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A compact chemical kinetic mechanism for modelling isocetane

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ABSTRACT

Developing a compact chemical kinetic mechanism for heavy hydrocarbons to facilitate their use within combustion simulation tools is an important contribution to the practical investigation of the fuels. Regarding the importance of isocetane for cetane number rating and as a candidate component of jet and diesel surrogates, the present work proposes a single simplified kinetic mechanism that can mimic the ignition behaviour, laminar burning velocity, and the concentration of the main oxidation products of this reference fuel with a good agreement compared to the empirical data. An initial lumped sub-mechanism of isocetane available from the literature was coupled to an available core mechanism. The performance of the mechanism in predicting the key combustion parameters was investigated with the aid of the Chemkin-Pro software package and the available empirical data in the literature. Since the initial raw mechanism need to be optimized, modifications including adding missing reactions were applied to improve the developed model performance. The final compact mechanism includes 179 species and 1325 reactions and demonstrates an improved performance over existing larger mechanisms in terms of predicting the ignition delay data for a wide range of temperatures covering low and high limits. Laminar burning velocity simulation at 443 K was conducted for isocetane and the result was compared with the available experiment data. It was found that there was good agreement between the modelling results and the experimental data. It was also found that the developed model can predict the main oxidation products of isocetane at lean and stoichiometric conditions with a close agreement, compared to the available experimental data.

1. Introduction

Developing chemical kinetic reaction mechanisms of fuels is of great importance, since it is a useful tool to understand the combustion characteristics of practical fuels that can lead to the development of cleaner and more efficient combustors. However, considering the current computational resources and the multicomponent nature of practical hydrocarbon fuels having complex molecular structures, it is difficult to model the combustion of such fuels in the combustion engine simulators. Thus, we need to apply simplifications such as surrogate development with a limited number of components, in order to produce a chemical kinetic mechanism computationally reasonable and viable to run.

Practical kinetic investigations such as multicomponent surrogate development and representation of complex geometries of combustion system via Equivalent Reactor Networks or computational fluid dynamic models require a compact chemical model to run smoothly and minimise the computational expense. One of the approaches which can fulfil this requirement is using a lumped version of chemical kinetics mechanisms. Instead of using a detailed kinetics mechanism that creates chemical complexities and a large-sized model infeasible or expensive to run, a reduced model including a limited number of species and reactions with a good predictive ability can be used.

One of the important hydrocarbon fuels is isocetane since it is used for cetane number rating and as a candidate component of jet and diesel surrogates [1–4]. Despites its importance, it is not a well-understood species and kinetic modelling of this important fuel is rare since its modelling is very difficult. This highly branched iso-alkane has a complex molecular structure with five different carbon sites hosting seven methyl groups that leads to a complicated chemical kinetic analysis on a large number of reactions. Based on the authors best knowledge, just one work has been conducted experimentally and numerically in recent years to develop a detailed mechanism for isocetane over low to high temperatures, in order to predict autoignition behaviour of this fuel for a wide range of conditions [5]. It is also noteworthy that the low vapor pressure of this high molecular weight species makes a gas phase empirical investigation on it very hard, due to the difficulty of keeping a

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Nomenclature

Atm	Atmospher
ATJ	Alcohol to jet
IC16	Iso-cetane
IDT	Ignition delay time
JSR	Jet-stirred reactor
NTC	Negative temperature coefficient
PSR	Perfectly stirred reactor
OOQOOH	Peroxy alkylhydroperoxides
QOOH	Hydroperoxy-alkyl radicals
R	Fuel radical
R’& R˝	Products of the unimolecular decomposition
RCM	Rapid compression machine
RO_2	Alkylperoxy radicals
ST	Shock tube
T	Temperature

sufficient fuel concentration in the reactant mixture.

Isocetane was firstly modelled by Agosta et al. [2] who developed a lumped kinetic mechanism and challenged the simulation ability of the mechanism compared to their experiment, on the low-temperature (600–800 K) reactivity and product speciation of this fuel in a flow reactor. Dagaut and Hadj-Ali [6] measured species concentrations of isocetane in a jet-stirred reactor (JSR) and developed a kinetic mechanism to model the oxidation of isocetane in the JSR. Guzman et al. [7] recently proposed a high-temperature oxidation mechanism for isocetane as a minor component of an alcohol-to-jet (ATJ) fuel, during their investigation on the pyrolytic and oxidative decomposition products of ATJ fuel in a single pulse shock tube.

The ignition chemistry of heavy hydrocarbons can be divided into two distinct temperature ranges of reactivity at low and high temperatures. There is also a regime of so-called negative temperate coefficient (NTC), for which the overall rate of reaction decreases with the increase of temperature, and the temperature up to the end of the NTC regime where the ignition delay starts to reduce again is usually considered the low temperature region. Although it is not the same for all hydrocarbon species, the range for the low-temperature regime is 600–1000 K, and for the high-temperature regime is > 1000 K. In terms of autoignition, there a few works dedicated to investigate this aspect of isocetane. The first kinetic mechanism for the autoignition of isocetane was developed by Oehlschlaeger et al., in 2009 [8], who conducted experiments on isocetane/air mixtures in a heated shock tube. The simulation results showed a good agreement against the experimental data at just moderate to high temperatures in different conditions. This mechanism was later updated by Yu et al., in 2019 [9], when they conducted experiments on the autoignition of isocetane at the temperature range of 620–880 K and for a wide range of equivalence ratios. In an investigation on the autoignition of isocetane/1-methylnaphthalene binary blends, Kukkadapu and Sung [10] experimentally investigated ignition delays of isocetane between 729 and 856 K at stoichiometric condition and 15 bar in a rapid compression machine (RCM).

Later in 2020, Raza et al. improved the performance of the detailed mechanism developed by Yu et al. by updating various reactions and rate constants [5]. The simulation results could emulate the ignition behaviour of isocetane compare to the empirical data, at equivalence ratios of $\Phi = 0.5$–2.0, pressures of 10–20 bar and temperature range of 838–1617 K.

