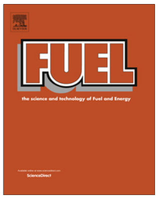
Fuel 191 (2017) 339–349

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel



Full Length Article

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

Tong Yao [a,b,c,*], Yuanjiang Pei [d], Bei-Jing Zhong [b,*], Sibendu Som [d], Tianfeng Lu [c], Kai Hong Luo [a,e]

[a] *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*
[b] *School of Aerospace Engineering, Tsinghua University, Beijing 100084, China*
[c] *Department of Mechanical Engineering, University of Connecticut, Storrs, CT 06269-3139, USA*
[d] *Energy System Division, Argonne National Laboratory, Argonne, IL 60439, USA*
[e] *Department of Mechanical Engineering, University College London, Torrington Place, London WC1E 7JE, UK*

ARTICLE INFO

Article history:
Received 13 August 2016
Received in revised form 7 November 2016
Accepted 22 November 2016
Available online 1 December 2016

Keywords:
n-Dodecane
Surrogate
Spray flames
Ignition delay
Skeletal mechanism

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 (RFA), 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 remained unchanged. The skeletal mechanism was validated for auto-ignition, perfectly 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).

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]. Despite of the multi-component nature of diesel fuels, single-component surrogate can also be useful in predicting selected flame behaviors of diesel fuels at relatively lower computational cost compared with the multi-component surrogates. For instance, *n*-heptane has been widely adopted as a diesel surrogate [2–4]. The number of carbon atoms in practical diesel fuels can range from 10 to 25. Compared with *n*-heptane, *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 [5–15]. Moreover, *n*-dodecane features boiling characteristics in the mid-range of diesel fuels, hence is expected to better mimic the fuel-air mixing processes associated with spray evaporation than *n*-heptane. 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 [16–20]. For instance, the detailed mechanism developed by Westbrook et al. [17] 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 developed [21]. Reduced mechanisms can be obtained by removing

---

* Corresponding authors at: 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 (T. Yao).

E-mail addresses: dy-369@163.com (T. Yao), zhongbj@tsinghua.edu.cn (B.-J. Zhong).

http://dx.doi.org/10.1016/j.fuel.2016.11.083
0016-2361/

unimportant species and reactions from the detailed mechanisms and lumping of similar species and reactions, using such methods as reaction flow analysis (RFA) [22], sensitivity analysis [23–25], principal component analysis (PCA) [26], detailed reduction [27], directed relation graph (DRG) [28–31] and variants[32–34], path flux analysis (PFA) [35] and isomer-lumping [36,37]. However, reduced mechanisms for large hydrocarbon fuels with low-T chemistry obtained by such methods may still be large [5,38–42]. For example, a skeletal mechanism for *n*-dodecane developed by Luo et al. [5] consists of 106 species and 420 reactions. The mechanism was developed using DRG with expert knowledge (DRGX) [39] and DRGASA [33] based on a detailed LLNL mechanism [17]. This mechanism and its variants [10,11] were coupled to different turbulent combustion models in Spray A flame simulations [8,10–14] and compared with the experimental data from the Engine Combustion Network (ECN). Narayanaswamy et al. [40] reduced the improved detailed LLNL mechanism [16] to a skeletal *n*-dodecane mechanism with 255 species and 2289 reactions through multi-stage reduction strategy involving DRGEP [32] and chemical lumping [36]. The reduced mechanism was implemented in a tabulated-chemistry combustion model by Ayyapureddi et al. [41] to simulate the Spray A flames. D'Errico et al. [42] developed two reduced mechanisms of *n*-dodecane (104 species and 1335 reactions, 88 species and 1158 reactions) 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. These two mechanisms were 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 [8,10,12,13], or high-fidelity LES studies [14]. 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, are employed to obtain a skeletal mechanism for *n*-dodecane based on a semi-detailed mechanism developed by You et al. [43]. The semi-detailed mechanism consists of 171 species and 1306 reactions and has been extensively validated for high temperature (high-T) conditions, 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 fast at high-T conditions and can be decoupled from the oxidation kinetics of the H_2 and C_1-C_4 fragments [43]. In the development of the skeletal mechanism, the C_5-C_{12} sub-mechanism from a detailed mechanism is first 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 procedures are further discussed in the following.

The detailed C_5-C_{12} mechanism developed by You et al. [43] 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 these paths lead to. Species associated with reaction pathways accumulatively contributing to, for example, 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 [37], 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 is fast at high-T conditions 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 by Vie et al. [44] is adopted. This core was reduced from USC-MECH II (111 species and 784 reactions) [45] for high-T oxidation. 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 is not considered by Vie et al. [44], 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 [46] is modified to be suitable for *n*-dodecane and appended to the skeletal mechanism to capture the NTC behavior. Transition between low-T and high-T conditions 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 [46] and has been fully investigated for *n*-heptane in [47,48]. 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 times predicted by SK54a are compared with experimental measurements by Vasu et al. [49] and detailed mechanisms [16,43] in Fig. 1. Simulations are performed under constant-pressure, adiabatic conditions by the SENKIN program [50]. It is seen that the ignition delay times at low-T conditions ($T < 900$ K) are significantly over-predicted by the You et al. mechanism [43] and SK54a while predictions by the LLNL [16] 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 experimental flame conditions listed in Table 1. The simulation setup has been reported in our previous studies [12,51] 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 [52]. The traditional Lagrangian-Eulerian method is employed, where the liquid phase