A compact skeletal mechanism for *n*-dodecane with optimized semi-global low-temperature chemistry for diesel engine simulations

Tong Yao[1, 2, 3*], Yuanjiang Pei[4], Bei-Jing Zhong[2*], Sibendu Som[4], Tianfeng Lu[3] , Kai Hong Luo[1,5]

[1]*Center for Combustion Energy, Key Laboratory for Thermal Science and Power Engineering of Ministry of Education, Department of Thermal Engineering, Tsinghua University, Beijing 100084, China*

[2]*School of Aerospace Engineering, Tsinghua University, Beijing 100084, China*

[3]*Department of Mechanical Engineering, University of Connecticut, Storrs, CT 06269-3139, USA*

[4]*Energy System Division, Argonne National Laboratory, Argonne, IL-60439, USA*

[5]*Department of Mechanical Engineering, University College London, Torrington Place, London WC1E 7JE, UK*

[*]*Corresponding Authors: dy-369@163.com; zhongbj@tsinghua.edu.cn*

Abstract: A skeletal mechanism with 54 species and 269 reactions was developed to predict pyrolysis and oxidation of *n*-dodecane as a diesel fuel surrogate involving both high-temperature (high-T) and low-temperature (low-T) conditions. The skeletal mechanism was developed from a semi-detailed mechanism developed at the University of Southern California (USC). Species and reactions for high-T pyrolysis and oxidation of C_5-C_{12} were reduced by using reaction flow analysis, isomer lumping, and then merged into a skeletal C_0-C_4 core to form a high-T sub-mechanism. Species and lumped semi-global reactions for low-T chemistry were then added to the high-T sub-mechanism and a 54-species skeletal mechanism is obtained. The rate parameters of the low-T reactions were tuned against a detailed mechanism by the Lawrence Livermore National Laboratory (LLNL), as well as the Spray A flame experimental data, to improve the prediction of ignition delay at low-T conditions, while the high-T chemistry remains unchanged. The skeletal mechanism was

validated for auto-ignition, perfect stirred reactors (PSR), flow reactors and laminar premixed flames over a wide range of flame conditions. The skeletal mechanism was then employed to simulate three-dimensional turbulent spray flames at compression ignition engine conditions and validated against experimental data from the Engine Combustion Network (ECN).

Keywords: n-dodecane; surrogate; spray flames; ignition delay; skeletal mechanism

1. Introduction

Accurate prediction of diesel engine combustion requires realistic chemical kinetics. However, diesel fuels consist of a large number of components and involve an even larger number of intermediate species and reactions during the combustion process, and thus it is difficult to employ fully detailed mechanisms in practical engine simulations as the computational cost would be intractable. As a simplification, surrogate mixtures with one or a few components have been developed to mimic the physicochemical behaviors of the real diesel fuels [1]. For instance, *n*-dodecane features a molecular size close to that of average diesel components, and has been employed recently as a surrogate fuel to model diesel fuel combustion [2-12]. Detailed mechanisms for large hydrocarbons, e.g. *n*-dodecane, can consist of thousands of species and reactions when low temperature (low-T) chemistry is involved [13-17]. For instance, the detailed mechanism developed by Westbrook et al. [14] for *n*-alkanes from *n*-octane to *n*-hexadecane consists of 2775 species and 11,173 reactions. Such large mechanisms need to be reduced for computationally tractable three-dimensional (3-D) simulations.

Mechanism reduction has been extensively studied in the last few decades and a number of reduction methodologies have been brought up [18]. Reduced mechanisms can be obtained by removing unimportant species and reactions from the detailed mechanisms and lumping of similar species and reactions, using such methods as reaction flow analysis (RFA) [19], sensitivity analysis [20-22], principal component analysis (PCA) [23], detailed reduction [24], directed relation graph (DRG) [25-28] and variants[29-31], path flux analysis (PFA) [32] and isomer-lumping [33,34]. However, reduced mechanisms for practical engine fuels with low-T chemistry obtained by such methods may still be large [2,35]. For example, a

skeletal mechanism for *n*-dodecane developed by Luo *et al.* [2] consists of 106 species and 420 reactions. The mechanism was developed using DRG with expert knowledge (DRGX) [36] and DRGASA [30] based on a detailed LLNL mechanism [13]. This mechanism and its variants [7, 8] have been coupled to different turbulent combustion models in Spray A flame simulations [5,7-11] and compared with the experimental data from the Engine Combustion Network (ECN). Narayanaswamy *et al.* [37] reduced the detailed LLNL mechanism to a skeletal *n*-dodecane mechanism with 255 species and 2289 reactions through multi-stage reduction strategy involving DRGEP [29] and chemical lumping [33]. The reduced mechanism was implemented in a tabulated-chemistry combustion model by Ayyapureddi *et al.* [38] to simulate the Spray A flames. D'Errico *et al.* [39] developed a reduced mechanism of *n*-dodecane using a reduction algorithm combining sensitivity and flux analysis starting from a much smaller detailed mechanism that consists of 435 species and 13,532 reactions. This mechanism was also used to simulate the Spray A flames for validation under engine-relevant conditions. These mechanisms are still relatively large and can be expensive for engine simulations, especially when the mechanisms are coupled to advanced combustion models [5, 7, 9,10], or high-fidelity LES studies [11]. More importantly, all of these reduced mechanisms show increased errors in low ambient temperature conditions for Spray A flames, and thus a compact and more accurate mechanism is needed for engine simulations.

