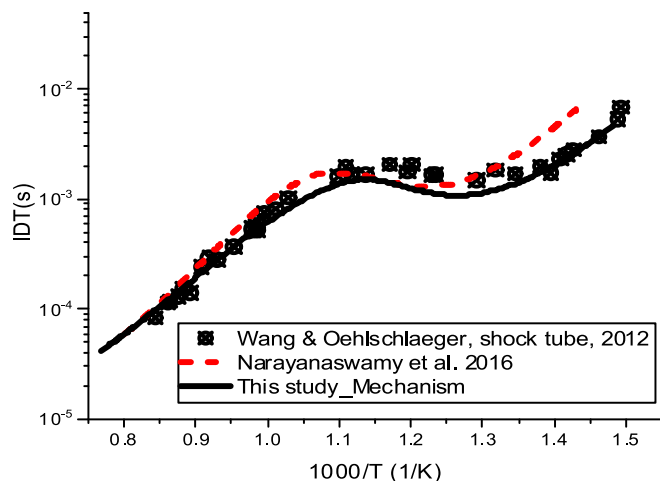


Fig. 4. IDT results of the developed mechanism of this study, against the mechanisms in the literature [37] and the experimental data at  $P = 20$  bar for rich condition ( $\Phi = 1.5$ ) [39].

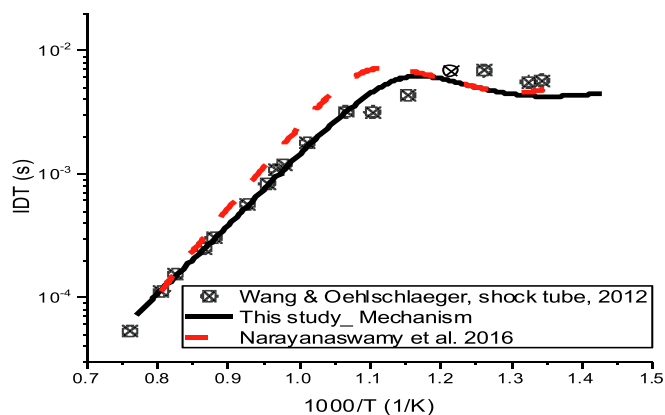


Fig. 5. IDT results of the developed mechanism of this study, against the mechanisms in the literature [37] and the experimental data at  $P = 12$  bar for stoichiometric condition [39].

of other detailed mechanisms is usually limited on one intended combustion parameter such as ignition delay, this core model could satisfactorily predict the important species mole fraction of heavy hydrocarbons, in addition to the ignition delay and the laminar flame speed.

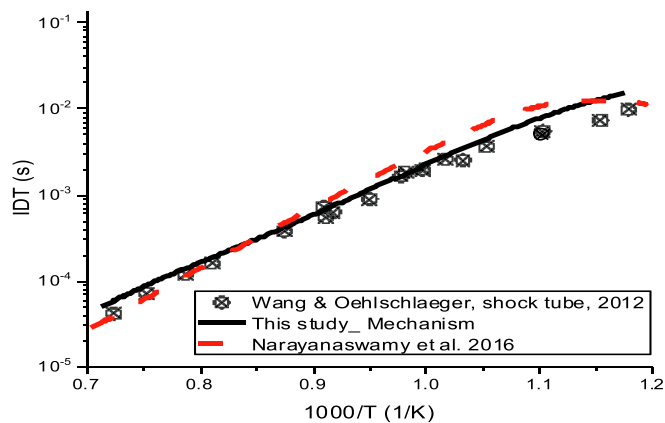


Fig. 6. IDT results of the developed mechanism of this study, against the mechanisms in the literature [37] and the experimental data at  $P = 8$  bar for stoichiometric condition [39].

