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On the development of multipurpose skeletal core combustion chemical kinetic mechanisms

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Abstract: Core combustion kinetic mechanisms for small $C_0 - C_4$ fuel molecules are not only of the utmost importance in understanding their individual combustion properties, but they are also the foundation for the development of kinetic models of real fuels. This brief communication intends to develop efficient skeletal core combustion mechanisms for the oxidation of $C_0 - C_3/C_4$ fuels using the recently developed NUIGMech1.1 as the detailed mechanism. A combination of different skeletal mechanism reduction methods is employed to produce two skeletal mechanisms for $C_0 - C_3$ and $C_0 - C_4$ fuels, respectively. The skeletal mechanisms have been validated by comparing against a wide range of combustion targets, and the maximum error in ignition delay time predictions is less than 10% for all the targeted fuels. The $C_0 - C_3$ skeletal mechanism is also employed as the core mechanism in the development of a five-component skeletal mechanism for real gasoline. The developed skeletal mechanisms should represent a valuable resource for mechanism development and kinetic modeling within the combustion community.

Keywords: Core combustion kinetics; skeletal reduction; gasoline surrogate

1. Introduction

The development of detailed kinetic models to predict the pyrolysis and oxidation properties of various fuels has received significant attention over the past number of decades. This is due to the need for reliable kinetic models for use in the rational design of practical combustors.[1-3] Owing to the hierarchical nature of combustion chemistry,[1] the core kinetic models usually recognized as the models for $C_0 - C_3/C_4$ hydrocarbons are not only of the utmost importance in understanding the combustion properties of the small components themselves, but they are also the foundation for the development of kinetic models of real fuels. The first universally successful attempt to develop such a kinetic model for natural gas combustion was probably GRI-Mech,[4] which was involuntary adopted as a core mechanism. However, due to extensions in combustion ranges, GRI-Mech shows poor predictability beyond its original validated range of applicability.[5, 6] Much progress has been made since the GRI-Mech effort. Currently, almost every major combustion mechanism development group has built and maintains its own core mechanism, with most developed for specific purposes. In order to develop a unified core kinetic model, the mechanism development group at NUI Galway have re-evaluated the kinetics and thermochemistry of $C_0 - C_4$ base chemistry based on recent ab-initio studies and experimental diagnostics. The widely used AramcoMech mechanisms[7-9] have been updated and recently published as NUIGMech1.1, which has been comprehensively validated against a large database for combustion properties of $C_0 - C_4$ hydrocarbon and oxygenated hydrocarbon fuels.[6, 10-12] However, its large size limits its applicability. Although a series of reduced mechanisms for small fuels were developed,[13-18] almost all of them were targeted for specific fuels or combustion conditions, limiting their applications as a core mechanism for the development of detailed mechanisms of large fuels. For this purpose, this work intends to develop multipurpose skeletal core combustion mechanisms for base fuels and validate their performance in the development of real fuels by using the comprehensively validated NUIGMech 1.1 as the starting point.

2. Mechanism reduction methods

The detailed NUIGMech1.1 mechanism includes 771 species and 3783 reactions to predict the

pyrolysis and oxidation of various $C_0 - C_4$ fuels.[6, 10, 12, 19-27] A combination of skeletal mechanism reduction methods is used to generate minimal skeletal mechanisms for core fuel molecules, including methane, methanol, ethane, ethylene, acetylene, ethanol, propene, propane, allene, propyne, the isomers of butene and butane, 1,3-butadiene, and benzene. These mechanisms are merged to form multi-purpose skeletal core kinetic models. Specifically, reaction state points densely sampled from auto-ignition simulations covering a wide range of temperatures ($\sim 750 - 1600$ K), pressures ($1 - 50$ bar), and equivalence ratios ($0.5 - 2.0$) are used in the reduction process. It has been confirmed that, in mechanism reduction, skeletal mechanisms still exhibit good performance in predicting combustion properties with reaction states only sampled from auto-ignition.[28-30] In addition, there are significantly more important reactions for ignition rather than for species profiles from jet-stirred reactors (JSR) or flame speed (FS) since JSR experiments are mostly relevant to low- to intermediate temperature chemistry and FS experiments are related to high-temperature chemistry. Thus, reaction state points sampled from ignition are used for mechanism reduction. The fuel molecule, and oxygen are naturally selected as the targeted species. In addition, the hydrogen atom is also selected since it is an important species for all of the fuels and plays a crucial role in flame simulations.[13, 31] To achieve a maximum reduction of the detailed mechanism,[32] different skeletal reduction methods are combined together and used sequentially. The original directed relation graph (DRG) method is firstly employed due to its computational efficiency, and then the two-stage DRG with error propagation (DRGEP) method with slightly larger computational cost but much more efficiency is used to further remove unimportant species. The brute-force sensitivity analysis method requiring large computational cost is finally used to derive minimal skeletal mechanisms of each fuel with a maximum error in ignition delay time (IDT) of less than 10%. Mechanism reduction is performed via an in-house code coupled with Chemkin 2.0 program.[33, 34]