The recent works mentioned above and the detailed mechanism recently developed for isocetane, made an important contribution to elucidate the chemical kinetics of this important fuel and to get a good understanding of its combustion parameters. Despite these developments, there is still the lack of a compact mechanism that is experimentally well-validated and could provide a close emulation for the autoignition behaviour of IC16 (isocetane) over a wide range of conditions, while delivering a good prediction for the laminar flame velocity and the concentration of the important species such as the main oxidation products. In this regard, this study was conducted to provide a small sized mechanism through coupling a lumped sub-mechanism to a core detailed mechanism, imitating the autoignition behaviour of IC16 with a good agreement against the available experimental data. In addition to ignition delay, the predictive ability of the proposed mechanism for simulating laminar flame speed and the mole fraction of the fuel and the main oxidation products including CO, CO_2, and H_2O was investigated with the aid of Ansys Chemkin-Pro and compared to available experimental data.

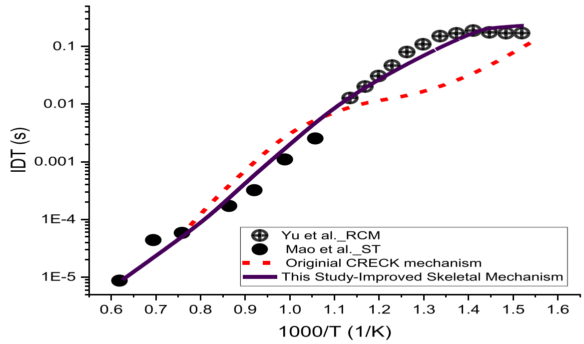
2. Theoretical framework

The criteria for the development of a model for this study is satisfying the goal of developing a simplified mechanism to target one intended combustion parameter, such as ignition delay, or even more, with a good prediction compared to experimental data. Since the construction of a compact mechanism for heavy fuels through the decoupling methodology [11] has been proven to be a successful method in developing a relatively simple chemical kinetics model, it is implicated in this study to provide a well-validated small size mechanism for IC16. The methodology procedure includes the incorporation of a detail/semi-detail core mechanism to a simplified sub-mechanism with a reduced number of species and reactions for the intended heavy fuel species, so that, one representative species of the hydrocarbon classes which are required for the prediction of a target combustion parameter has been just considered for inclusion in the sub-mechanism. In a comparison of the decoupling methodology with that of reduced methodologies [11], it was demonstrated that a small-sized mechanism constructed via the decoupling methodology can satisfactory simulate all the combustion properties (ignition delay, laminar flame speed, species concentration) of heavy hydrocarbons. While the reduced mechanisms using the global reduction methods usually cannot provide a good prediction for more than one combustion property, and are still relatively large for use in practical applications. Researchers also compared the reduction power of a decoupling methodology to DRGEP method [12] and reported that a detailed mechanism for butanol isomers including more than 300 species and thousands of reactions could be reduced to 66 species and 196 reactions with the aid of a decoupling methodology, while the DRGEP method reduced the detailed mechanism to more than 100 species and 800 reactions. An analysis on three developed skeletal mechanisms for iso-octane that couldn’t provide a good prediction for laminar flame speed in all the temperature and pressure conditions showed that [13] a global reduction process from small to large molecules and low to high temperature reactions does not necessarily retain those characteristics that coupled in these reactions. It was noted that the small radical and molecule reactions are those that play the dominating role on the key characteristics of laminar flame speed, and not those in the low temperature oxidation and large molecule decomposition. On the other hand, a mechanism with a more substantial small size developed by a decoupling methodology showed a good prediction ability through just reducing the large molecule mechanism component and holding the small radicals and molecules with the original form in order to keep most essential information of the combustion process. It is reported that [14] the global reduction methods like direct relation graph suffers from the limitation to considerably decrease the size of a detailed mechanism and negatively affect the accuracy of the detailed mechanism. Moreover, reduced mechanisms have a restricted usage since they are reduced based on specific conditions and are inherently system dependent. But, in a decoupling methodology, the core mechanism selected for the mechanism construction is a detailed/semi-detailed model which includes the small species and the reactions required for the good prediction of laminar flame speed, extinction strain rate, heat release rate, and the important species concentrations under a wide range of conditions. Application of such a mature core model that didn't go through a global reduction process avoids the final developed mechanism from additional optimization of the reaction rate or mitigates it. On the other hand, developing a sub-mechanism by just a focus on the prediction of the auto-ignition characteristics of the target fuel makes the size of a model as small as possible, since only a limited number of the required species and reactions in the sub-mechanism are included for the simulation of ignition delay.

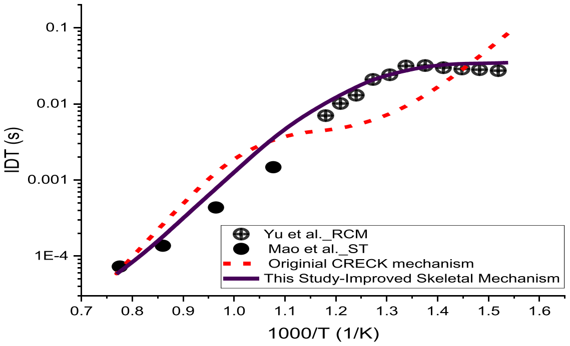
With the aid of the decoupling methodology, a skeletal mechanism was generated through coupling an extracted small size lumped sub-mechanism of IC16 as the target fuel species from a comprehensive detailed mechanism [15] to a well-validated core detailed mechanism of C0–C5 chemistry [16,17]. A schematic of the initial raw lumped sub-mechanism can be observed in Fig. 1. The C0–C5 core mechanism used in this study is a semi-detailed model which is simple in comparison with many other available detailed mechanisms, while it includes the important small species and reactions that have a dominating role for the prediction of the laminar flame speed of jet fuels and the detail description of the fuel emissions.