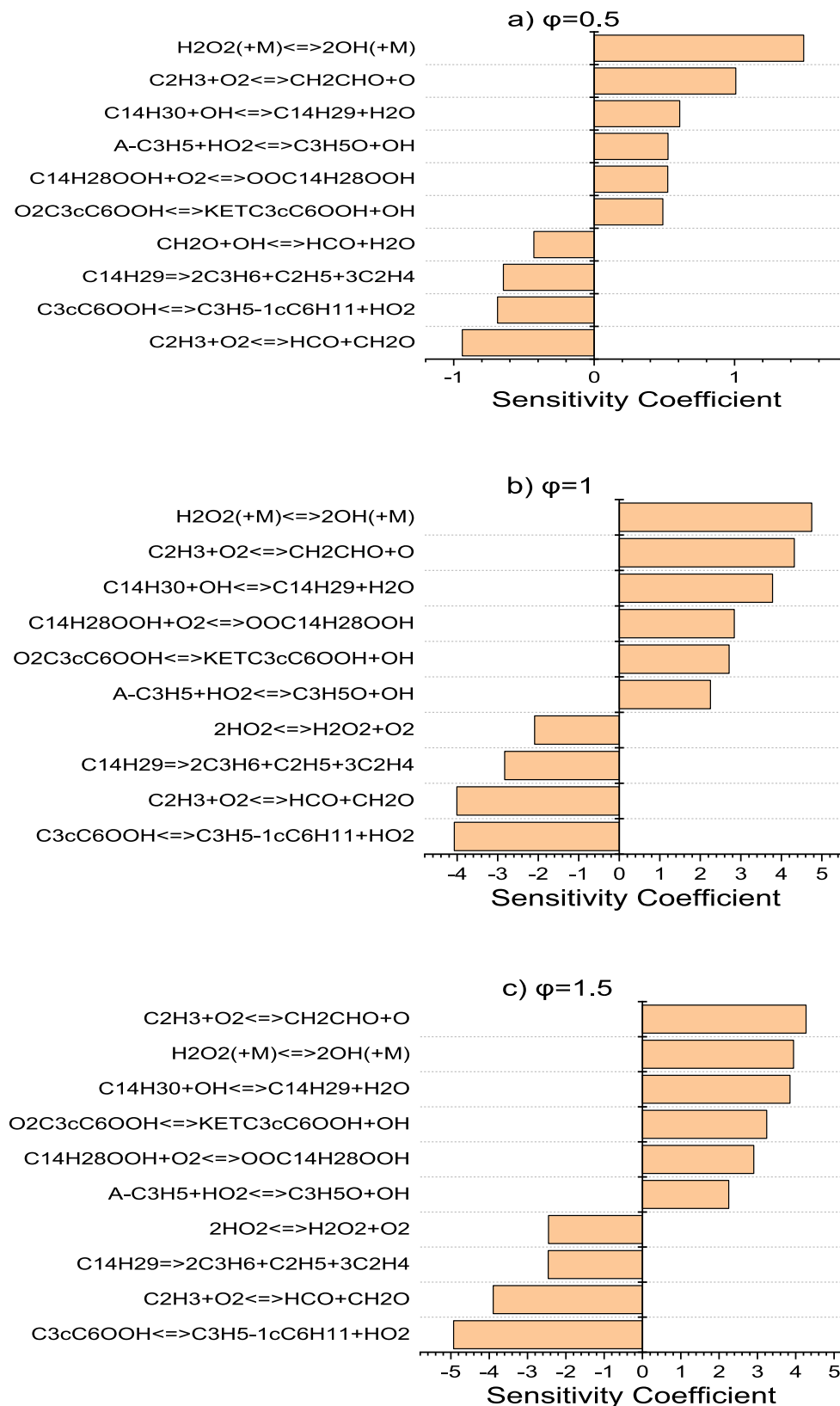


Fig. 7. Sensitivity analysis at 20 bar for lean (a), stoichiometric (b), and rich (c) conditions at low temperature (800 K).

### 3. Ignition delay time (IDT)

The simulations were conducted for a series of pressures and equivalence ratios where experimental data was available in the literature. Providing simulations for  $\phi = 1$  at 20 bar is the most important, as

most works from other researchers' mechanisms and surrogates (for jet A fuel) have been conducted under this condition, and thus, it can provide an opportunity for forming a comparison to other works.

As it can be observed in Fig. 2, the simulation in this study has the closest behaviour to the experiment data at all temperature zones (high