In the present work, multiple reduction methods, including RFA and isomer-lumping, will be employed to obtain a skeletal mechanism for n-dodecane based on a semi-detailed mechanism developed by You *et al.* [40]. The semi-detailed mechanism consists of 171 species and 1306 reactions and has been widely validated, which is a good candidate to start with. Semi-global reactions for low-T chemistry are merged to the skeletal mechanism and subsequently optimized to better predict the negative temperature coefficient (NTC) behavior. The final mechanism consists of 54 species and 269 reactions in the skeletal form and is validated against detailed mechanisms and available experimental data. The mechanism is further tuned for and applied in 3-D lifted diesel spray flame simulations.

2. Mechanism development

2.1 Skeletal mechanism development

For a range of conditions in ignition and combustion, the kinetics of fuel decomposition to smaller fragments, which is described by C_5-C_{12} sub-mechanism, is always fast and can be decoupled from the oxidation kinetics of the H_2 and C_1-C_4 fragments [40]. In the development of the skeletal mechanism, the C_5-C_{12} sub-mechanism from a detailed mechanism is firstly simplified by eliminating unimportant species and reactions, and isomer lumping is also employed. The simplified C_5-C_{12} sub-mechanism is then merged into the simplified H_2/CO/C_1-C_4 base mechanism. Lumped low-T reactions are then added and tuned, resulting in an optimized skeletal mechanism with 54 species and 269 reactions. The reduction and tuning procedure is further discussed in the following.

The detailed C_5-C_{12} mechanism developed by You *et al.* [40] consists of 60 species and 522 reactions. In the present study, reduction is based on data sampled from homogeneous, adiabatic, isobaric reactors. The parameter range covers pressure of 1–80 bar, equivalence ratio of 0.5–2.0, and initial temperature of 800–1600 K. RFA is first employed to quantify the contribution of each reaction to the generation and consumption of each species. Analysis is conducted from the reactant n-dodecane as the starting point. Reaction pathways that are not important to the consumption of *n*-dodecane are removed along with the species that the path leads to. Species associated with reaction pathways contributing e.g. 95% of the total consumption of *n*-dodecane are retained. This reduction is performed successively until all the retaining C_5-C_{12} species find their main pathways to translate into C_1-C_4 fragments. By further applying radical isomers equilibrium assumptions [34], isomers of n-dodecyl and other alkyls are lumped to three and one representatives, respectively. The reduced C_5-C_{12} sub-mechanism obtained after performing species and reactions elimination and isomer lumping consists of 18 species and 60 reactions. It is worth noting that fuel cracking process goes fast during the oxidation of n-dodecane and many intermediates are in steady state, only the main reaction pathways that are important for the decomposition of n-dodecane to fragments are needed to reproduce this process.

In order to obtain a compact C_0-C_4 sub-mechanism, the C_0-C_4 core in a reduced high-T mechanism for *n*-dodecane oxidation in Vie *et al.* [41] is adopted. This core is reduced from USC-MECH II (111 species and 784 reactions) [42] for high temperature oxidation (high-T). Two species, namely C_4H_7 and pC_4H_9, and the involved reactions are added to accommodate the C_5-C_{12} sub-mechanism and more accurately predict the C_4 species concentrations in pyrolysis, which was not considered by Vie *et al.* [41], resulting in a new C_0-C_4 core with 32 species and 191 reactions.

In the end, a semi-global scheme involving 4 species and 18 reactions for low-T chemistry of *n*-decane developed by Bikas and Peters [43] is modified to be suitable for *n*-dodecane and appended to the skeletal mechanism to capture the NTC behavior. Transition between low and high temperatures showing the negative temperature dependence can be well reproduced by applying the Low-T sub-mechanism with lumped reaction steps, which is rather efficient for practical engine simulations [43] and has been fully investigated for *n*-heptane in [44, 45]. A 54-species skeletal mechanism (SK54a) is thereby obtained, which can be found in the supplementary material.

2.2 Need for further tuning

The ignition delay time of SK54a is compared with experimental measurement by Vasu *et al.* [46] and detailed mechanisms [13, 40] in Fig. 1. Simulations were performed under constant-pressure, adiabatic conditions by the Senkin program package [47]. It is seen that the ignition delay time at low-T (~700 K) is significantly over-predicted by the You *et al.* mechanism [40] and SK54a while predictions by the LLNL [13] show improved agreement with experimental data.