As it was expected, the initial raw developed model predicted simulation results similar to the IC16 original model in the main detailed mechanism (the red dashed/dotted line results in Figs. 2–5), and exhibited a significant discrepancy over the low to high temperature regions compared to the experimental data. It implies that the sub-mechanism suffers from some missing reaction classes and untuned reaction rates, as the isocetane reaction kinetics in the detailed mechanism is based on an old lumped version model with a limited number of species and reactions.

a) Lean



b) Stoichiometric



c) Rich

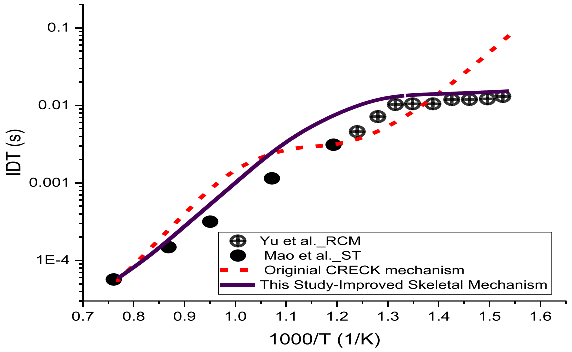


Fig. 2. IDT modelling results against the experimental data at P = 20 bar for (a) lean (φ = 0.5), (b) stoichiometric (φ = 1), and (c) rich (φ = 1.5) conditions [5].

The recent developed mechanisms [5,7,9] that include the missing reaction classes and also a combination of experimental and theoretical rate parameters, were utilized to improve the agreement and provide a close emulation for IDT based on the empirical data. A comparison was made between the sensitivity analyses of the initial developed model in this study and the abovementioned mechanisms in the literature. The structure of the utilized mechanisms [5,7,9] were also followed. These

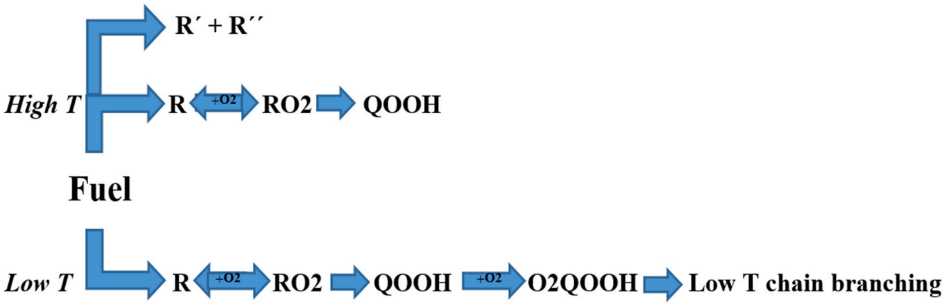


Fig. 1. Schematic diagram of the original lumped IC16 sub-mechanism.
T = Temperature, R = Fuel radical, R'& R'' = products of the unimolecular decomposition.

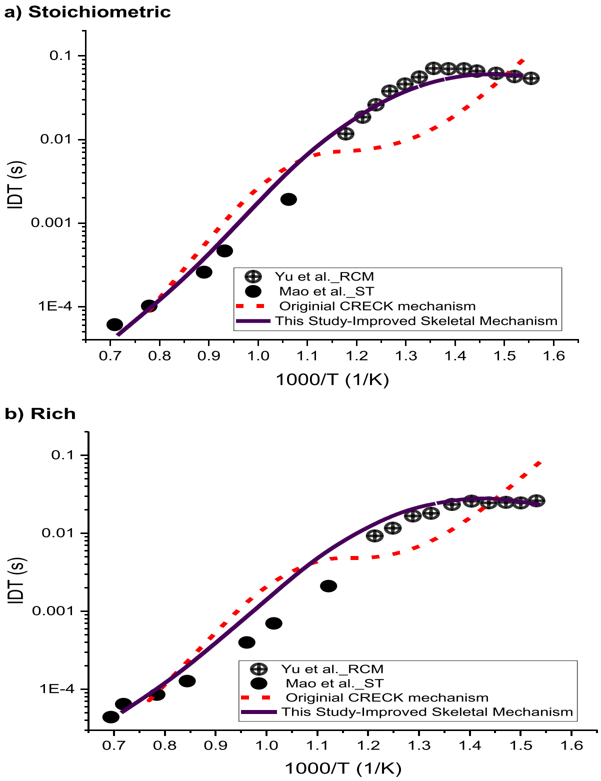


Fig. 3. IDT modelling results against the experimental data at P = 15 bar for (a) stoichiometric (φ = 1), and (b) rich (φ = 1.5) conditions [5].

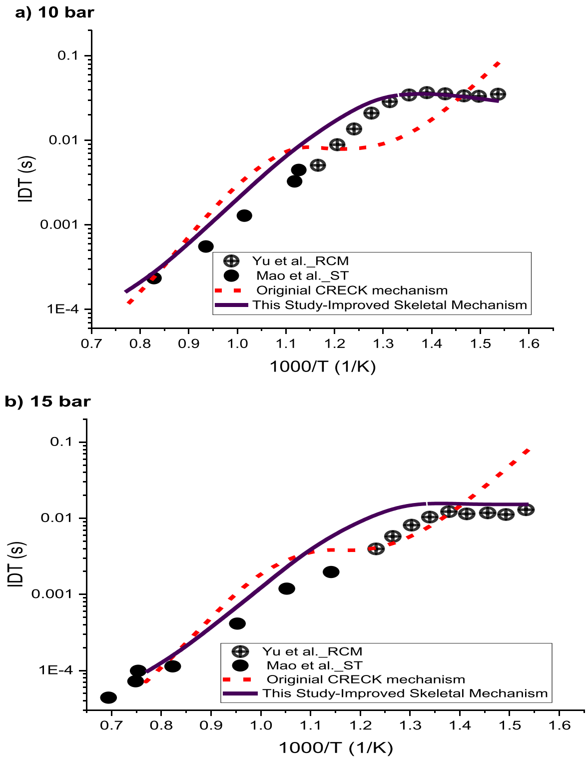


Fig. 4. IDT modelling results against the experimental data at φ = 2 for (a) 10 bar and (b) 15 bar [5].