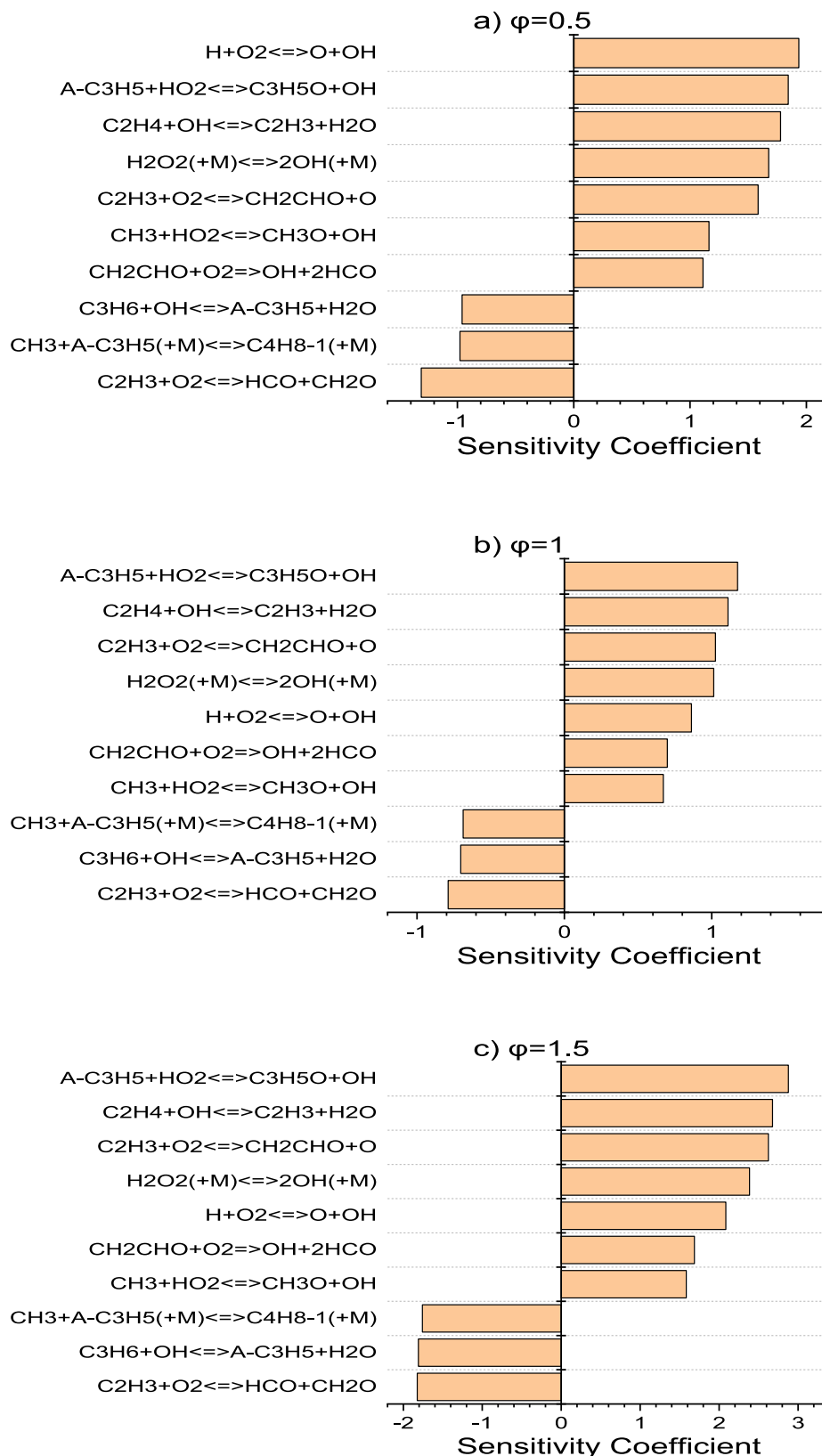


Fig. 8. Sensitivity analysis at 20 bar for lean (a), stoichiometric (b), and rich (c) conditions at high temperature (1200 K).

temperature, NTC, and cool flame) among other developed surrogates and mechanisms, and it has a very good agreement with experimental data. In addition to these conditions, simulations were performed for other equivalence ratios at 20 atm (Figs. 3 and 4) and also other

pressures (8 and 12 bar), see Figs. 5 and 6. Although the results are not as good as for  $\phi = 1$  (at pressure = 20 bar), these results are still produce the best agreement to the experiment data when compared to the published results [37] under these conditions. While Narayanaswamy et al.

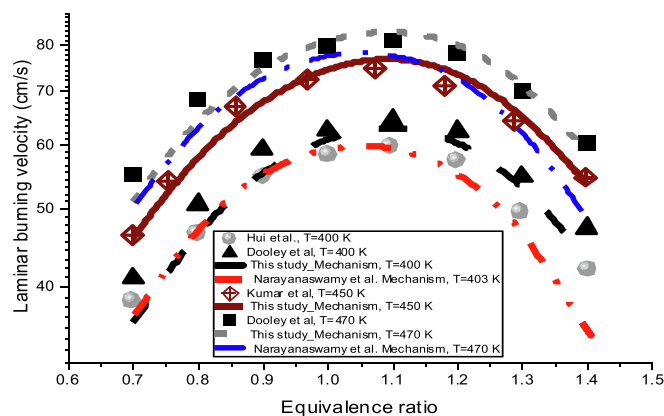


Fig. 9. Laminar flame speed simulation results of the developed mechanism of this study at the unburned temperatures of 400 K, 450 K, and 470 K, against the experimental data of jet A fuel at  $P = 1$  bar [17,40,41].

[37] considered 3 hydrocarbon classes and gave the composition (30.3 % n-alkane, 21.2 % aromatics, and 48.5 % *cyclo*-alkane) based on an optimization process that does not match to the real mass fractions of the target jet A fuel, this study simulated parameters by maintaining approximately the original mass fractions of the jet A fuel and considering all 4 major hydrocarbon classes.

To identify the key reactions in the ignition delay simulations and thus the candidate reactions to which modifications may help to improve the ignition delay at  $p = 20$  bar and  $\phi = 0.5$  where there is discrepancy between the simulations and the experiment at low temperature conditions, a series of sensitivity analyses at three equivalence ratios were performed for the ignition delay time of the developed model at 800 K and 1200 K, as the representatives of the low and high temperature regimes. The normalized sensitivity coefficients represent the fractional change in concentration  $c_i$  caused by a fractional change of parameter  $k_j$  in the normalized matrix of the local sensitivity coefficients:

$$S = \left( \frac{k_i}{c_i} \right) \times \left( \frac{\partial c_i}{\partial k_i} \right) = \left( \frac{\partial \ln c_i}{\partial \ln k_i} \right) \quad (3.1)$$