3. Results and discussion

Table 1 lists the size of the generated skeletal mechanism for each fuel with the predicted error of IDT less than 10%, and the maximum and mean absolute errors (MAE) of the predicted IDT via

the merged $C_0 - C_3$ and $C_0 - C_4$ skeletal mechanisms, which include 170 species and 1002 reactions and 341 species and 1977 reactions, respectively. Unlike previously derived skeletal mechanisms for small fuels, the current skeletal mechanisms include comprehensive core fuel molecules, especially the sub-mechanisms for allene and propyne which are critical for the prediction of soot formation from non-aromatic fuels.[10, 11] The two skeletal mechanisms are validated against IDT, laminar flame speed (LFS), and species profiles from JSR and flow reactor (FR) over a wide range of combustion conditions from an extensive literature review, with details given as Supplementary material. Table 2 summarizes these experimental conditions of various $C_0 - C_4$ fuels utilized for validation of the two skeletal mechanisms. The current skeletal mechanisms show high-fidelity compared to the detailed NUIGMech1.1, which was significantly improved for the prediction of IDT and LFS of propene, propyne and isobutene and the pyrolysis process of alkenes[11, 19, 20] compared to AramcoMech3.0.[9] Figure 1 shows the predicted IDT and LFS for propene (C_3H_6), isobutene (iC_4H_8), and n-butane using the generated skeletal mechanisms and the detailed NUIGMech1.1 and AramcoMech3.0 mechanisms. For propene it can be seen that the detailed and skeletal mechanisms exhibit reasonable prediction of IDT at the studied conditions due to the optimization of key reaction rate constants,[20] while the older AramcoMech3.0 mechanism tends to overestimate the IDT and even no ignition was found with pressure of 30 bar for the interested low-temperature conditions. The updated detailed NUIGMech1.1 mechanism also better predicts IDT and LFS data for isobutene, as discussed in a previous reference,[22] indicating the necessity to continuously improve the core mechanism.

An efficient core skeletal mechanism is the foundation in the development of kinetic models for larger fuels, specifically in the decoupling or hybrid chemistry methods.[11, 35] For this purpose, the derived skeletal mechanism is validated against a 5-component gasoline surrogate model via a decoupling method. Specifically, the $C_0 - C_3$ skeletal mechanism is coupled with the lumped global mechanisms for the five components including iso-octane, n-heptane, iso-hexane, 1-hexene, and toluene with the compositions of 39.91%, 6.99%, 9.31%, 9.28%, and 34.51% (mole %) respectively to describe the high-temperature pyrolysis and oxidation at negative temperature coefficients (NTC)

regions, which has been detailed previously.[11, 36, 37] Fig. 1 shows the predicted IDT and LFS using the derived skeletal mechanism for gasoline. The validation results indicate that the prediction accuracy of the 5-component gasoline surrogate model with the skeletal mechanism can also well re-produce the modeling results compared to the detailed mechanism.[11] It is worth noting that the developed detailed mechanisms for real fuels can still be further reduced for engine simulations. Following a similar procedure to derive the core skeletal mechanism together with the computational singular perturbation method to remove unimportant reactions, the constructed reaction mechanism of the 5-component gasoline surrogate model is further reduced under engine conditions to a skeletal mechanism with only 95 species and 321 reactions, and the performance for IDTs and LFS under typical conditions against the detailed mechanism is provided as Fig. 3. The reduced skeletal mechanism exhibits good predictions compared with the detailed mechanism. The CSP method is used for the deletion of unimportant reactions due to its clarity in the description of reaction contributions to the production rate of a species and computational efficiency compared with other methods, such as sensitivity and principal component analysis.[28, 38]

Although this concept of a $C_0 - C_4$ core mechanism was used in the HyChem approach,[39, 40] the present work shows different characteristics. The $C_0 - C_4$ core mechanism in the HyChem approach mainly focused on high-temperature combustion conditions, while this work aims to derive a skeletal core kinetic mechanism covering a wide range of applicability for these small fuels. The HyChem approach is physics-based, and the development of kinetic models for larger fuels generally requires fuel pyrolysis studies. The skeletal mechanisms in this work are mainly intended for use as the foundation for the development of detailed kinetic models of large fuels to understand their combustion chemistry. More specifically, in addition to their use in understanding the individual combustion properties of these small fuels, the $C_0 - C_3$ core skeletal mechanism is recommended for use in the decoupling method for the development of lumped mechanisms for large/real fuels as demonstrated here in the five-component surrogate model for gasoline. Moreover, the $C_0 - C_4$ core mechanism is mainly intended as a starting point in the development of detailed combustion models

for large fuels or surrogate models for real fuels. The users can develop suitable detailed mechanisms based on the developed skeletal core mechanisms of real fuels and further reduce the developed mechanisms for their interested operating conditions.

4. Conclusions

This work presents an extensive skeletal mechanism reduction and validation study of $C_0 - C_4$ fuels starting with the detailed NUIGMech1.1 mechanism. The derived skeletal mechanisms for each fuel in addition to two merged skeletal mechanisms for $C_0 - C_3$ and $C_0 - C_4$ skeletal mechanisms are comprehensively validated, and significant improvement in the prediction of experimental results for C_3 and C_4 fuels are achieved using both the detailed and skeletal mechanisms. The derived skeletal mechanisms are also used as the base model for a recently developed 5-component surrogate model for real gasoline, and good prediction accuracy is found. The resulted skeletal mechanisms should not only be a valuable resource for mechanism development and kinetic modeling but can also contribute significantly to the ongoing development of a unified core mechanism within the combustion community.