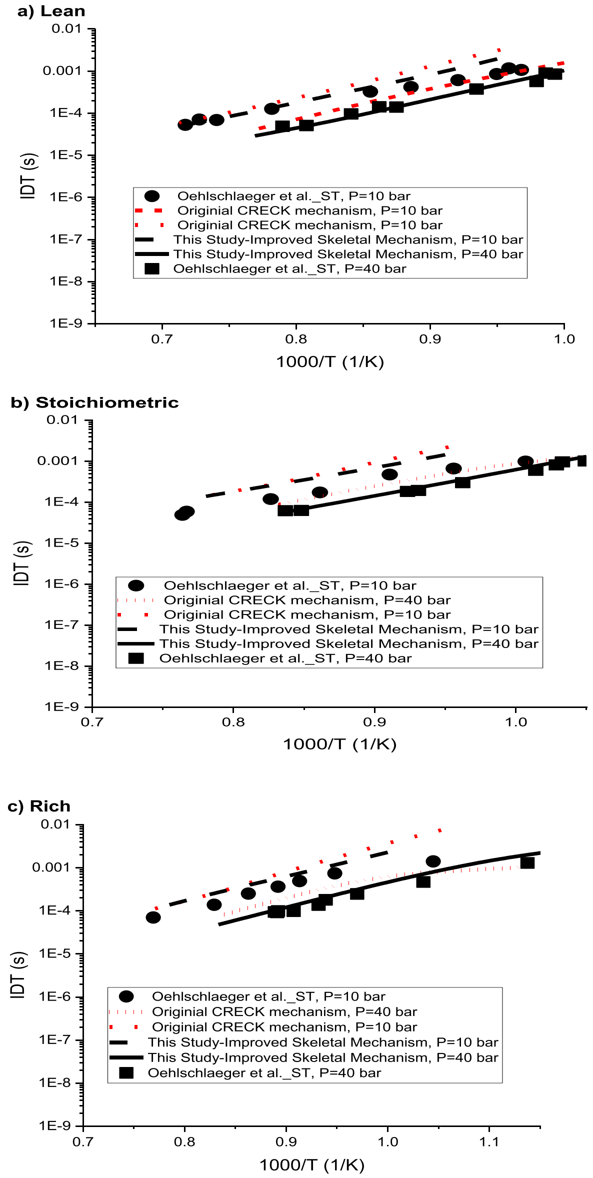


Fig. 5. IDT modelling results against experimental data at P = 10 and 40 bar, for (a) lean (φ = 0.5), (b) stoichiometric (φ = 1), and (c) rich (φ = 1.5) conditions [5].

two steps were conducted in order to identify the important missing reactions to be added and the most important reaction rates to be modified. Then, the required modifications were then applied for the initial model developed in this research.

The added important reactions in the sub-mechanism that had a great contribution to optimize the mechanism performance and match the experimental data in a wide range of conditions can be seen in Table 1.

The optimized kinetic model is able to predict oxidation at low through high temperatures for a wide range of conditions in a more compact size and a closer agreement against the experimental data, compared to the available IC16 mechanisms [5,8,9].

The ignition behaviour of the improved IC16 mechanism was investigated at varying conditions using the closed homogeneous batch reactor model in the Chemkin-Pro software. Then, the simulation results were compared to the available experimental data at three regimes of low, intermediate and the high temperature. Reduction in IDTs for higher pressures and typical NTC behaviour was observed for all the

Table 1

The list of the added important reactions missing in the original sub-mechanism (cm^3, mole, s, cal/mol units).

Reaction class	reaction	Arrhenius equation parameters		
ROOH = RO + OH	HMN-R2OOH = HMN-R2O + OH	1.5E16	0.0	4.25E4
	C8H17+N–C7H15CHO = HMN-R2O	1.0E11	0.0	1.29E4
	TC4H9CHO + X4C11H23 = HMN-R2O	1.0E+011	0.0	1.29E4
RO2 + H2O2 = ROOH + HO2	IC16H33-OO + H2O2 = HMN-R2OOH + HO2	2.4E12	0.0	1.0E4
		REV/2.4E12	0.0	1.0E4/
R + HO2 = RO + OH	IC16H33+HO2=HMN-R2O + OH	7.0E12	0.0	−1.0E3
	IC16H33-OO=IC16H32+HO2	REV/1.967E18	−1.37	2.889E4/
		1.26E8	1.32	2.79E4
RO2 + HO2 = ROOH + O2	IC16H33-OO + HO2=HMN-R2OOH + O2	1.75E10	0.0	−3.275E3
		REV/5.974E13	−8.5E-1	3.49E4/
H atom abstraction from olefins	IC16H32+OH=IC16H31+H2O	7.49E8	1.61	−3.5E1
	IC16H32+O2=>IC16H31+HO2	1.0E12	0.0	3.72E4
	IC16H32+HO2=IC16H31+H2O2	2.0E4	3.37	1.372E4
	IC16H32+H=>IC16H31+H2	3.7E13	0.0	3.9E3
	IC16H32+CH3=IC16H31+CH4 IC16H32+O=IC16H31+OH	1.0E12	0.0	7.3E3
		1.0E12	0.0	4.0E3
Alkenyl radical decomposition	IC16H31=>C8H15+2I–C4H8	1.254E13	0.3	2.832E4
	IC16H31=>C8H15+C8H16-1	1.254E13	0.3	2.832E4
	IC16H31 = C5H11+I–C4H7+C7H13 IC16H31+HO2=>TC4H9CHO + P–C3H4 + C8H17+OH	1.254E13	0.3	2.832E4
		1.0E43	−8.7	2.1071E4
QOOH = Q + HO2	IC16-QOOH = IC16H32+HO2	1.22E11	0.57	1.51E4
		REV/1.0E11	0.0	1.153E4/
	IC16H32=>C8H17+C8H15	1.0E16	0.0	7.1E4
Retro-one decomposition	IC16H32 = IC12H24+I–C4H8	3.98E12	0.0	5.7629E4
Unimolecular decomposition	IC12H25+T-C4H9 = IC16H34	3.6E13	0.0	0.0E0
	2C8H17 = IC16H34	3.6E13	0.0	0.0E0

conditions in accordance with the experimental data. The optimized developed model showed a good agreement against the empirical data for most temperatures, and at different pressures and the equivalence ratios. However, some discrepancies at certain temperatures were observed. The discrepancy can be related to the experimental uncertainty of the measurements and the considerable heat loss effect that can occur in RCM tests (due to the production of the active radicals [18]) and the structure of the lumped mechanism that is expected, since the lumped reactions and their associated rate restrict the performance of the mechanism at some temperature points, an equivalence ratio, or a pressure condition. Considering the discrepancies, the kinetic model showed a very close emulation for the autoignition behaviour of IC16. Thus, this small size mechanism with a good predictive capability can be a suitable candidate for application as a surrogate for fuels and practical simulations.