As can be seen in Fig. 7 for sensitivity at 800 K, a combination of some small species reactions from the core mechanism and the fuel related reactions of the surrogate components sub-mechanisms such as H abstraction reactions, the isomerization of OOQOOH to the ketohydroperoxides, the formation of OOQOOH by oxygen addition, fuel radical decomposition, and the concerted elimination reaction are among the top promoting and inhibiting sensitive reactions. The application of the sensitivity analysis for making improvement in a combustion parameter is a complicated process as there are interconnections between the conditions of a combustion parameter. In this study, the presence of common reactions at different conditions in the sensitivity analysis for the ignition delay is an obstacle to make modification in the reaction rates. For example, a change in the rate coefficients of a reaction affecting the ignition delay at a specified low temperature at  $p = 20$  bar and  $\phi = 0.5$  has a negative effect on the excellent simulation result for the ignition delay at  $\phi = 1$  ( $p = 20$  bar) at that temperature, because of the common reactions that exist in both of these conditions. Moreover, while we need to apply modifications in the common sensitive reactions in order to make the ignition delay longer at around 800 K for  $\phi = 1.5$ , we should make it shorter for  $\phi = 0.5$  at the temperature point.

For high temperature, Fig. 8 demonstrates that the reactions of small species are the key reactions showing strong promoting and inhibiting effects, dominating the reactivity of the system. The reactions of small species that only produce more active radicals are in the top list as the strongest promoter.

#### 4. Laminar flame velocity

The simulations for laminar flame speed were conducted at 1 atm for three unburned combustion temperatures (400, 450, 470 K) and a range of equivalence ratios (0.7 to 1.4). The results were compared to the results of the mechanisms in the literature and the available experimental data as illustrated in Fig. 9. In comparison with the mechanism in the literature developed for jet-A fuel, the simulated flame speed

