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Experimental validation and analysis of seven different chemical kinetic mechanisms for n-dodecane using a Rapid Compression-Expansion Machine

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ABSTRACT

Seven different chemical kinetic mechanisms for n-dodecane, two detailed and five reduced, have been evaluated under Engine Combustion Network (ECN) thermodynamic conditions by comparison to experimental measurements in a Rapid Compression-Expansion Machine (RCEM). The target ECN conditions are imposed at Top Dead Center (TDC), which cover a wide range of temperatures (from 850 *K* to 1000 *K*), oxygen molar fractions (0.21 and 0.15) and equivalence ratios (0.8, 0.9 and 1), while the pressure is fixed to keep a constant density at TDC equal to 22.8 kg/m^3. The results obtained have been used to validate the chemical kinetic simulations, which have been performed with CHEMKIN, by comparing both cool flames and high temperature ignition delays, as well as the heat released in each stage of the combustion process in case of having a two-stage ignition pattern. The experimental results show good agreement with the chemical kinetic simulations. In fact, the mean relative deviation in ignition delay between experiments and simulations among all the chemical mechanisms is equal to 18.0% (3 *CAD*) for both cool flames and high temperature ignition. In general, closer correspondence has been obtained for the ignition delay referred to the high-temperature stage of the process, being the cool flames phenomenon more difficult to reproduce. Moreover, the differences between the reduced mechanisms and the most detailed one have been analyzed, concluding that the enhanced specific reaction rates of the most reduced mechanisms cause differences not only on the ignition delays, but also on the Negative Temperature Coefficient (NTC) behavior and on the heat released during cool flames.

1. Introduction, justification and objective

The Engine Combustion Network (ECN) is a worldwide group of institutions in which an experimental and modeling collaboration dedicated to the improvement of the spray and combustion knowledge under engine conditions is performed. The ECN database is composed by quantitative information about reacting and non-reacting sprays, including spray characteristics related to evaporation and mixing, such as the liquid and vapor penetration lengths or the spray angle, as well as other characteristics related to combustion, such as the lift-off length or the ignition delay. These data are usually obtained from combustion vessels under fully-controlled high-temperature and high-pressure conditions, providing high-quality information for the improvement of Computational Fluid Dynamics (CFD) models under realistic engine conditions. For instance, some contributions to the ECN experimental database have been performed by Pickett et al. [1] or Malbec et al. [2], while the use of such database for model validation can be seen in the works of Pei et al. [3] or Novella et al. [4].

A current topic at ECN is the analysis of the effects of using different chemical kinetic mechanisms in CFD applications [5]. Although ignition can be properly simulated by means of advanced CFD codes coupled to detailed chemistry, the required computing time can be too long, since the conservation of species equations for all the species involved in the mechanism have to be solved for each cell of the domain. This is the reason why the higher the spatial resolution, the simpler the chemical mechanism employed to solve the reaction paths, i.e., the use of detailed chemical kinetic mechanisms coupled to CFD codes is limited by the physical discretization of the domain. Thus, the computational cost of solving detailed chemistry in cases with a high number of cells could be unacceptable, imposing the use of reduced mechanisms.

The reduction of a chemical kinetic mechanism can be performed following different strategies [6], as e.g., principal component analysis [7], sensitivity analysis [8], Jacobian analysis [9],

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Notation

A	pre-exponential factor for the Arrhenius expression
BDC	bottom dead center
CFD	computational fluid dynamics
CR	compression ratio
Da	damköhler number
DRG	directed relation graph
$DRGASA$	directed relation graph-aided sensitivity analysis
$DRG-X$	directed relation graph with expert knowledge
Ea	activation energy for the Arrhenius expression
ECN	engine combustion network
EGR	exhaust gas recirculation
Fr	working equivalence ratio
$LLNL$	Lawrence Livermore national laboratory
n	temperature index for the Arrhenius expression
NTC	negative temperature coefficient
P	pressure
P_i	initial pressure
PAH	polycyclic aromatic hydrocarbons
$Q_{cool\_flames}/Q_{released}$	percent of heat released during cool flames with respect to the total amount of heat
R^2	Pearson's coefficient of correlation
$RCEM$	rapid compression-expansion machine
T_i	initial temperature
TDC	top dead center
$t_{i,\,1}$	ignition delay referred to cool flames
$t_{i,\,2}$	ignition delay referred to the high-temperature stage of the process
$t_{i,2-1}$	time interval between cool flames and the high-temperature ignition stage
X_{O2}	oxygen molar fraction
ϵ	percentage deviation in ignition delay between experimental and simulation results
$\lvert\bar{\epsilon}\rvert$	mean absolute deviation between experimental and simulation results
τ	ignition delay under constant conditions of pressure and temperature