3-D simulations of Spray A flames are further performed by a three-dimensional computational fluid dynamics code CONVERGE with the flame condition listed in Table 1. The simulation setup has been reported in our previous studies [9, 48] and will be briefly described here. The Reynolds-averaged Navier-Stokes (RANS) method is used along with the Re-normalization Group (RNG) k-ε turbulence model [49]. The traditional Lagrangian-Eulerian method is employed, where the liquid phase is treated as Lagrangian discrete parcels and the gas-phase is solved on a Eulerian mesh. Source terms are used to exchange mass, momentum, and energy between the two-phases. The “blob” injection method [50] is used with the Kelvin-

Helmholtz and Rayleigh-Taylor (KH-RT) model [51, 52] for primary and droplet secondary breakup. A dynamic drag model [53] was used to account for the droplet drag. Droplet evaporation is modeled using the Frossling correlation [54]. The gas phase reaction is modeled by a delta function combustion model [55]. The computational region is a cube with dimension of 108 mm in each direction. Adaptive mesh refinement (AMR) is employed to refine the mesh. The minimum cell size is 0.25 mm with peak cell counts in the order of one million. Based on a previous study, this resolution is deemed to be grid convergent for RANS calculations [56]. Lift-off length (LOL) and ignition delay data measured under a wide range of ambient conditions are used for validation of the developed n-dodecane skeletal mechanism. The conditions involve ambient gas temperature of 800-1100 K, fuel injection pressure of 150 MPa, ambient oxygen concentration of (X_{O2}) 15%, ambient gas density of 22.8 Kg/m^3. Ignition delay obtained using SK54a and the previous 106-species mechanism (SK106) [2] are compared with the ECN data [57-59] in Fig. 2 for different ambient temperatures. It is seen that the predictions at 1100 K and 1000 K are better for the SK54a mechanism, showing an advantage of SK54a at high temperatures. At 800 K, SK54a however significantly over-predicts the ignition delay (which is longer than 6 ms and not shown here), showing the need for further tuning of the semi-global low-T reactions.

2.3 Mechanism Tuning

Mechanism tuning is conducted against the detailed LLNL mechanism in auto-ignition. Although there are uncertainties in the detailed mechanism as well but at least with this approach the tuned mechanism will match a published detailed one, wherever experimental data is rare and more scattered. Simulations are performed under representative conditions of pressure p = 20 bar, initial temperature T_0 = 800 K and various equivalence ratios as shown in Fig. 3. It is seen that the ignition delay time is over-predicted by SK54a at lean conditions, while better agreement is observed for rich mixtures. As a result, ignition delay in Spray A flames predicted using SK54a at T = 800 K is expected to be longer than that of SK106 which is reduced from LLNL.

Sensitivity analysis is then performed using SK54a at p = 20 bar, ϕ = 0.5, 1.0, 2.0, and T_0 = 800 K in the NTC regime to identify the reactions important for low-T ignition. Sensitivity Coefficients (SC) are

defined as the resulting percentage change in the ignition delay time (τ) by doubling the rate constant of the *i*th reaction, *ki* [60].

$$SC_i = \frac{\tau(2k_i) - \tau(k_i)}{\tau(k_i)}$$

Eight reactions with the largest SC are selected and summarized in Fig. 4. Reactions with positive SC decelerate ignition and make ignition delays longer, and those with negative SC accelerate ignition and result in shorter ignition delays. Sensitivity analysis is also performed under other engine relevant conditions, for example p = 50 bar and 80 bar, which shows the same tendency as in p = 20 bar and is not showing here.

It can be seen from Fig. 4 that ignition delay times under fuel rich conditions (ϕ = 2.0) have larger sensitivity to Low-T reactions (R3, R4, R5) than lean conditions (ϕ = 0.5), which makes it impossible to change ignition delay time at lean conditions without affecting rich conditions by tuning these reactions. R1, R2, R6, R7 and R8 are involved in the high-T sub-mechanism and cannot be changed. Then we observed that R1 is more sensitive for lean conditions, for the formation of vinoxy radical (CH_2CHO) facilitates the chain branching of the overall reactivity and the facilitation is more inclined in lean conditions than rich conditions [60]. Although R1 cannot be tuned for its significant influence to high temperature oxidation, decomposition reaction of ketohydroperoxide $OC_{12}H_{23}OOH$ (R9) can be tuned to accelerate CH_2CHO formation which leads to small species through one step reaction ($OC_{12}H_{23}OOH \rightarrow CH_2O+3C_2H_4+C_2H_5+C_2H_3CHO+OH$). As the products of R9 are appointed arbitrarily with reference to Bikas and Peters [43], the $OC_{12}H_{23}OOH$ decomposition reaction is changed to the following formation: $OC_{12}H_{23}OOH \rightarrow 3C_2H_4+C_2H_5+2CH_2CHO+OH$, to produce vinoxy radicals (CH_2CHO) that can facilitate the chain branching of low temperature reactivity. And the rate constant of this reaction is tuned down by a factor of two to accommodate the new mechanism, resulting in SK54b mechanism, which can be found in the supplementary material. Performance of SK54b can be seen in Fig. 3, which shows improvement after the above tuning.