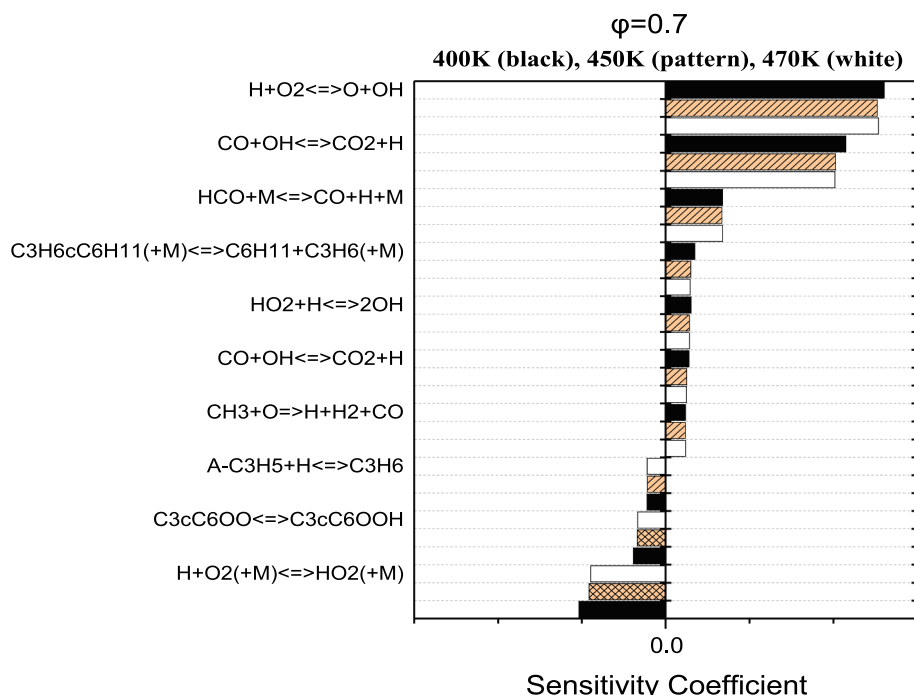
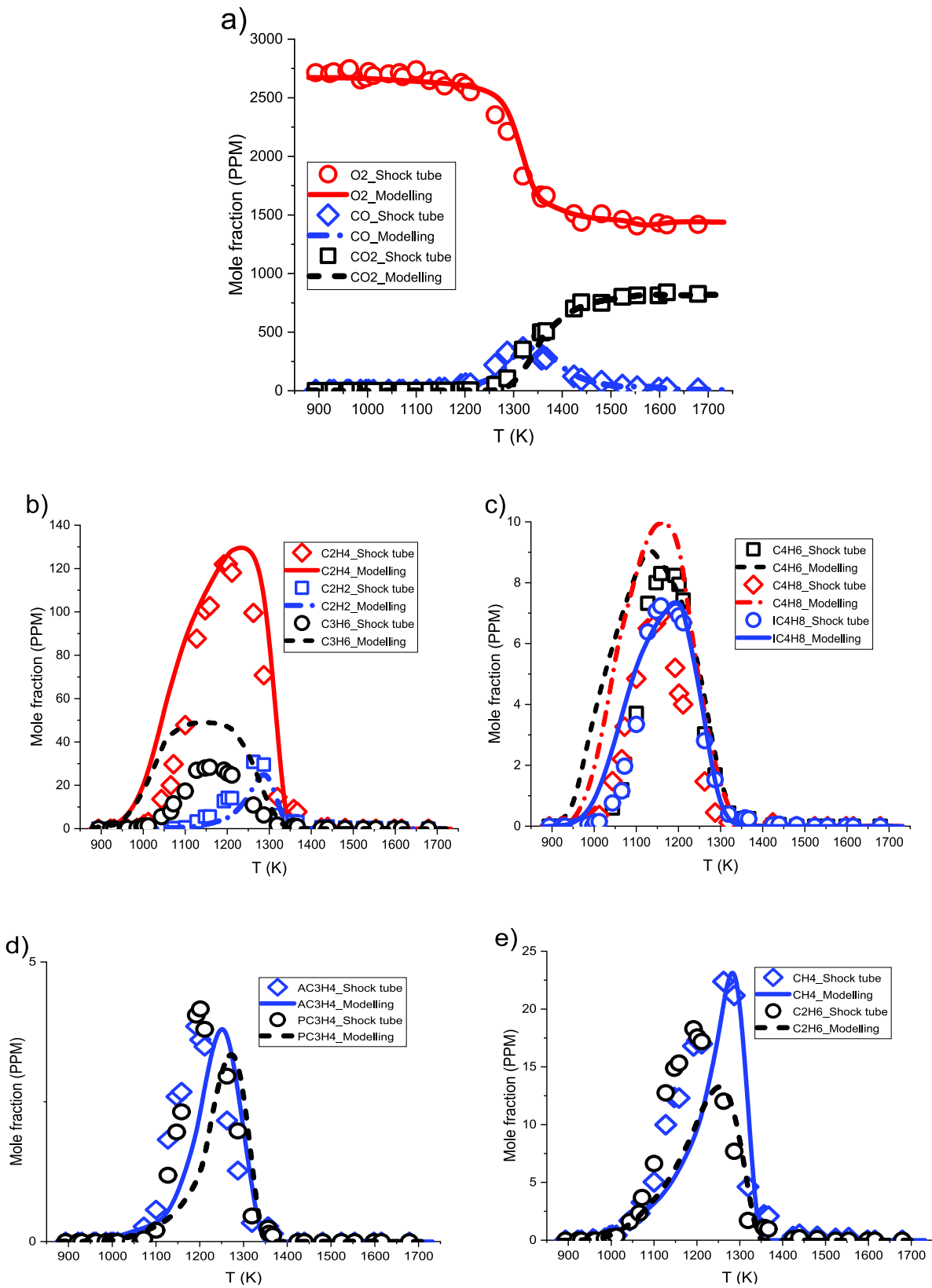
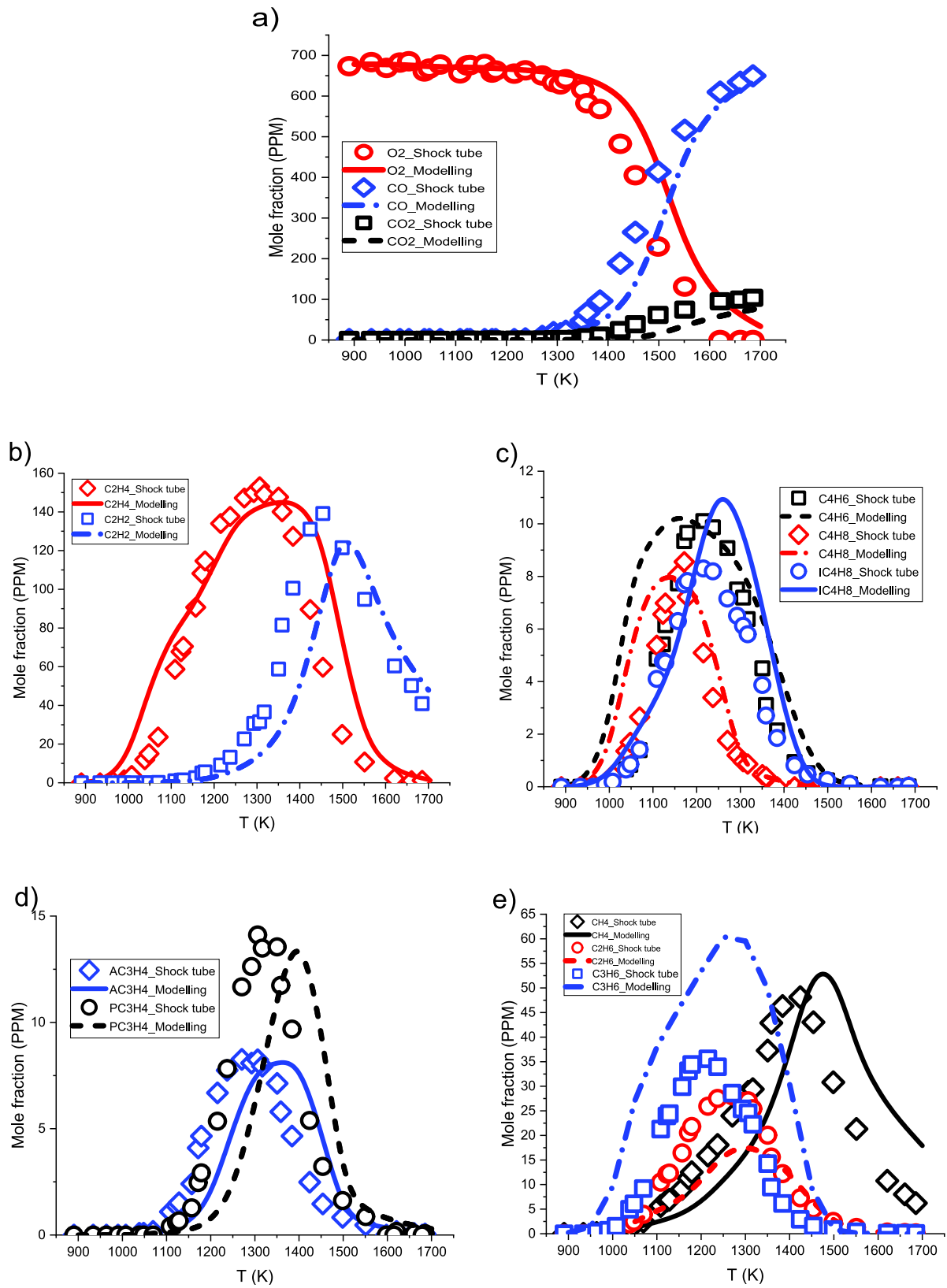