3. Kinetic analysis

An investigation on the contribution of each reaction to the production and consumption of the major species with the aid of reaction

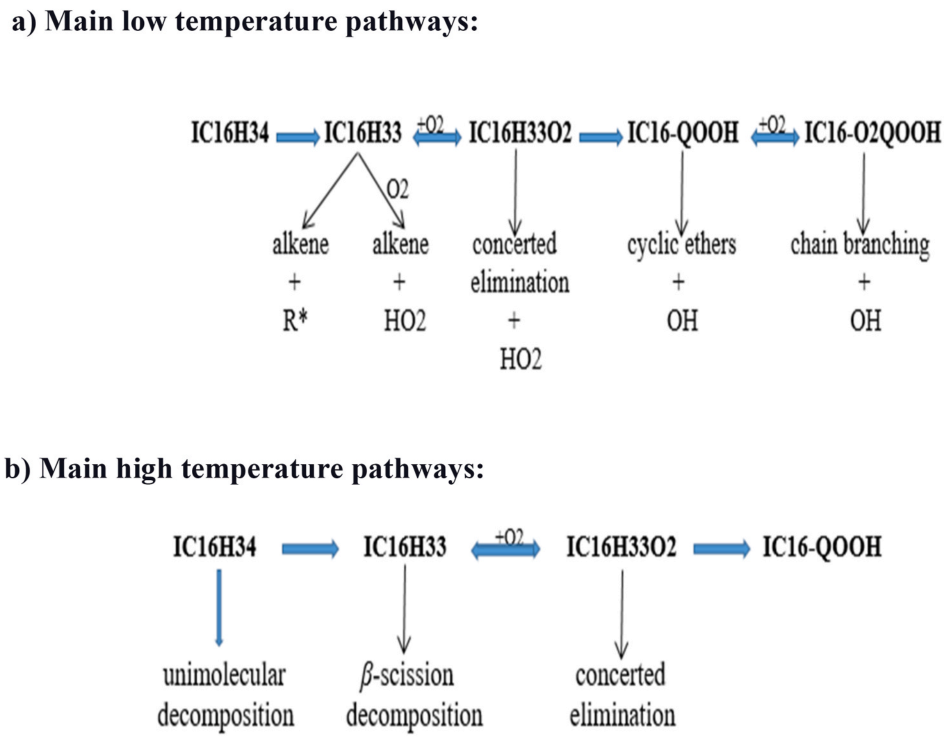


Fig. 6. Schematic diagram of IC16 main pathways of this study mechanism at low (a) and high (b) temperatures.

pathway analysis at low temperature (Fig. 6a) showed that, fuel is mostly consumed by H-atom abstraction reactions with subsequent reactions beginning with oxygen addition. The produced fuel radicals generate alkylperoxy radicals (RO_2) via O_2 addition process, as the start of chain branching reaction sequences of low temperature. Then, alkylperoxy radicals form hydroperoxy-alkyl radicals (QOOH) which in turn generate peroxy-alkylhydroperoxides (OOQOOH) through another O_2 addition process, leading to the low temperature chain branching that enhances the rate of the fuel consumption. The OOQOOH radical can decompose to ketohydroperoxides which finally leads to the formation of β-scission products. The concerted elimination reactions that generates olefin species (reducing the overall reactivity) are the alternative channel competing with the main low temperature pathways. For the high temperature regime (Fig. 6b), most of fuel molecules are consumed through H atom abstraction and also unimolecular decomposition. The fuel radicals formed by H atom abstraction reactions generates alkylperoxy radicals and β-scission decomposition. The C–C and C–H bonds in fuel radicals are opened via β-scission and then generate olefins and alkyl radicals which in turn undergo successive β-scission reactions, ultimately decomposing to generate small molecules and radicals that are depleted according to the provided core mechanism. Therefore, the β-scission reactions and the reactions of small species play a significant role in the high temperature regime.

Sensitivity analysis is a tool that identifies the reactions having the greatest impact on ignition delay time. To identify the key reactions, sensitivity analyses were performed for the ignition delay time of the developed model at 800 K and 1200 K, as the representatives of low and high temperature regimes. As can be seen in Fig. 7 for sensitivity at 800 K, the formation of OOQOOH by oxygen addition, H abstraction reactions, and alkenyl decomposition to active radicals, are the reactions with the greatest promoting effect on ignition delay time. The reaction of H abstraction from fuel by HO_2 that have a great promoting effect, has a boosting role in the combustion process, since it leads to the generation of hydrogen peroxide by producing two reactive OH radicals through $H_2O_2 \rightleftharpoons 2OH$. The reactions of $A\text{-}C_3H_5 + HO_2 \rightleftharpoons C_3H_5O + OH$ and $C_2H_3 + O_2 \rightleftharpoons CH_2CHO + OH$ that undergo branching reaction and form two kinds of radicals also have an important promoting effect. On the other hand, the decomposition of hydroperoxy-alkyl radicals to more stable olefins is the strongest inhibitor and has a great impact on the reduction of the fuel overall reactivity. The reactions of small species radicals that produce a more stable species, and also the alkenyl decomposition reactions that generate an alkene in their products, are the other key reactions having an inhibitor role in the ignition of IC16.

For high temperature, Fig. 7b demonstrates that the fuel unimolecular decomposition, the β-scission reactions, and the reactions of small species are the key reactions showing strong promoting and inhibiting effects, dominating the reactivity of the system in the high temperature regime. The small species reactions of the coupled core mechanism which only generate more active radicals are in the top list as the strongest promoter. The unimolecular decomposition of fuel is the other strong promoting reaction at this temperature. For the inhibitor key reactions, the small species producing stable alkenes showing the strongest inhibiting effect.