The tuned mechanism (SK54b) was then employed in 3-D Spray A flame simulations, and predictions of ignition delay time are shown in Fig. 5. Over-prediction of ignition delay by ~25% is still observed at the 800 K ambient temperature, which is also observed with SK106 in Fig.2. Since the first stage ignition was found to occur in the lean mixtures and the main ignition in rich mixture [11], ignition delay of rich cases (e.g., ϕ = 2.0) at 800 K is further tuned down by ~25% using another round of reaction tuning based on sensitivity analysis, resulting in a final mechanism (SK54).

The second round of sensitivity analysis is performed using SK54b to identify important low-T reactions that are sensitive to ignition delay times at p = 20 bar, ϕ = 0.5, 1.0, 2.0 and T_0 = 800 K, 900 K. Selected reactions with high sensitivities are shown in Fig. 6. It can be seen that R2 mostly facilitates ignition in all investigated cases with negative sensitivity coefficient. And R6 accelerates ignition of fuel rich condition and decelerates ignition of fuel lean condition at T_0 = 800 K, which however has little influence on ignition delay time at T_0 = 900 K. Therefore, tuning up rate constants of R2 and R6 will result in a further decrease of ignition delay time at ϕ = 2.0, T_0 = 800 K and ignition delay times at T_0 = 900 K and ϕ = 0.5, T = 800 K nearly unaffected. The tuning of these two reactions (R2 and R6) is conducted through careful trial and error, leading to the final mechanism (SK54), which can be found in the supplementary material. Performance of SK54 after this round of tuning can be found in Fig. 5. Improvement achieved can be seen here that ignition delay time at T_0 =800 K can be better reproduced by SK54.

3. Mechanism Validation

3.1 Validation for elementary reactors and flames

The mechanism is first validated for shock tube ignition delay data [46,61] at various pressures and equivalence ratios. Fig. 7 shows comparison between experimental data and predicted ignition delay for pressure of 20 bar and 50 bar, and various equivalence ratios. It is seen that the present mechanism agrees well with the experimental data, and the overall discrepancy is smaller than that using the detailed LLNL mechanism due to the tuning of low-T chemistry. It is therefore expected that the auto-ignition delay of

homogeneous mixtures can be more accurately captured for flames that fall within the above parameter range, which is relevant to the Spray A flame conditions.

To further verify the performance of the mechanisms, especially the simplified C_5-C_{12} fuel cracking sub-mechanism, pyrolysis of *n*-dodecane in stirred reactors [62] and flow reactors [63] was simulated with the present mechanism and compared with the experimental data by Herbinet *et al.* [64] and Dahm *et al.* [65]. Fig. 8 shows the comparison of the *n*-dodecane conversion rate calculated with different mechanisms [13, 40] in comparison with experimental data. Species profiles during the pyrolysis processes are further compared in Figs. 9-10. It is seen that the reduced mechanism shows overall similar accuracy in the different pyrolysis cases to that of the more detailed You *et al.* mechanism, for these two mechanisms share the high temperature chemistry, while the LLNL mechanism shows overall larger discrepancies.

Figure 11 shows extended validations of the laminar flame speed of *n*-dodecane/air mixtures during one-dimensional (1-D) flame simulations [66] evaluated using SK54 and You *et al.* mechanism [40], in comparison with experimental data in literature [67-69]. Agreement between SK54 and You *et al.* mechanism is of the order of the scatter of the experimental data at various conditions of pressures, inlet temperatures and equivalence ratios. This is expected since the flame speed is primarily controlled by high temperature chemistry, while You *et al.* mechanism and SK54 share the high temperature C_0-C_4 core, which has been extensively validated against flame speed data, although some discrepancy exists for the simplification. Also, the present skeletal mechanism is primarily developed for simulations of diesel engine relevant conditions for which absolutely accurate prediction of laminar flame speed is not so necessary [2].

3.2 Validation for 3-D spray flame simulations

The newly developed skeletal mechanism SK54 is further applied to simulate spray flames. The simulation results are compared with experimental data performed under compression-ignition (CI) engine conditions from the ECN [57,70-72]. The experimental and computational configurations are shown in Table 1. Details of the 3D simulations are described in section 2.2.