Fig. 10. Sensitivity analysis of laminar flame speed for equivalence ratio = 0.7, at 400 K, 450 K, and 470 K.



**Fig. 11.** Species concentration simulation results of the developed mechanism of this study at the equivalence ratio = 0.46, the resident time = 3 s, and  $p = 22.4$  bar, against the experimental data at the temperature range of 900 to 1700 K [17].



**Fig. 12.** Species concentration simulation results of the developed mechanism of this study at the equivalence ratio = 1.86, the resident time = 3 s, and  $p = 20.6$  bar, against the experimental data at the temperature range of 900 to 1700 K [17].

variations obtained in this study demonstrated a closer behavior to the experimental data. Discrepancy was observed in lean conditions for 400 and 470 K against the empirical results. Similar to the sensitivity analysis for ignition delay, there are common reactions in the sensitivity analysis for the flame speed presented in Fig. 10 at 400 and 470 K in comparison with 450 K that prevents further improvements in the lean conditions for 400 and 470 K. Another limitation is that the reactions have a key role in the ignition delay and they could not be selected for the modifications since they would negatively affect the results of ignition delay significantly. It can be seen from Fig. 10 that the dominant chain branching reaction of  $H + O_2 \rightleftharpoons O + OH$  and the main oxidation reaction of CO ( $CO + OH \rightleftharpoons CO_2 + H$ ) that generate more active radicals of H, O, and OH are the most important elementary reactions having the strongest promoting effects on the laminar flame velocity, respectively. On the other hand, the reaction of  $H + O_2 (+M) \rightleftharpoons HO_2 (+M)$  which leads to the termination of the radical chain process demonstrates the highest inhibiting effect and has a suppressing role on the flame speed.

## 5. Species mole fraction

Simulation of the species concentration for some important species at lean and rich conditions were extracted with the closed homogeneous batch reactor model in Chemkin-Pro based on the experimental conditions [17] that was conducted for a mixture of jet A and  $O_2$  diluted in argon, in a high pressure shock tube (HPST), over a temperature range of 900 to 1700 K, and the nominal pressures of 22.4 bar for lean conditions and 20.6 bar for rich conditions. As can be seen in Figs. 11 and 12, for most species, the modelling results show a close emulation compared to the experimental results. However for some intermediate species, there is a considerable overestimation on the results that have been reported by other researchers as well, where they used surrogates to model the species concentration of real jet fuels [17,18,42]. It is a common problem for species simulation of heavy hydrocarbons which have a complicated composition that includes hundreds of species from different hydrocarbon classes. In the oxidation process of the real fuel, specific hydrocarbons intermediates are not formed in significant amounts, as there are an extensive variety of hydrocarbons in the structure of the fuel. While, a surrogate fuel usually consists of only two to four components of the target fuel components, and therefore, the concentration of some intermediates generated by the specific surrogate components is unrealistically higher in the absence of the other components that exist in the real target fuel.

## 6. Conclusion

In this study, an investigation was conducted for the development of a well-validated surrogate for jet A, to address the requirement for a surrogate and its associated kinetics mechanism to have a small size and a good prediction ability for the all key combustion parameters in a wide range of temperatures, pressures and equivalence rates conditions. A surrogate consisting of 4 components was developed based on the major components of the real fuel and the similar property targets to the target fuel. Then, a reaction kinetic mechanism consisting of a core semi-detailed mechanism and 4 simplified sub-mechanisms including tetradecane, iso-dodecane, n-propylcyclohexane, and toluene was developed for the proposed surrogate with the aid of a decoupling methodology. Three parameters, including ignition delay time, laminar flame speed, and species concentration are simulated by use of ANSYS Chemkin-Pro under zero dimensional homogeneous closed reactors, one dimensional freely-propagating laminar flame speed calculations, and zero dimensional perfectly-stirred reactors, respectively. The simulation results for these parameters are validated against the available data in the literature. In general, the results showed a good agreement for ignition delay, laminar flame speed, and most species concentration profiles compared to the experimental data, though discrepancy was observed for a few conditions. The compact model of this study could provide a closer

emulation of the empirical data for ignition delay and laminar flame speed, in comparison to the previous developed models for jet A. A series of sensitivity analyses were provided to gain a deeper understanding of the developed mechanism. The compact size and the predictive ability of the developed simplified mechanism of the proposed surrogate make it a good candidate for researchers to use the model for functional kinetic investigations and the combustion investigation of aviation kerosene in some 3-D simulations such as Equivalent Reactor Network Analyses.