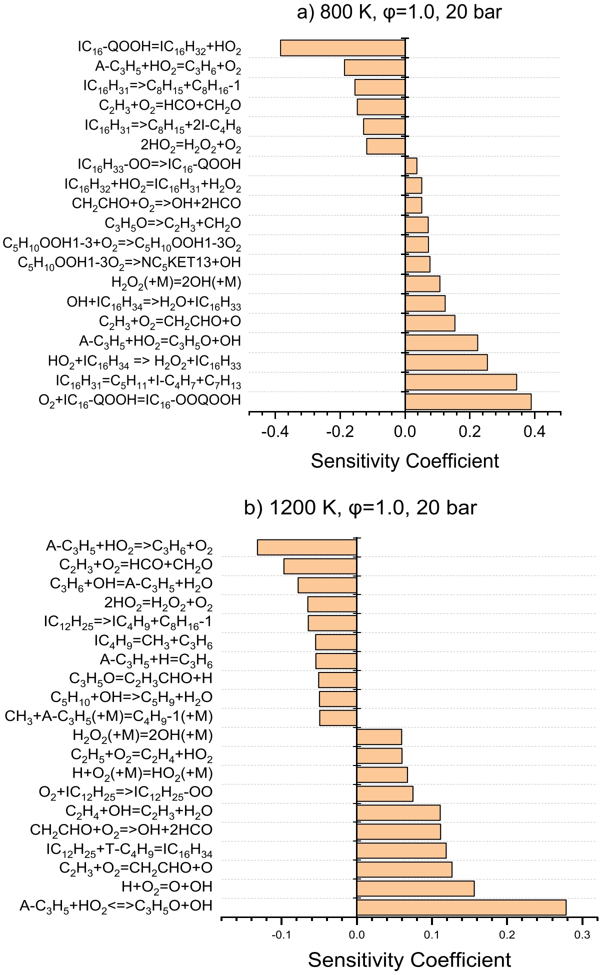


Fig. 7. Sensitivity analysis at 20 bar for stoichiometric condition at low (a) and high (b) temperatures.

4. Laminar flame speed

The simulations of the laminar flame speed given in Fig. 8 were conducted at 1 bar for the inlet gas temperature of 443 K and a range of equivalence ratios. The results were compared to the results of the available experimental data for isocetane [19]. Since the simulation result by the original mechanism didn't show a good agreement compared to the experimental data, some reactions rates of the core mechanism were optimized to achieve a closer simulation. The modifications were given in the Table 2. The optimized reactions were selected based on the fact that they shouldn't affect the ignition delay results negatively, and the new rates in the reliable mechanisms in the literature are available. The skeletal mechanism, in general, demonstrates a good agreement for the laminar flame speed, compared to the empirical data. However, discrepancies are observed between the modelling and experimental results. A slight under-prediction is seen for the fuel-rich side, but the over-prediction at the fuel-lean side for equivalence ratio of 0.8 is considerable.

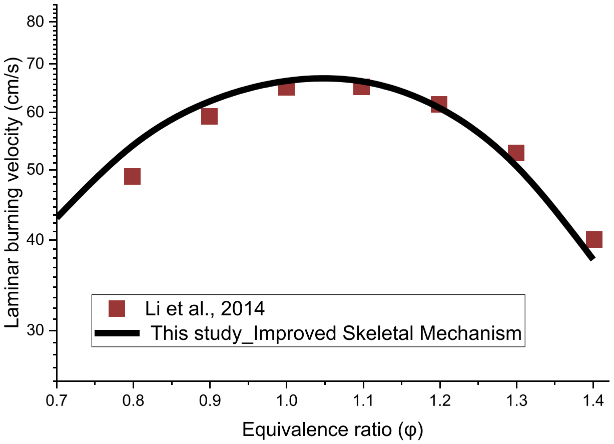


Fig. 8. Isocetane/air laminar flame speed of the developed mechanism of this study at the unburned temperature of 443 K, against the experimental data at P = 1 bar [19].

Table 2
The optimized reactions of the developed mechanism for the simulation of the laminar flame velocity. (cm^3, mole, s, cal/mol units).

Reaction	Original Arrhenius equation parameters	New Arrhenius equation parameters	New rate References
T-CH2+O2=>CO2+2H	5.8E12 0.0 1.5E3	2.64E12 0.0 1.5E3	[15]
CH3+O═CH2O + H	5.06E13 0.0 0.0	8.43E13 0.0 0.0	[20]
C2H2+O = T-CH2+CO	1.25E7 2.0 1.9E3	7.395E8 1.28 2.472E3	[15]
C3H6+O=>CH3CHCO+2H	2.5E7 1.76 7.6E1	3.05E+06 1.88 1.83E2	[15]

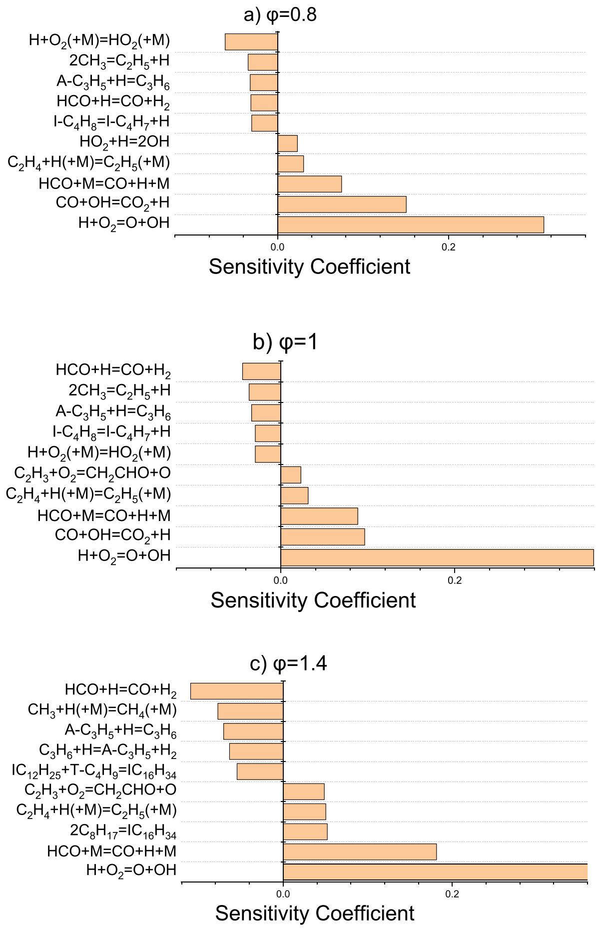


Fig. 9. Sensitivity analysis of laminar flame velocity for isocetane/air mixture at 1 bar and 443 K, for equivalence ratios of 0.8 (a) 1 (b) and 1.4 (c).