Figure 12 shows the comparison of experimental data and predicted ignition delay and LOL at fuel injection pressure of 150 MPa, ambient oxygen concentration of (XO_2) 15%, ambient gas density of 22.8 Kg/m^3 and various ambient temperatures. It is seen from Fig. 12a that the ignition delays are well reproduced at high temperatures (T > 1000 K), indicating the high fidelity of the high-T sub-mechanism in the skeletal mechanism. Some discrepancies are observed at low-T conditions wherein ignition delays are under-predicted at ambient temperatures of 900 K and 850 K, and slightly over-predicted at 800 K. The differences may be due to the simplification of the lumped low-T oxidation sub-mechanism. It is noted that the prediction at 800 K is within the experimental uncertainty range. The LOL comparison is reported in Fig. 12b. It is seen that the present mechanism accurately reproduces the experimental LOL data at both low and high temperature conditions. Overall, the predictions of the present mechanism are reasonably good compared to the measurements for the wide range of ambient temperatures investigated.

Figures 13 and14 show the comparisons of ignition delay and LOL between the experimental data and predictions at ambient gas temperature of 900 K, ambient gas density of 22.8 Kg/m^3, different fuel injection pressures and ambient oxygen concentrations. Overall, the simulations capture the experimental trends well. As the present mechanism under-predicts ignition delay at the condition T=900 K, all cases in Fig. 13a show about 10-20% shorter ignition delay time compared to the experimental data. Similar observation is made in Fig. 14a also at different oxygen concentrations. However, the predictions of LOL presented in Figs. 13b and 14b are in good agreement with experiments.

Comparisons of ignition delay and LOL at ambient gas temperature of 900 K, fuel injection pressure of 150 MPa, ambient oxygen concentration of (X_{O2}) 15% and different ambient densities are shown in Fig. 15. Again, the ignition delay is under-predicted with larger discrepancies at lower ambient densities. Overall, the ignition delay and LOL at these ambient densities are reasonably reproduced by the skeletal kinetic mechanism.

4. Conclusions

A compact skeletal mechanism with 54 species and 269 reactions was developed for *n*-dodecane using a hybrid and decoupling approach. The high temperature C_5-C_{12} mechanism module is firstly simplified from the detailed mechanism of You *et al*. [40] by eliminating unimportant species and reactions and isomer lumping, guided by RFA. The C_5-C_{12} sub-mechanism is then merged to a reduced C_0-C_4 core based on the USC-Mech II [42]. Semi-global reactions for NTC chemistry are added and tuned against the detailed LLNL mechanism and experimental data to eventually obtain a 54-species skeletal mechanism.

The tuned mechanism was validated against experimental data for shock tubes, stirred reactors, flow reactors, and laminar flame speed, and compared with other mechanisms. It is shown that the skeletal mechanism performs well over a wide range of parameters in elementary flame experiments. Furthermore, the skeletal mechanism was applied for 3-D Spray A flame simulations. Comparison with experimental data obtained from the ECN shows that the ignition delay and flame LOL are reasonably well reproduced by the tuned skeletal mechanism under various conditions, thus providing a valid option for efficient and accurate multi-dimensional engine combustion simulations.

5. Acknowledgements

This work was supported by the National Science Foundation and the Department of Energy through the NSF-DOE Partnership on Advanced Combustion Engines Program under Grant CBET-1258646. The work at Tsinghua was supported by the Natural Science Foundation of China under Contracts No. 91441113 and No. 91441120.

The submitted manuscript has been created by UChicago Argonne, LLC, Operator of Argonne National Laboratory ("Argonne"). Argonne, a U.S. Department of Energy Office of Science laboratory, is operated under Contract No. DE-AC02-06CH11357. This research was funded by DOE's Office of Vehicle Technologies, Office of Energy Efficiency and Renewable Energy under Contract No. DE-AC02-06CH11357. The authors wish to thank Gurpreet Singh and Leo Breton, program managers at DOE, for their support.

We gratefully acknowledge the computing resources provided on "Fusion," a 320-node computing cluster operated by the Laboratory Computing Resource Center at Argonne National Laboratory. We also acknowledge Convergent Sciences Inc. for providing us with the CONVERGE software and related support.

6. Supplementary material

Supplementary data including newly developed mechanisms (SK54a, SK54b, SK54) associated with this article can be accessed on online.

7. References

[1] Pitz WJ, Mueller CJ. Recent progress in the development of diesel surrogate fuels. Prog Energy Combust Sci 2011;37(3):330–50.

[2] Luo Z, Som S, Sarathy SM, Plomer M, Pitz WJ, Longman DE, et al. Development and validation of an *n*-dodecane skeletal mechanism for spray combustion applications. Combust Theory Model 2014;18(2):187–203.

[3] Wang H, Ra Y, Jia M, Reitz RD. Development of a reduced *n*-dodecane-PAH mechanism and its application for *n*-dodecane soot predictions. Fuel 2014;136(10):25–36.

[4] Gong C, Jangi M, Bai XS. Large eddy simulation of *n*-dodecane spray combustion in a high pressure combustion vessel. Appl Energy 2014; 136:373–81.