Supporting Information

Developed skeletal core combustion mechanisms; reduced skeletal mechanism for gasoline surrogate model; detailed NUIGMech1.1 mechanism; validation results for the skeletal mechanisms.

Reference

1. Curran, H. J., Developing detailed chemical kinetic mechanisms for fuel combustion. *Proc. Combust. Inst.* **2019,** *37* (1), 57-81.

2. Yao, W., Kerosene-fueled supersonic combustion modeling based on skeletal mechanisms. *Acta Mech. Sin.* **2019,** *35* (6), 1155-1177.

3. Yao, W.; Wu, K.; Fan, X., Development of Skeletal Kerosene Mechanisms and Application to Supersonic Combustion. *Energy Fuels* **2018,** *32* (12), 12992-13003.

4. Smith, G. P.; Golden, D. M.; Frenklach, M.; Moriarty, N. W.; Eiteneer, B.; Goldenberg, M.; Bowman, C. T.; Hanson, R. K.; Song, S.; Gardiner Jr, W. C., *GRI 3.0 Mechanism, http://combustion.berkeley.edu/gri-mech/releases.html* **1999**.

5. Mulvihill, C. R.; Mathieu, O.; Petersen, E. L., H_2O time histories in the H_2-NO_2 system for validation of NOx hydrocarbon kinetics mechanisms. *Int. J. Chem. Kinet.* **2019,** *51* (9), 669-678.

6. Baigmohammadi, M.; Patel, V.; Martinez, S.; Panigrahy, S.; Ramalingam, A.; Burke, U.; Somers, K. P.; Heufer, K. A.; Pekalski, A.; Curran, H. J., A comprehensive experimental and simulation study of ignition delay time characteristics of single fuel $C_1 – C_2$ hydrocarbons over a wide range of temperatures, pressures, equivalence ratios, and dilutions. *Energy Fuels* **2020,** *34* (3), 3755-3771.

7. Metcalfe, W. K.; Burke, S. M.; Ahmed, S. S.; Curran, H. J., A Hierarchical and Comparative Kinetic Modeling Study of C_1-C_2 Hydrocarbon and Oxygenated Fuels. *Int. J. Chem. Kinet.* **2013,** *45* (10), 638-675.

8. Li, Y.; Zhou, C. W.; Somers, K. P.; Zhang, K. W.; Curran, H. J., 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), 403-411.

9. Zhou, C. W.; Li, Y.; Burke, U.; Banyon, C.; Somers, K. P.; Ding, S. T.; Khan, S.; Hargis, J. W.; Sikes, T.; Mathieu, O.; Petersen, E. L.; AlAbbad, M.; Farooq, A.; Pan, Y. S.; Zhang, Y. J.; Huang, Z. H.; Lopez, J.; Loparo, Z.; Vasu, S. S.; Curran, H. J., An experimental and chemical kinetic modeling study of 1,3-butadiene combustion: Ignition delay time and laminar flame speed measurements. *Combust. Flame* **2018,** *197*, 423-438.

10. Panigrahy, S.; Jinhu, L.; Nagaraja, S. S.; Kim, G.; MacDougall, T.; Vasu, S. S.; Curran, H. J., A comprehensive experimental and improved kinetic modeling study on the pyrolysis and oxidation of propyne. *Proc. Combust. Inst.* **2020,** doi: 10.1016/j.proci.2020.06.320.

11. Yang, S.; Wang, Q.; Curran, H. J.; Jia, M., Development of a 5-component gasoline surrogate model using recent advancements in the detailed $H_2/O_2/CO/C_1$-C_3 mechanism for decoupling methodology. *Fuel* **2021,** *283*, 118793.

12. Mohamed, A. A. E.-S.; Panigrahy, S.; Sahu, A. B.; Bourque, G.; Curran, H., An experimental and kinetic modeling study of the auto-ignition of natural gas blends containing C_1-C_7 alkanes. *Proc. Combust. Inst.* **2020,** doi: 10.1016/j.proci.2020.06.015.

13. Luo, Z.; Lu, T.; Liu, J., A reduced mechanism for ethylene/methane mixtures with excessive NO enrichment. *Combust. Flame* **2011,** *158* (7), 1245-1254.

14. Zsely, I. G.; Nagy, T.; Simmie, J. M.; Curran, H. J., Reduction of a detailed kinetic model for the ignition of methane/propane mixtures at gas turbine conditions using simulation error minimization methods. *Combust. Flame* **2011,** *158* (8), 1469-1479.

15. Wang, Q.-D., Skeletal Mechanism Generation for High-Temperature Combustion of H-2/CO/C-1-C-4 Hydrocarbons. *Energy Fuels* **2013,** *27* (7), 4021-4030.

16. Sharma, D.; Mahapatra, S.; Garnayak, S.; Arghode, V. K.; Bandopadhyay, A.; Dash, S. K.; Reddy, V. M., Development of the Reduced Chemical Kinetic Mechanism for Combustion of H2/CO/C1–C4 Hydrocarbons. *Energy Fuels* **2021,** *35* (1), 718-742.

17. Zettervall, N.; Fureby, C.; Nilsson, E. J. K., Small Skeletal Kinetic Reaction Mechanism for Ethylene–Air Combustion. *Energy Fuels* **2017,** *31* (12), 14138-14149.