detailed reduction [10], directed relation graph (DRG) [11] or path flux analysis [12], among others. An evaluation of the skeletal mechanism accuracy relative to that of the original one has great interest as a method to analyze the mechanism reduction process. It should be noted that the more complex the hydrocarbon, the higher the number of species and reactions needed to describe its oxidation. For instance, one of the most detailed mechanisms to describe the n-dodecane oxidation has been developed by Lawrence Livermore National Laboratory (LLNL) [13], and it is composed by 2885 species and 11754 reactions. However, it is important to note that even detailed chemical kinetic mechanisms have to be validated by comparison to experimental results over a wide range of temperatures, pressures and equivalence ratios. This detailed chemical kinetic mechanism has been reduced by several authors in order to obtain skeletal mechanisms that can be more easily coupled to CFD codes to perform spray simulations in the frame of the ECN, where n-dodecane is the standard fuel.

Lu et al. [14] reduced the detailed mechanism for n-dodecane from LLNL using a combination of a DRG with expert knowledge (DRG-X) method and a DRG combined with sensitivity analysis (DRGASA), both coupled with isomer lumping. The resulting mechanism is composed by 163 species and 887 reactions. The DRG-X method tries to reduce a give mechanism paying attention to a given combustion parameter that is intended to be correctly predicted. To do so, the main chemical paths, as well as the corresponding more relevant species are identified. Thus, high accuracy is imposed for the relevant species while higher errors are allowed for the other species. This reduced mechanism has been successfully applied to CFD spray simulations. However, experimental validation under homogeneous conditions should be performed to decouple the accuracy of the CFD models from the accuracy of the mechanism itself.

Luo et al. [15] developed a skeletal mechanism for n-dodecane with 105 species and 420 reactions, specially adjusted for spray combustion simulations. An algorithm combining DRG-X and sensitivity analysis was employed for the reduction. The skeletal mechanism was validated by comparison to the detailed one according to autoignition characteristics, jet stirred reactor results, laminar premixed flame velocities and diffusion flame velocities. Moreover, an additional validation was performed in CFD spray combustion simulations under engine conditions. However, a wide experimental validation under homogeneous conditions, where the chemical kinetics can be traced, for high pressures as the ones reached in diesel engines is needed.

Narayanaswamy et al. [16] proposed a reduced chemical kinetic mechanism composed by 225 species and 1509 reactions that describes the oxidation of n-dodecane. Despite the fact that the skeletal mechanism includes both the low and high-temperature oxidation paths, which are based on [13] and [17], respectively, some specific reaction rates were changed to improve the calculations. Besides, this mechanism also includes aromatic chemistry from [18]. A wide validation has been performed by comparison to experimental data from shock tubes, rapid compression machines, pressurized flow reactors and burners; and not only according to ignition delays, but also according to species concentrations and burning velocities. However, most of this extensive validation was carried out at low pressures (from 7 *bar* to 40 *bar*), and an extension to ECN conditions (P$\approx$ 60 *bar*) can be interesting.

Wang et al. [19] proposed a skeletal chemical kinetic mechanism for n-dodecane composed by 100 species and 432 reactions, which was reduced from the archived detailed mechanism for n-alkanes developed by the LLNL [20]. The mechanism includes a PAH sub-mechanism for soot production and oxidation and it was compared with the optical measurements carried out in a constant volume vessel from the ECN by coupling the mechanism with a soot model. Simulations can reproduce the main trends of the soot formation process. However, unsuccessful comparisons versus a reference n-heptane mechanism [21] show that the n-dodecane mechanism tends to predict shorter ignition delays under spray combustion conditions, although the predicted ignition delays of n-heptane are very close (or even shorter) to the values for n-dodecane under homogeneous conditions, which is nonsense. Therefore, chemical kinetic mechanisms should be continuously improved, specially those that describe such a long chain hydrocarbon as n-dodecane.

Yao et al. [22] developed a skeletal mechanism with 54 species and 269 reactions to predict the n-dodecane oxidation. The mechanism was reduced from the more detailed mechanism of You et al. [23] by means of reaction flow analysis, sensitivity analysis and isomer lumping methods. The resulting reactions have been combined with San Diego's mechanism [24] to generate a block of reactions for the high-temperature oxidation paths. The low-temperature branching was described by semi-global reactions