[5] Bhattacharjee S, Haworth DC. Simulations of transient *n*-heptane and *n*-dodecane spray flames under engine-relevant conditions using a transported PDF method. Combust Flame 2013;160(10):2083–102.

[6] Manin J, Bardi M, Pickett LM, Dahms RN, Oefelein JC. Microscopic investigation of the atomization and mixing processes of diesel sprays injected into high pressure and temperature environments. Fuel 2014;134(9):531–43.

[7] Pei Y, Hawkes ER, Kook S, Goldin GM, Lu T. Modeling *n*-dodecane spray and combustion with the transported probability density function method. Combust Flame 2015;162(5):2006–19.

[8] Som S, Longman DE, Luo Z, Plomer M, Lu T. Three dimensional simulations of diesel sprays using *n*-dodecane as a surrogate. In: Fall Technical Meeting of Eastern States Section of the Combustion Institute, USA; 2011.

[9] Kundu P, Pei Y, Wang M, Mandhapati R, Som S. Evaluation of turbulence-chemistry interaction under diesel engine conditions with multi-flamelet RIF model. Atomization and Sprays 2014;24(9):779–800.

[10] D'Errico G, Lucchini T, Contino F, Jangi M, Bai X-S. Comparison of well-mixed and multiple representative interactive flamelet approaches for diesel spray combustion modelling. Combust Theory Model 2014;18(1):65–88.

[11] Pei Y, Kundu P, Goldin GM, Som S. Large eddy simulation of a reacting spray flame under diesel engine conditions. SAE Paper 2015: 2015-01-1844.

[12] Pei Y, Davis MJ, Pickett LM, Som S. Engine Combustion Network (ECN): Global sensitivity analysis of Spray A for different combustion vessels. Combust Flame 2015;162(6):2337–47.

[13] Sarathy SM, Westbrook CK, Mehl M, Pitz WJ, Togbe C, Dagaut P, et al. Comprehensive chemical kinetic modeling of the oxidation of 2-methylalkanes from C_7 to C_{20}. Combust Flame 2011;158(12):2338–57.

[14] Westbrook CK, Pitz WJ, Herbinet O, Curran HJ, Silke EJ. A comprehensive detailed chemical kinetic reaction mechanism for combustion of n-alkane hydrocarbons from n-octane to n-hexadecane. Combust Flame 2009;156(1):181–99.

[15] Mzéahmed A, Hadjali K, Dagaut P, Dayma G. Experimental and modeling study of the oxidation kinetics of *n*-undecane and *n*-dodecane in a Jet-Stirred Reactor. Energy Fuels 2012; 26(7):4253-68.

[16] Biet J, Hakka MH, Warth V, Glaude P-A, Battin-Leclerc F. Experimental and modeling study of the low-temperature oxidation of large alkanes. Energy Fuels 2008;22(4):2258–69.

[17] Battin-Leclerc F. Detailed chemical kinetic models for the low-temperature combustion of hydrocarbons with application to gasoline and diesel fuel surrogates. Prog Energy Combust Sci 2008;34(4):440–98.

[18] Lu T, Law CK. Toward accommodating realistic fuel chemistry in large-scale computations. Prog Energy Combust Sci 2009;35(2):192–215.

[19] Warnatz J, Maas U, Dibble RW. Combustion: physical and chemical fundamentals, modeling and simulation, experiments, pollutant formation. Springer; 2006.

[20] Rabitz H, Kramer M, Dacol D. Sensitivity analysis in chemical kinetics. Annu Rev Phys Chem 1983;34(1):419–61.

[21] Tomlin AS, Pilling MJ, Turányi T, Merkin JH, Brindley J. Mechanism reduction for the oscillatory oxidation of hydrogen: sensitivity and quasi-steady-state analyses. Combust Flame 1992;91(2):107–30.

[22] Turányi T. Sensitivity analysis of complex kinetic systems. Tools and applications. J Math Chem 1990;5(3):203–48.

[23] Vajda S, Valko P, Turanyi T. Principal component analysis of kinetic models. Int J Chem Kinet 1985;17(1):55–81.

[24] Wang H, Frenklach M. Detailed reduction of reaction mechanisms for flame modeling. Combust Flame 1991;87(3):365–70.

[25] Lu T, Law CK. A directed relation graph method for mechanism reduction. Proc Combust Inst 2005;30(1):1333–41.

[26] Lu T, Law CK. Linear time reduction of large kinetic mechanisms with directed relation graph: *n*-Heptane and *iso*-octane. Combust Flame 2006;144(1):24–36.

[27] Lu T, Law CK. On the applicability of directed relation graphs to the reduction of reaction mechanisms. Combust Flame 2006;146(3):472–83.

[28] Luo Z, Lu T, Maciaszek MJ, Som S, Longman DE. A reduced mechanism for high-temperature oxidation of biodiesel surrogates. Energy Fuels 2010;24(12):6283–93.