7

18. Hu, X.; Yu, Q.; Li, Y.; Liu, J., A Minimal Skeletal Mechanism for Combustion of CH4/O2/CO2 Mixtures. *Energy Fuels* **2016,** *30* (2), 1407-1414.

19. Nagaraja, S. S.; Liang, J. H.; Dong, S. J.; Panigrahy, S.; Sahu, A.; Kukkadapu, G.; Wagnon, S. W.; Pitz, W. J.; Curran, H. J., A hierarchical single-pulse shock tube pyrolysis study of C_2-C_6 1-alkenes. *Combust. Flame* **2020,** *219*, 456-466.

20. Ramalingam, A.; Panigrahy, S.; Fenard, Y.; Curran, H.; Heufer, K. A., A chemical kinetic perspective on the low-temperature oxidation of propane/propene mixtures through experiments and kinetic analyses. *Combust. Flame* **2021,** *223*, 361-375.

21. Baigmohammadi, M.; Patel, V.; Nagaraja, S.; Ramalingam, A.; Martinez, S.; Panigrahy, S.; Mohamed, A. A. E.-S.; Somers, K. P.; Burke, U.; Heufer, K. A.; Pekalski, A.; Curran, H. J., Comprehensive Experimental and Simulation Study of the Ignition Delay Time Characteristics of Binary Blended Methane, Ethane, and Ethylene over a Wide Range of Temperature, Pressure, Equivalence Ratio, and Dilution. *Energy Fuels* **2020,** *34* (7), 8808-8823.

22. Lokachari, N.; Panigrahy, S.; Kukkadapu, G.; Kim, G.; Vasu, S. S.; Pitz, W. J.; Curran, H. J., The influence of iso-butene kinetics on the reactivity of di-isobutylene and iso-octane. *Combust. Flame* **2020,** *222*, 186-195.

23. Dong, S.; Zhang, K.; Ninnemann, E. M.; Najjar, A.; Kukkadapu, G.; Baker, J.; Arafin, F.; Wang, Z.; Pitz, W. J.; Vasu, S. S.; Sarathy, S. M.; Senecal, P. K.; Curran, H. J., A comprehensive experimental and kinetic modeling study of 1- and 2-pentene. *Combust. Flame* **2021,** *223*, 166-180.

24. Lokachari, N.; Wagnon, S. W.; Kukkadapu, G.; Pitz, W. J.; Curran, H. J., An experimental and kinetic modeling study of cyclopentane and dimethyl ether blends. *Combust. Flame* **2021,** *225*, 255-271.

25. Nagaraja, S. S.; Power, J.; Kukkadapu, G.; Dong, S.; Wagnon, S. W.; Pitz, W. J.; Curran, H. J., A single pulse shock tube study of pentene isomer pyrolysis. *Proc. Combust. Inst.* **2020,** doi: 10.1016/j.proci.2020.06.069.

26. Dong, S.; Zhang, K.; Senecal, P. K.; Kukkadapu, G.; Wagnon, S. W.; Barrett, S.; Lokachari, N.; Panigaphy, S.; Pitz, W. J.; Curran, H. J., A comparative reactivity study of 1-alkene fuels from ethylene to 1-heptene. *Proc. Combust. Inst.* **2020,** doi: 10.1016/j.proci.2020.07.053.

27. Nagaraja, S. S.; Kukkadapu, G.; Panigrahy, S.; Liang, J. H.; Lu, H. T.; Pitz, W. J.; Curran, H. J., A pyrolysis study of allylic hydrocarbon fuels. *Int. J. Chem. Kinet.* **2020,** *52* (12), 964-978.

28. Lu, T.; Law, C. K., Toward accommodating realistic fuel chemistry in large-scale computations. *Prog. Energy Combust. Sci.* **2009,** *35* (2), 192-215.

29. Wang, Q.-D.; Fang, Y.-M.; Wang, F.; Li, X.-Y., Skeletal mechanism generation for high-temperature oxidation of kerosene surrogates. *Combust. Flame* **2012,** *159* (1), 91-102.

30. Lu, T.; Law, C., Strategies for mechanism reduction for large hydrocarbons: n-heptane. *Combust. Flame* **2008,** *154* (1-2), 153-163.

31. Ranzi, E.; Frassoldati, A.; Grana, R.; Cuoci, A.; Faravelli, T.; Kelley, A. P.; Law, C. K., Hierarchical and comparative kinetic modeling of laminar flame speeds of hydrocarbon and oxygenated fuels. *Prog. Energy Combust. Sci.* **2012,** *38* (4), 468-501.

32. Lu, T. F.; Law, C. K., Toward accommodating realistic fuel chemistry in large-scale computations. *Prog. Energy Combust. Sci.* **2009,** *35* (2), 192-215.

33. Kee, R. J.; Rupley, F. M.; Miller, J. A. *Chemkin-II: A Fortran chemical kinetics package for the analysis of gas-phase chemical kinetics*; Sandia National Laboratories Report SAND89-8009; 1989.

34. Lutz, A. E.; Kee, R. J.; Miller, J. A. *Senkin: A Fortran Program for Predicting Homogeneous Gas Phase Chemical Kinetics with Sensitivity Analysis*; Sandia National Laboratories Report SAND87-8248; 1990.