## CRedit authorship contribution statement

**Hossein S. Saraee:** Writing – original draft, Visualization, Validation, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Kevin J. Hughes:** Writing – review & editing, Supervision. **Mohamed Pourkashanian:** Supervision.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

**Supplementary material** including mechanism files is appended to this paper.

## Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.fuel.2024.131896>.

## References

- [1] Jenkins RW, Moore CM, Semelsberger TA, Chuck CJ, Gordon JC, Sutton AD. The effect of functional groups in bio-derived fuel candidates. *ChemSusChem* 2016;9(9):922–31.
- [2] Owoyele O, Pal P. ChemNODE: a neural ordinary differential equations framework for efficient chemical kinetic solvers. *Energy and AI* 2022;7:100118.
- [3] Reuter, C. B., Farouk, T. I., Tuttle, S. G. (2022). Preferential Vaporization Effects on the Droplet Burning and Lift-off Behaviors of Jet Fuel Surrogates. In *AIAA SCITECH 2022 Forum* (p. 1258).
- [4] Edwards T, Maurice LQ. Surrogate mixtures to represent complex aviation and rocket fuels. *J Propul Power* 2001;17:461–6.
- [5] Dagaut P, Cathonnet M. The ignition, oxidation, and combustion of kerosene: A review of experimental and kinetic modeling. *Prog Energy Combust Sci* 2006;32(1):48–92.
- [6] Luche J, Reuillon M, Boettner JC, Cathonnet M. Reduction of large detailed kinetic mechanisms: Application to kerosene/air combustion. *Combust Sci Technol* 2004;176:1935–63.
- [7] Patterson PM, Kyne AG, Pourkashanian M, Williams A. Combustion of kerosene in counterflow diffusion flames. *J Propul Power* 2001;17:453–60.
- [8] Dagaut P, Reuillon M, Boettner JC, Cathonnet M. Kerosene combustion at pressures up to 40 atm: Experimental study and detailed chemical kinetic modeling. *Symp (Int) Combust* 1994;25(1):919–26.
- [9] Cathonnet, M., Voisin, D., Etsouli, A., Sferdean, C., Reuillon, M., Boettner, J.C., Dagaut, P., (1999). Kerosene combustion modelling using detailed and reduced chemical kinetic mechanisms. RTO Meeting proceedings 16, *Aircraft Weapon System Compatibility and Integration, September 1998*, Chester, UK. France: Nato research.
- [10] Dagaut P. On the kinetics of hydrocarbons oxidation from natural gas to kerosene and diesel fuel. *PCCP* 2002;4(11):2079–94.
- [11] Doute C, Delfau J-L, Akkrich R, Vovelle C. Chemical structure of atmospheric pressure premixed n-decane and kerosene flames. *Combust Sci Technol* 1995;106(4–6):327–44.
- [12] Violi A, Yan S, Eddings EG, Sarofim AF, Granata S, Faravelli T, et al. Experimental formulation and kinetic model for JP-8 surrogate mixtures. *Combust Sci Technol* 2002;174(11–12):399–417.
- [13] Vasu SS, Davidson DF, Hanson RK. Jet fuel ignition delay times: shock tube experiments over wide conditions and surrogate model predictions. *Combust Flame* 2008;152(1–2):125–43.
- [14] Dagaut P, El Bakali A, Ristori A. The combustion of kerosene: Experimental results and kinetic modelling using 1-to 3-component surrogate model fuels. *Fuel* 2006;85(7–8):944–56.