[29] Pepiot-Desjardins P, Pitsch H. An efficient error-propagation-based reduction method for large chemical kinetic mechanisms. Combust Flame 2008;154(1):67–81.

[30] Zheng XL, Lu T, Law CK. Experimental counterflow ignition temperatures and reaction mechanisms of 1, 3-butadiene. Proc Combust Inst 2007;31(1):367–75.

[31] Lu T, Law CK. Strategies for mechanism reduction for large hydrocarbons: *n*-heptane. Combust Flame 2008;154(1):153–63.

[32] Sun W, Chen Z, Gou X, Ju Y. A path flux analysis method for the reduction of detailed chemical kinetic mechanisms. Combust Flame 2010;157(7):1298–307.

[33] Pepiot-Desjardins P, Pitsch H. An automatic chemical lumping method for the reduction of large chemical kinetic mechanisms. Combust Theory Model 2008;12(6):1089–108.

[34] Zeppieri SP, Klotz SD, Dryer FL. Modeling concepts for larger carbon number alkanes: a partially reduced skeletal mechanism for *n*-decane oxidation and pyrolysis. Proc Combust Inst 2000;28(2):1587–95.

[35] Saylam A, Ribaucour M, Pitz WJ, Minetti R. Reduction of large detailed chemical kinetic mechanisms for autoignition using joint analyses of reaction rates and sensitivities. Int J Chem Kinet 2007;39(4):181–96.

[36] Lu T, Plomer M, Luo Z, Sarathy SM, Pitz WJ, Som S, et al. Directed relation graph with expert knowledge for skeletal mechanism reduction. in: 7th US National Combustion Meeting, 2011.

[37] Narayanaswamy K, Pepiot P, Pitsch H. A chemical mechanism for low to high temperature oxidation of *n*-dodecane as a component of transportation fuel surrogates. Combust Flame 2014;161(4):866–84.

[38] Ayyapureddi S, Egüz U, Bekdemir C, Somers LMT, De Goey LPH. Application of the FGM method to spray conditions of the ECN database. in: The 12th Triennial International Conference on Liquid Atomization and Spray Systems, Heidelberg, Germany: 2012.

[39] D'Errico G, Lucchini T, Stagni A, Frassoldati A, Faravelli T, Ranzi E. Reduced kinetic mechanisms for diesel spray combustion simulations. SAE Technical Paper 2013.

[40] You X, Egolfopoulos FN, Wang H. Detailed and simplified kinetic models of *n*-dodecane oxidation: The role of fuel cracking in aliphatic hydrocarbon combustion. Proc Combust Inst 2009;32(1):403–10.

[41] Vié A, Franzelli B, Gao Y, Lu T, Wang H, Ihme M. Analysis of segregation and bifurcation in turbulent spray flames: A 3D counterflow configuration. Proc Combust Inst 2015;35(2):1675–83.

[42] Wang H, You X, Joshi AV, Davis SG, Laskin A, Egolfopoulos F, et al. USC MECH Version II High-temperature combustion reaction model of H_2/CO/C_1-C_4 compounds, 2007. <http://ignis.usc.edu/USC_Mech_II.htm>.

[43] Bikas G, Peters N. Kinetic modelling of *n*-decane combustion and autoignition. Combust Flame 2001;126(1):1456–75.

[44] Peters N, Paczko G, Seiser R, Seshadri K. Temperature cross-over and non-thermal runaway at two-stage ignition of *n*-heptane. Combust Flame 2002;128(1-2):38–59.

[45] Kazakov A, Chaos M, Zhao Z, Dryer FL. Computational singular perturbation analysis of two-stage ignition of large hydrocarbons. J Phys Chem A 2006;110(21):7003–9.

[46] Vasu SS, Davidson DF, Hong Z, Vasudevan V, *n*-Dodecane oxidation at high-pressures: Measurements of ignition delay times and OH concentration time-histories. Proc Combust Inst 2009;32(1):173–80.

[47] Lutz AE, Kee RJ, Miller JA. SENKIN: A FORTRAN program for predicting homogeneous gas phase chemical kinetics with sensitivity analysis. Sandia National Laboratories: Livermore, CA, 1988; Sandia National Laboratories Report SAND-87-8248.

[48] Pei Y, Mehl M, Liu W, Lu T, Pitz WJ, Som S. A multicomponent blend as a diesel fuel surrogate for compression ignition engine applications. ASME. J. Eng. Gas Turbines Power. 2015;137(11):111502-111502-9.

[49] Han Z, Reitz RD. Turbulence modeling of internal combustion engines using RNG κ-ε models. Combust Sci Technol 1995;106(4-6):267–95.

[50] Reitz RD, Diwakar R. Structure of high-pressure fuel sprays. SAE Technical Paper, 870598; 1987.