35. Wang, K.; Xu, R.; Parise, T.; Shao, J.; Movaghar, A.; Lee, D. J.; Park, J.-W.; Gao, Y.; Lu, T.; Egolfopoulos, F. N.; Davidson, D. F.; Hanson, R. K.; Bowman, C. T.; Wang, H., A physics-based approach to modeling real-fuel combustion chemistry - IV. HyChem modeling of combustion kinetics of a bio-derived jet fuel and its blends with a conventional Jet A. *Combust. Flame* **2018,** *198*, 477-489.

36. Tsurushima, T., A new skeletal PRF kinetic model for HCCI combustion. *Proc. Combust. Inst.* **2009,** *32*, 2835-2841.

37. Tanaka, S.; Ayala, F.; Keck, J. C., A reduced chemical kinetic model for HCCI combustion of primary reference fuels in a rapid compression machine. *Combust. Flame* **2003,** *133* (4), 467-481.

38. Lu, T.; Law, C. K., A criterion based on computational singular perturbation for the identification of quasi steady state species: A reduced mechanism for methane oxidation with NO chemistry. *Combust. Flame* **2008,** *154* (4), 761-774.

39. Xu, R.; Saggese, C.; Lawson, R.; Movaghar, A.; Parise, T.; Shao, J. K.; Choudhary, R.; Park, J. W.; Lu, T. F.; Hanson, R. K.; Davidson, D. F.; Egolfopoulos, F. N.; Aradi, A.; Prakash, A.; Mohan, V. R. R.; Cracknell, R.; Wang, H., A physics-based approach to modeling real-fuel combustion chemistry - VI. Predictive kinetic models of gasoline fuels. *Combust. Flame* **2020,** *220*, 475-487.

40. Wang, K.; Xu, R.; Parise, T.; Shao, J.; Movaghar, A.; Lee, D. J.; Park, J. W.; Gao, Y.; Lu, T. F.; Egolfopoulos, F. N.; Davidson, D. F.; Hanson, R. K.; Bowman, C. T.; Wang, H., A physics based approach to modeling real-fuel combustion chemistry - IV. HyChem modeling of combustion kinetics of a bio-derived jet fuel and its blends with a conventional Jet A. *Combust. Flame* **2018,** *198*, 477-489.

41. Zhou, C. W.; Li, Y.; O'Connor, E.; Somers, K. P.; Thion, S.; Keesee, C.; Mathieu, O.; Petersen, E. L.; DeVerter, T. A.; Oehlschlaeger, M. A.; Kukkadapu, G.; Sung, C. J.; Alrefae, M.; Khaled, F.; Farooq, A.; Dirrenberger, P.; Glaude, P. A.; Battin-Leclerc, F.; Santner, J.; Ju, Y. G.; Held, T.; Haas, F. M.; Dryer, F. L.; Curran, H. J., A comprehensive experimental and modeling study of isobutene oxidation. *Combust. Flame* **2016,** *167*, 353-379.

42. Davis, S. G.; Law, C. K., Determination of and Fuel Structure Effects on Laminar Flame Speeds of C1 to C8 Hydrocarbons. *Combust. Sci. Technol.* **1998,** *140* (1-6), 427-449.

43. Hirasawa, T.; Sung, C. J.; Joshi, A.; Yang, Z.; Wang, H.; Law, C. K., Determination of laminar flame speeds using digital particle image velocimetry: Binary Fuel blends of ethylene, n-Butane, and toluene. *Proc. Combust. Inst.* **2002,** *29* (2), 1427-1434.

44. Bosschaart, K. J.; de Goey, L. P. H., The laminar burning velocity of flames propagating in mixtures of hydrocarbons and air measured with the heat flux method. *Combust. Flame* **2004,** *136* (3), 261-269.

45. Gauthier, B. M.; Davidson, D. F.; Hanson, R. K., Shock tube determination of ignition delay times in full-blend and surrogate fuel mixtures. *Combust. Flame* **2004,** *139* (4), 300-311.

46. Zhao, Z.; Conley, J. P.; Kazakov, A.; Dryer, F. L., Burning Velocities of Real Gasoline Fuel at 353 K and 500 K. SAE International: 2003; 2003-01-3265.

Table 1. Mechanism size for single fuels and the error of predicted IDT.

| Fuel	Species	Reactions	Maximum Error (%)		MAE (%)	
			$C_0 - C_3$ mech	$C_0 - C_4$ mech	$C_0 - C_3$ mech	$C_0 - C_4$ mech
methane (CH_4)	24	117	1.0	1.1	0.3	0.3
methanol (CH_3OH)	17	54	5.5	4.7	0.9	0.6
ethane (C_2H_6)	49	284	5.3	1.4	1.2	0.4
ethylene (C_2H_4)	54	305	7.5	6.1	3.5	1.5
acetylene (C_2H_2)	38	237	9.8	8.7	2.1	1.6
ethanol (C_2H_5OH)	38	265	6.9	3.9	1.4	0.8
propane (C_3H_8)	69	445	6.7	2.8	1.7	0.7
propene (C_3H_6)	80	487	8.9	8.6	4.9	2.7
allene (C_3H_4-a)	63	296	10.3	8.9	3.9	2.9
propyne (C_3H_4-p)	80	344	8.3	2.7	2.7	0.7
1-butene (C_4H_8-1)	87	464	–	7.2	–	2.5
2-butene (C_4H_8-2)	84	607	–	8.9	–	3.7
iso-butene (iC_4H_8)	96	548	–	8.5	–	2.3
n-butane (C_4H_{10})	111	703	–	9.6	–	1.6
iso-butane (iC_4H_{10})	120	791	–	3.7	–	1.4
1,3-butadiene (C_4H_6)	107	695	–	7.0	–	2.7
benzene (C_6H_6)	58	291	–	2.7	–	0.8