Sensitivity coefficients for laminar flame speed at equivalence ratios of 0.8, 1, 1.4 were conducted using Chemkin-Pro, to find out the most important reactions affecting the laminar flame velocity. It can be seen from Fig. 9 that the dominant chain branching reaction of $H + O_2 \rightleftharpoons O + OH$ generating too many OH and O radicals and having a great contribution to the flame with self-propagation characteristics [20], the main oxidation reaction of CO and the production of CO as the chain propagation and the chain initiation reactions that leading to the production of H radicals, are the most important elementary reactions for the laminar flame velocity of isocetane/air mixture. Since the mentioned reactions produce more active radicals of H, O, and OH, they have a promoting role on the laminar flame speed and increase it. On the other hand, the reaction of $HCO + H \rightleftharpoons CO + H_2$ which leads to the termination of the radical chain process and has a suppressing role on the flame speed, shows the highest negative sensitivity coefficient. The common reactions having an important effect on the flame speed at three equivalence ratios and the reactions with a considerable impact on the ignition delay of IC16, make it hard to further optimize the discrepancy observed for the lean condition, or the little disagreement between the simulation and experimental data at $\varphi = 1.4$. In addition, more experimental data are required to be certain about the experimental data of IC16 flame speed, and then, exerting the required optimizations for the laminar flame velocity at the equivalence ratios.

5. Species mole fraction

Providing a close simulation for the fuel consumption and emissions by a utilized reaction mechanism in CFD studies is of great importance. Therefore, the ability of the developed model for the prediction of the species with the available experimental data including the mole fraction profiles of IC16, CO, CO_2, and H_2O was challenged. While it was expected that a much simplified model developed for the prediction of ignition delay, particularly for a wide range of conditions, and/or laminar flame speed would not necessarily deliver a reasonable prediction for the important species mole fractions. It was found that the constructed mechanism of this study could predict the concentration profile for the fuel and the main oxidation products with a good agreement compared to the experimental results. The simulation was conducted with the aid of the perfectly stirred reactor (PSR) tool in Ansys Chemkin-Pro, to model the experiment that was conducted on a jet-stirred reactor (JSR) at the pressure of 10 atm, a constant residence time of 1 s, the temperature range of 770–1070 K, and for three equivalence ratios of 0.5, 1, and 2 [6]. It can be observed in Figs. 10–12 that the mechanism could satisfactorily emulate the experimental concentration profiles of the intended species with a good agreement.

The consumption of IC16 begins at 770 K, continues to decay until 900 K for the lean, stoichiometric and the rich conditions, where it completely decayed. Generally, the modelling results of IC16 could follow the experimental profiles with a relatively good agreement at the three equivalence ratios, particularly for the beginning and the termination areas of the consumption profile, though an overestimation is observed at 850–950 K. It might be as a result of the approximation used in the lumping process for the development of the lumped reaction rates that might have undergone the lack of enough precision.

While the modelling results for the all oxidation products could capture the parameters of the production and the magnitude compared to the experiment, the prediction of magnitude for H_2O at the lean

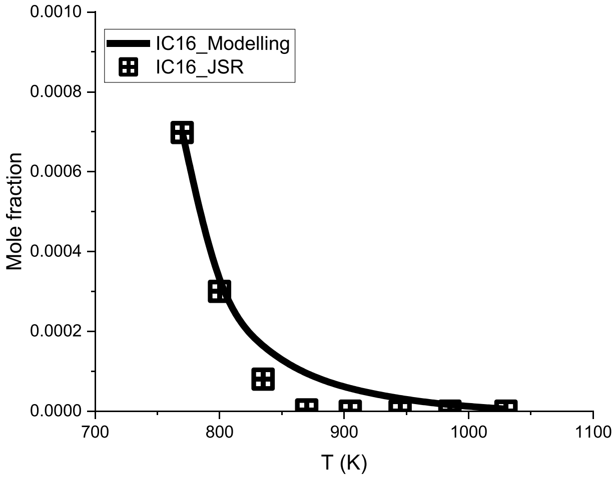


Fig. 10a. IC16H34 mole fraction simulation result of the developed mechanism of this study, against the experimental data at the equivalence ratio = 0.5 and the temperature range of 770–1030 K [6].

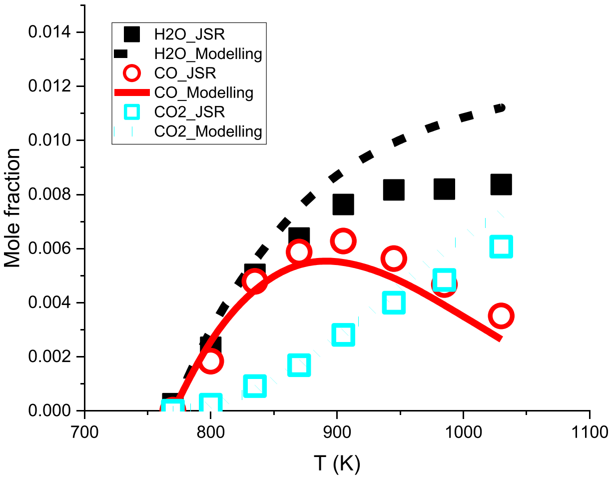


Fig. 10b. CO, CO_2, and H_2O mole fraction simulation results of the developed mechanism of this study, against the experimental data at the equivalence ratio = 0.5 and the temperature range of 770–1030 K [6].