[51] Reitz RD. Modeling atomization processes in high-pressure vaporizing sprays. Atomisation and Spray Technol 1987;3:309–37.

[52] Patterson MA, Reitz RD. Modeling the effects of fuel spray characteristics on diesel engine combustion and emission. In: International congress and exposition, Detroit, MI; 1998.

[53] Liu AB, Mather DK, Reitz RD. Modeling the effects of drop drag and breakup on fuel sprays. In: Proceedings of the international SAE congress and exposition, Detroit, MI; 1993.

[54] Frossling N. Evaporation, heat transfer, and velocity distribution in two dimensional and rotationally symmetrical laminar boundary-layer flow. N.A.C.A. 1956; 168: AD-B189

[55] Senecal PK, Pomraning E, Richards KJ, Briggs TE, Choi CY, McDavid RM, et al. Multi-dimensional modeling of direct-injection diesel spray liquid length and flame lift-off length using CFD and parallel detailed chemistry. SAE Technical Paper, 2003-01-1043; 2003.

[56] Senecal PK, Pomraning E, Richards KJ, Som S. Grid-convergent spray models for internal combustion engine CFD simulations. J Energy Res Technol 2013;136(1):12204.

[57] Sahetchian K, Champoussin JC, Brun M, Levy N, Blin-Simiand N, Aligrot C, et al. Experimental study and modeling of dodecane ignition in a Diesel engine. Combust Flame 1995;103(3):207–20.

[58] Pickett LM, Genzale CL, Bruneaux G, Malbec L-M, Hermant L, Christiansen CA, et al. Comparison of diesel spray combustion in different high-temperature, high-pressure facilities. SAE Int J Engines 2010;3(2):156–81.

[59] Pickett L, Bruneaux G, Payri R. Engine combustion network. Sandia National Laboratories, Livermore, CA, 2014. <http://www.ca.sandia.gov/ecn>.

[60] Kumar K, Mittal G, Sung C-J, Law CK. An experimental investigation of ethylene/O_2/diluent mixtures: Laminar flame speeds with preheat and ignition delays at high pressures. Combust Flame 2008;153(3):343–54.

[61] Pfahl U, Fieweger K, Adomeit G. Self-ignition of diesel-relevant hydrocarbon-air mixtures under engine conditions. in: Symposium (International) on Combustion, 1996; Elsevier: pp 781-789.

[62] Glarborg P, Kee RJ, Grcar JF, Miller JA. PSE: A Fortran program for modeling well-stirred reactors; Sandia National Laboratories: Livermore, CA, 1986; Sandia National Laboratories Report SAND-86-8209.

[63] Larson RS. PLUG: A Fortran program for the analysis of plug flow reactors with gas-phase and surface chemistry. Sandia National Laboratories: Livermore, CA, 1986; Sandia National Laboratories Report SAND-96-8211.

[64] Herbinet O, Marquaire P-M, Battin-Leclerc F, Fournet R. Thermal decomposition of *n*-dodecane: Experiments and kinetic modeling. J Anal Appl Pyrolysis 2007;78(2):419–29.

[65] Dahm KD, Virk PS, Bounaceur R, Battin-Leclerc F, Marquaire PM, Fournet R, et al. Experimental and modelling investigation of the thermal decomposition of *n*-dodecane. J Anal Appl Pyrolysis 2004;71(2):865–81.

[66] Kee RJ, Grcar JF; Smooke MD, Miller JA. A Fortran program for modeling steady laminar one-dimensional premixed flames; Sandia National Laboratories: Livermore, CA, 1985; Sandia National Laboratories Report SAND-85-8240.

[67] Ji C, Dames E, Wang YL, Wang H, Egolfopoulos FN. Propagation and extinction of premixed C_5–C_{12} *n*-alkane flames. Combust Flame 2010;157(2):277–87.

[68] Kumar K, Sung C-J. Laminar flame speeds and extinction limits of preheated *n*-decane/O_2/N_2 and *n*-dodecane/O_2/N_2 mixtures. Combust Flame 2007;151(1):209–24.

[69] Hui X, Sung C-J. Laminar flame speeds of transportation-relevant hydrocarbons and jet fuels at elevated temperatures and pressures. Fuel 2013;109:191–200.

[70] Pickett LM, Manin J, Genzale CL, Siebers DL, Musculus MP, Idicheria CA. Relationship between diesel fuel spray vapor penetration/dispersion and local fuel mixture fraction. SAE Int J Engines 2011;4(1):764–99.

[71] Payri R, García-Oliver JM, Bardi M, Manin J. Fuel temperature influence on diesel sprays in inert and reacting conditions. Appl Therm Eng 2012;35:185–95.

[72] Benajes J, Payri R, Bardi M, Martí-Aldaraví P. Experimental characterization of diesel ignition and lift-off length using a single-hole ECN injector. Appl Therm Eng 2013;58(1):554–63.