Table 2. Range of experimental conditions utilized for skeletal mechanism validation.

| Species	Shock tube (ST)	Rapid compression machine (RCM)	Jet-stirred reactor (JSR)	Flow reactor (FR)	Flame speed (FS)
H2/CO	✓	✓	✓	✘	✓
ΔT	975.0 – 1670 K	930.0 – 1040 K	840.0 – 1150 K	–	298.0 K
Δp	1.05 – 300.5 atm	8.0 – 32.0 atm	1.0 – 10.0 atm	–	1.0 atm
$\Delta \varphi$	0.3 – 1.0	0.5	0.1 – 2.5	–	0.5 – 5.0
CH$_3$OH	✓	✓	✓	✓	✓
ΔT	909.0 – 2180.0 K	817.0 – 980.0 K	697.2 – 1099.4 K	781.0 – 1043.0 K	298.0 – 423.0 K
Δp	0.99 – 51.71 atm	9.27 – 40.64 atm	10.0 – 10.0 atm	1.0 – 15.0 atm	1.0 – 5.0 atm
$\Delta \varphi$	0.38 – 6.0	0.5 – 2.0	0.2 – 0.2	0.42 – 2.59	0.6 – 1.6
CH$_4$	✓	✓	✓	✓	✓
ΔT	1041.0 – 2538.0 K	869.9 – 1178.19 K	1635.0 – 2400.0 K	1942.0 – 2374.0 K	298.0 K
Δp	0.54 – 260.0 atm	10.0 – 24.0 atm	0.9 – 1.66 atm	0.37 – 1.1 atm	1.0 – 20.0 atm
$\Delta \varphi$	0.1 – 6.0	0.3 – 2.0	100.0 – 100.0	0.5 – 4.0	0.6 – 1.6
C$_2$H$_2$	✓	✓	✘	✓	✓
ΔT	808.6 – 2319.0 K	711.25 – 953.14 K	–	600.0 – 1380.0 K	298.0 K
Δp	0.77 – 31.3 atm	9.04 – 30.37 atm	–	1.0 – 58.82 atm	1.0 – 2.0 atm
$\Delta \varphi$	0.06 – 2.0	0.5 – 2.0	–	0.05 – 5.56	0.6 – 2.0
C$_2$H$_4$	✓	✓	✓	✓	✓
ΔT	945.2 – 2226.3 K	773.0 – 990.33 K	597.81 – 1300.0 K	850.0 – 1163.0 K	298.0 K
Δp	0.94 – 40.98 atm	19.6 – 41.4 atm	1.0 – 59.22 atm	1.0 – 10.0 atm	1.0 – 5.0 atm
$\Delta \varphi$	0.3 – 3.0	0.5 – 2.0	0.5 – 10.0	0.75 – 2.5	0.6 – 1.6
C$_2$H$_5$OH	✓	✓	✓	✓	✓
ΔT	778.1 – 1669.8 K	650.0 – 983.12 K	799.0 – 1250.0 K	757.93 – 1400.5 K	298.0 – 428 K
Δp	1.8 – 91.5 atm	10.0 – 50.6 atm	1.0 – 10.0 atm	1.0 – 1.0 atm	1.0 atm
$\Delta \varphi$	0.25 – 2.0	0.3 – 2.0	0.25 – 2.0	0.03 – 1.37	0.5 – 1.7
C$_2$H$_6$	✓	✓	✓	✓	✓
ΔT	947.3 – 1862.0 K	830.0 – 999.0 K	895.5 – 1215.0 K	598.0 – 1073.0 K	298.0 K
Δp	0.57 – 40.56 atm	19.28 – 81.8 atm	1.0 – 1.0 atm	19.7 – 98.7 atm	1.0 – 10 atm
$\Delta \varphi$	0.1 – 2.0	0.5 – 2.0	0.1 – 1.5	0.034 – 47	0.5 – 1.6
C$_3$H$_6$	✓	✓	✓	✓	✓
ΔT	999.0 – 1820.0 K	0.0 – 1241.0 K	800.0 – 1426.0 K	800.0 – 1200.0 K	298.0 – 398 K
Δp	0.95 – 47.0 atm	0.0 – 41.62 atm	1.0 – 1.05 atm	1.0 – 15.0 atm	1.0 atm
$\Delta \varphi$	0.5 – 2.0	0.5 – 2.0	0.5 – 2.19	0.35 – 1.5	0.5 – 1.6
C$_3$H$_8$	✓	✓	✓	✓	✓
ΔT	847.5 – 2615.0 K	714.0 – 909.0 K	674.0 – 1350.0 K	548.0 – 1210.0 K	298.0 K