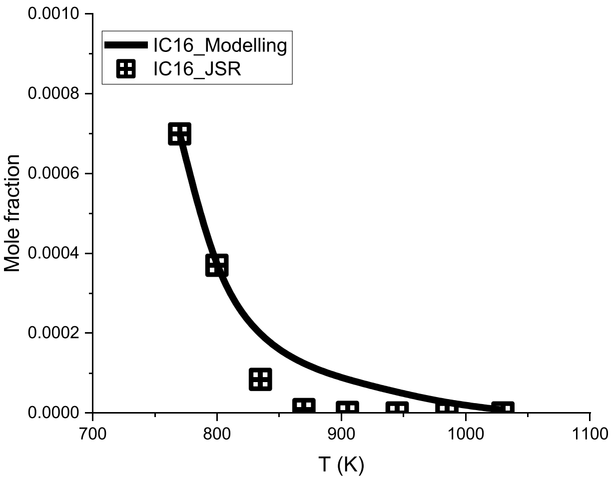


Fig. 11a. IC16H34 mol fraction simulation result of the developed mechanism of this study, against the experimental data at the equivalence ratio = 1 and the temperature range of 770–1030 K [6].

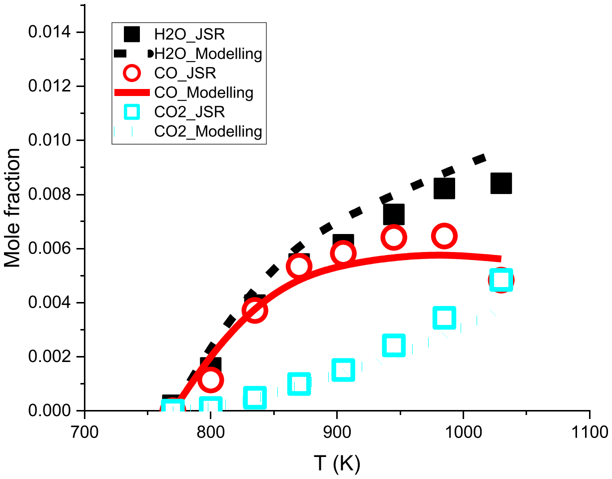


Fig. 11b. CO, CO_2, and H_2O mole fraction simulation results of the developed mechanism of this study, against the experimental data at the equivalence ratio = 1 and the temperature range of 770–1030 K [6].

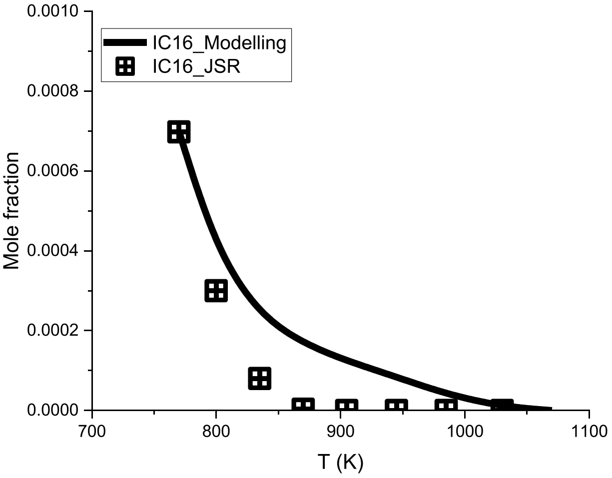


Fig. 12a. IC16H34 mol fraction simulation result of the developed mechanism of this study, against the experimental data at the equivalence ratio = 2 and the temperature range of 770–1070 K [6].

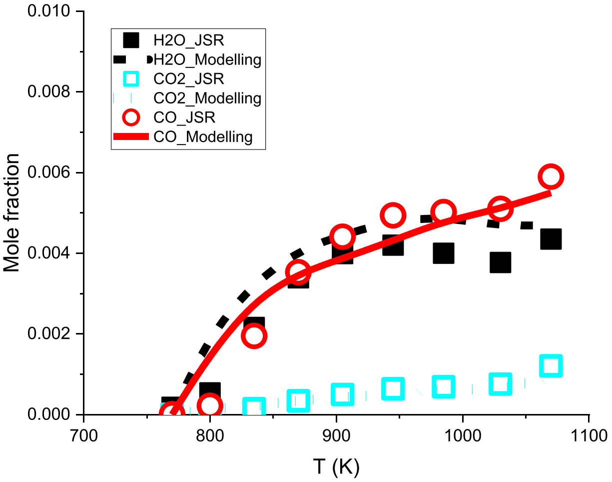


Fig. 12b. CO, CO_2, and H_2O mole fraction simulation results of the developed mechanism of this study, against the experimental data at the equivalence ratio = 2 and the temperature range of 770–1070 K [6].

condition showed a considerable over-prediction against the experimental profile at the area above 900 K. Since the model could satisfactorily predict the H_2O profile at stoichiometric with an excellent agreement and the rich conditions with a close agreement, the speculation firstly can be made for the accuracy of the experimental measurement of H_2O profile at the lean condition. The other scenario for consideration could be the simplification that has been applied for the initial mechanism.

6. Conclusion

A compact reaction kinetic mechanism has been developed for isocetane as an important surrogate component of jet and diesel fuels, using a decoupling methodology through coupling a well validated core mechanism to a sub-mechanism of isocetane.

- From mechanism enhancement, a very good agreement was observed between the mechanism predictions and measured ignition delay times.
- To our knowledge, this is the only mechanism for IC16 which satisfies both the targets of compact size and very close emulation of the

ignition behaviour over the low-to-high temperature range for lean, stoichiometric, and rich conditions at different pressures. However, discrepancies were still observed at certain temperature conditions between the modelling and empirical results, which can be due to the uncertainty for the experiments and the restrictions in the prediction power of the mechanism caused by using lumped reaction rates in the model.

- The main oxidation pathway of IC16 was explained and the key reactions were identified by sensitivity analysis.
- The simulation of the laminar flame speed was conducted for iso-cetane/air mixture at 1 bar and 443 K, and the result was found to be in good agreement with the experimental data.
- The concentration of the main oxidation products of IC16 were predicted against the experimental results at the lean, stoichiometric, and the rich conditions. The results showed that the model can simulate the mole fractions with a close emulation compared to the experimental results.
- All in all, the provided mechanism can be used as a surrogate for fuels and also for some practical simulation works, due to its high predictive capability of ignition delay, the close emulation of the laminar flame speed and the mole fraction of main oxidation species, and the small size of the model.

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.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.joei.2023.101253.

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