- [15] Gokulakrishnan P, Gaines G, Currano J, Klassen MS, Roby RJ. Experimental and kinetic modeling of kerosene-type fuels at gas turbine operating conditions. *J Eng Gas Turb Power* 2007;129:655–63.
- [16] Dooley S, Won SH, Chaos M, Heyne J, Ju Y, Dryer FL, et al. A jet fuel surrogate formulated by real fuel properties. *Combust Flame* 2010;157(12):2333–9.
- [17] Dooley S, Won SH, Heyne J, Farouk TI, Ju Y, Dryer FL, et al. The experimental evaluation of a methodology for surrogate fuel formulation to emulate gas phase combustion kinetic phenomena. *Combust Flame* 2012;159(4):1444–66.
- [18] Malewicki T, Gudiya S, Brezinsky K. Experimental and modeling study on the oxidation of Jet A and the n-dodecane/iso-octane/n-propylbenzene/1, 3, 5-trimethylbenzene surrogate fuel. *Combust Flame* 2013;160(1):17–30.
- [19] Kim D, Violi A. Hydrocarbons for the next generation of jet fuel surrogates. *Fuel* 2018;228:438–44.
- [20] Yu Z, Wei S, Wu C, Wu L, Sun L, Zhang Z. Development and verification of RP-3 aviation kerosene surrogate fuel models using a genetic algorithm. *Fuel* 2022;312:122853.
- [21] Liu YX, Richter S, Naumann C, Braun-Unkhoff M, Tian ZY. Combustion study of a surrogate jet fuel. *Combust Flame* 2019;202:252–61.
- [22] Zhong BJ, Peng HS. Development of a skeletal mechanism for aviation kerosene surrogate fuel. *J Propul Power* 2019;35(3):645–51.
- [23] Ranzi E, Frassoldati A, Stagni A, Pelucchi M, Cuoci A, Faravelli T. Reduced kinetic schemes of complex reaction systems: fossil and biomass-derived transportation fuels. *Int J Chem Kinet* 2014;46(9):512–42.
- [24] Xu R, Wang K, Banerjee S, Shao J, Parise T, Wang S, et al. A physics-based approach to modeling real-fuel combustion chemistry—II. Reaction kinetic models of jet and rocket fuels. *Combust Flame* 2018;193:520–37.
- [25] Kim D, Martz J, Violi A. Effects of fuel physical properties on direct injection spray and ignition behavior. *Fuel* 2016;180:481–96.
- [26] Kim D, Martz J, Violi A. A surrogate for emulating the physical and chemical properties of conventional jet fuel. *Combust Flame* 2014;161(6):1489–98.
- [27] Yu W, Tay K, Zhao F, Yang W, Li H, Xu H. Development of a new jet fuel surrogate and its associated reaction mechanism coupled with a multistep soot model for diesel engine combustion. *Appl Energy* 2018;228:42–56.
- [28] Li Y, Zhou CW, Somers KP, Zhang K, Curran HJ. The oxidation of 2-butene: A high pressure ignition delay, kinetic modeling study and reactivity comparison with isobutene and 1-butene. *Proc Combust Inst* 2017;36(1):403–11.
- [29] Canneaux S, Bohr F, Henon E. KiSThelP: a program to predict thermodynamic properties and rate constants from quantum chemistry results. *J Comput Chem* 2014;35(1):82–93.
- [30] Pires AP, Han Y, Kramlich J, Garcia-Perez M. Chemical composition and fuel properties of alternative jet fuels. *BioResources* 2018;13(2):2632–57.
- [31] Edwards JT. Reference jet fuels for combustion testing. In: In 55th AIAA aerospace sciences meeting; 2017. p. 0146.
- [32] Luning Prak DJ, Simms GR, Dickerson T, McDaniel A, Cowart JS. Formulation of 7-component surrogate mixtures for military jet fuel and testing in diesel engine. *ACS Omega* 2022;7(2):2275–85.
- [33] Kim D, Violi A. Uncertainty-based weight determination for surrogate optimization. *Combust Flame* 2022;237:111850.
- [34] Saraee HS, Hughes KJ, Shi S, Ingham DB, Pourkashanian M. Skeletal and compact validated mechanisms for iso-dodecane using a decoupling methodology. *Energy Fuel* 2023. <https://doi.org/10.1021/acs.energyfuels.2c03539>.
- [35] Saraee HS, Hughes KJ, Pourkashanian M. Construction of a small-sized simplified chemical kinetics model for the simulation of n-propylcyclohexane combustion properties. *Energies* 2024;17(5):1103. <https://doi.org/10.3390/en17051103>.
- [36] Chang Y, Jia M, Li Y, Liu Y, Xie M, Wang H, et al. Development of a skeletal mechanism for diesel surrogate fuel by using a decoupling methodology. *Combust Flame* 2015;162(10):3785–802.
- [37] Narayanaswamy K, Pitsch H, Pepiot P. A component library framework for deriving kinetic mechanisms for multi-component fuel surrogates: Application for jet fuel surrogates. *Combust Flame* 2016;165:288–309.
- [38] Sheyyab M, Abdulrahman M, Hossain S, Lynch PT, Mayhew EK, Brezinsky K. Method for generating kinetically relevant fuel surrogates based on chemical functional group compositions. *Combust Flame* 2024;259:113185.
- [39] Wang H, Oehlschlaeger MA. Autoignition studies of conventional and Fischer-Tropsch jet fuels. *Fuel* 2012;98:249–58.
- [40] Hui X, Kumar K, Sung CJ, Edwards T, Gardner D. Experimental studies on the combustion characteristics of alternative jet fuels. *Fuel* 2012;98:176–82.
- [41] Kumar K, Sung CJ, Hui X. Laminar flame speeds and extinction limits of conventional and alternative jet fuels. *Fuel* 2011;90(3):1004–11.
- [42] Dagaut P, Karsenty F, Dayma G, Dievart P, Hadj-Ali K, Mze-Ahmed A, et al. Experimental and detailed kinetic model for the oxidation of a Gas to Liquid (GtL) jet fuel. *Combust Flame* 2014;161(3):835–47.