Δp	0.82 – 41.34 atm	30.0 – 50.0 atm	1.0 – 10.0 atm	1.0 – 98.7 atm	1.0 – 5.0 atm
$\Delta\varphi$	0.125 – 2.0	1.0	0.4 – 1.5	0.02 – 4.0	0.5 – 1.6
C$_3$H$_4$-a	✓	✗	✓	✗	✗
ΔT	1175.0 – 1896.0 K	–	801.6 – 1261.0 K	–	–
Δp	1.81 – 5.29 atm	–	1.0 – 10.0 atm	–	–
$\Delta\varphi$	0.5 – 2.0	–	0.2 – 2.0	–	–
C$_3$H$_4$-p	✓	✓	✓	✓	✗
ΔT	1131.0 – 2037.0 K	714.0 – 910.0 K	796.0 – 1265.0 K	1170 K	–
Δp	1.8 – 5.26 atm	10.0 – 30.0 atm	1.0 – 10.0 atm	1.0 atm	–
$\Delta\varphi$	0.5 – 2.0	0.5 – 2.0	0.2 – 2.0	0.7	–
C$_4$H$_6$	✓	✗	✗	✗	✓
ΔT	954.0 – 1781.7 K	–	–	–	298.0 K
Δp	0.91 – 42.05 atm	–	–	–	1.0 atm
$\Delta\varphi$	0.3 – 2.0	–	–	–	0.5 – 1.6
C$_4$H$_8$ –1	✓	✗	✗	✗	✓
ΔT	899.3 – 1834.5 K	–	–	–	298.0 K
Δp	1.19 – 53.14 atm	–	–	–	1.0 atm
$\Delta\varphi$	0.5 – 2.0	–	–	–	0.5 – 1.6
C$_4$H$_{10}$	✓	✗	✗	✗	✓
ΔT	1000.0 – 1430.7 K	–	–	–	298.0 K
Δp	1.0 – 45.05 atm	–	–	–	1.0 atm
$\Delta\varphi$	0.3 – 2.0	–	–	–	0.5 – 1.6
iC$_4$H$_8$	✓	✓	✗	✗	✓
ΔT	987.3 – 1436.5 K	712.0 – 976.0 K	–	–	298.0 – 398 K
Δp	10.0 – 50.0 atm	10.4 – 50.4 atm	–	–	1.0 atm
$\Delta\varphi$	0.3 – 2.0	0.3 – 1.0	–	–	0.5 – 1.6
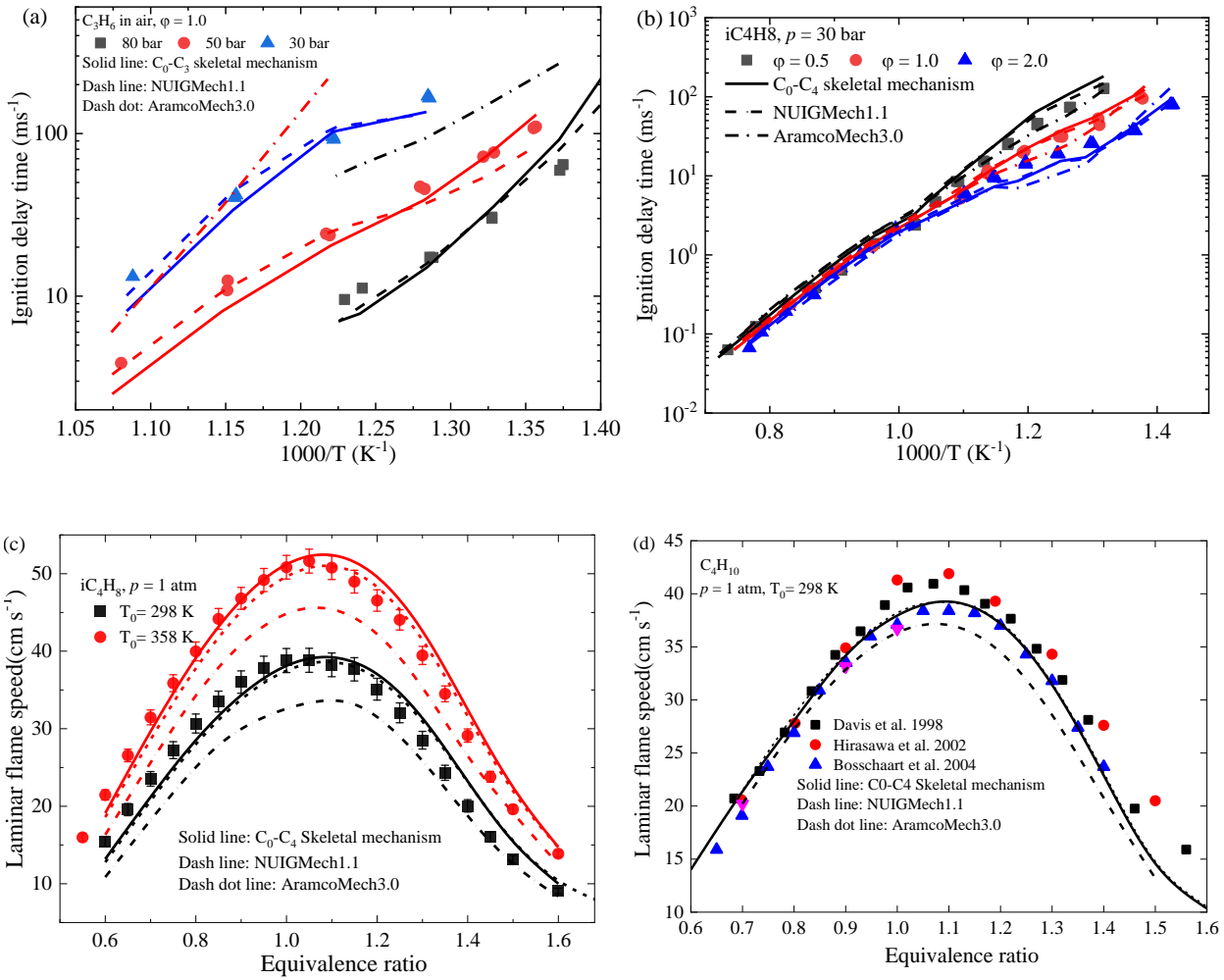
Fig.1. Comparisons of predicted IDTs and LFSs for important fuels by using the derived skeletal mechanisms, the detailed NUIGMech1.1 and AramcoMech3.0 mechanisms, respectively. (a) IDTs for propene;[20] (b) IDTs for isobutene;[41] (c)LFSs for isobutene;[41] (d)LFSs for *n*-butane: Davis et al.;[42] Hirasawa et al.;[43] Bosschaart et al.[44]
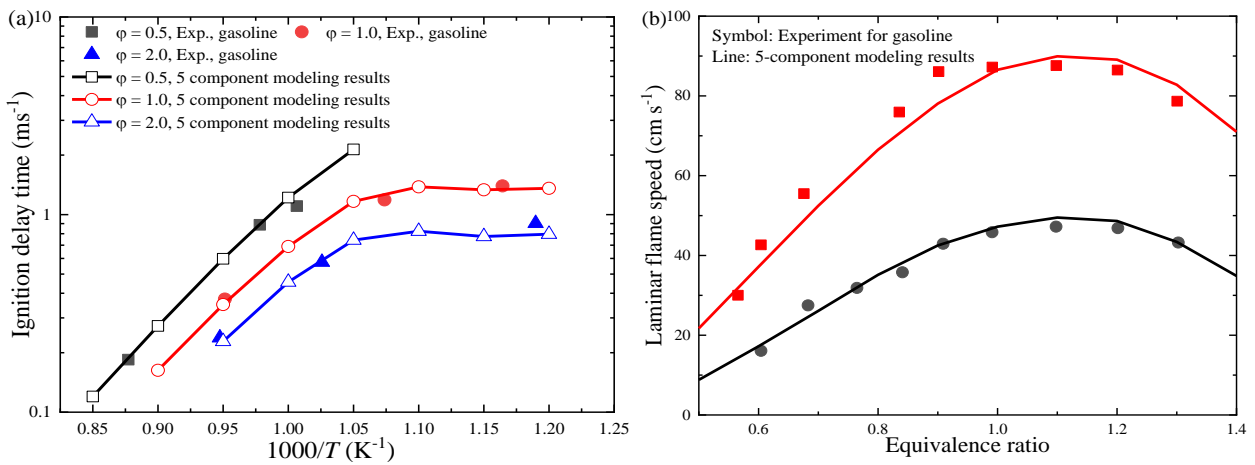
Fig. 2. Simulated ignition delay time and laminar flame speeds using the 5-component surrogate model with the reduced skeletal mechanism and comparisons with experimental data[45, 46] for gasoline/air mixtures.
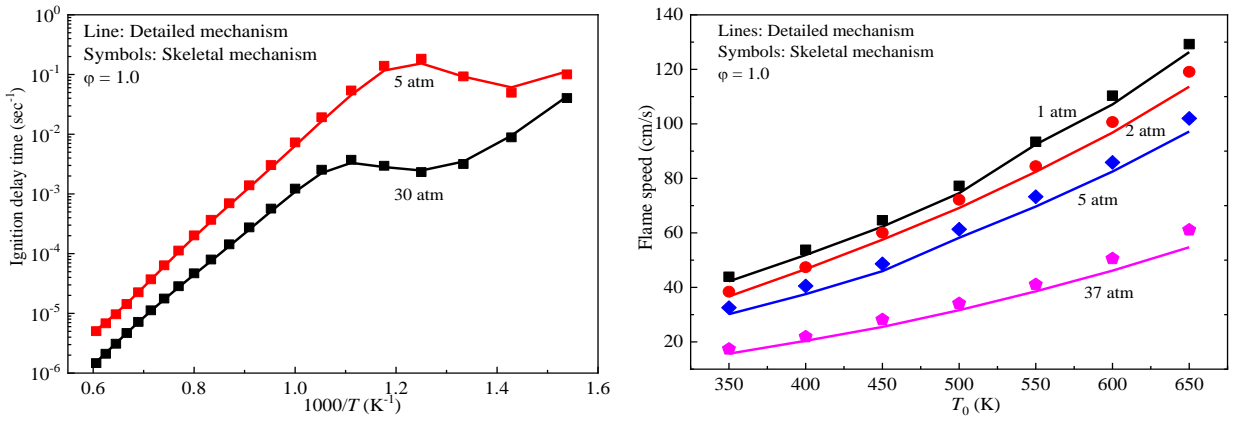
Fig.3. Validation of the reduced skeletal mechanism for 5-component surrogate model under typical engine conditions against the detailed kinetic model for fuel/air mixture.

TOC Graphic