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Evaluation of chemical-kinetics models for *n*-heptane combustion using a multidimensional CFD code

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ABSTRACT

Computational fluid dynamics (CFDs)-based predictions are presented for nonpremixed and partially premixed flames burning vaporized *n*-heptane fuel. Three state-of-the-art chemical kinetics models are incorporated into a time-dependent, two-dimensional, CFD model known as UNICORN. The first mechanism is the San Diego (SD) mechanism (52 species and 544 reactions), the second one is the Lawrence Livermore National Laboratory (LLNL) mechanism (160 species and 1540 reactions), and the third one is the National Institute of Standards and Technology (NIST) mechanism (197 species and 2926 reactions). Soot model based on acetylene, and radiation model based on optically thin media assumption are included. Two-dimensional calculations are made for the detailed structures of nonpremixed and partially premixed flames, strain-induced extinction and diffusion-controlled autoignition and the results are compared with the available experimental data. Diffusion-controlled autoignition characteristics are also compared with the ignition delay times calculated in homogeneous stoichiometric mixture of *n*-heptane and air. Through the simulation of complete flowfields between the opposing fuel and air ducts reasons for the flame curvature seen in some experiments are explained. Compared to the traditional one-dimensional models for opposing-jet flames, two-dimensional simulations are found to give results closer to the experimental values when the flames are highly stretched. While LLNL mechanism predicted extinction of a nonpremixed flame better, NIST mechanism predicted the autoignition behavior in the flowfield established by the opposing jets of fuel and heated air better. However, all three mechanisms predicted both the nonpremixed and partially premixed *n*-heptane flames very well. Surprisingly, SD mechanism with less than one-third of the species used in the other two mechanisms predicted flame structures with nearly the same accuracy. Comparisons made with the available experimental data could not suggest which mechanism is better in predicting the minor species concentrations. Computations could not predict the temperature rise detected in the experiments in the premixed-combustion zone of a partially premixed flame when it was subjected to a moderately high stretch rate.

1. Introduction

Detailed chemical kinetics for describing combustion of hydrocarbon fuels involves several hundred species and several thousand elementary reactions. Accurate chemical-kinetics models help not only in understanding the combustion phenomena but also for modeling the combustion processes in various practical devices and, thereby, making combustion more efficient and less polluting. The need for more accurate and presumably larger chemical-kinetic mechanisms is being strongly driven by the escalating costs of petroleum-based fuels and the search for alternate and renewable fuels. Significant progress has been reported in recent years in the development of detailed reaction mechanisms for simple as well as complex hydrocarbon fuels. A considerable part of this effort has focused on the oxidation chemistry of methane (CH_4) and *n*-heptane (*n*-C_7H_{16}), as these two fuels are considered as the most representative gaseous and liquid fuels, respectively. Moreover, methane is the dominant constituent of natural gas, while *n*-heptane is a primary reference fuel for octane rating in internal combustion engines, and also a good surrogate for gasoline [1,2] and diesel [3,4] fuels. Consequently, several detailed mechanisms have been developed and validated for these two fuels. The mechanisms for methane oxidation include GRI-3.0 [5], HPNGB-1 [6], and Curran [7] mechanisms. Similarly, several detailed reaction mechanisms have been reported for *n*-heptane oxidation [8–10].

Detailed chemical-kinetics mechanisms for fuels are generally validated using some specific targets, such as flow reactor data, ignition delay times from shock tube experiments, and laminar

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flame speeds. The validation process then involves performing zero- and one-dimensional simulations using codes such as RUN1DL [11], OPPDIF [12], and CHEMKIN [13] and comparing the results with the available experimental data. Extensive experimental data for the intermediate species concentrations are required for obtaining a reasonably built or validated kinetics mechanism. However, it is not always feasible to obtain concentrations of the numerous hydrocarbon intermediates generated during the combustion of complex hydrocarbon fuels. As a result, validation of complex chemical-kinetics mechanisms using the traditional zero- and one-dimensional experimental/numerical studies can be performed only partially. Alternatively, one could include more target flames, such as coaxial nonpremixed [14], Bunsen [15], and center-body flames [16], and validate the mechanisms for predicting flame shapes, lift-off heights, blowout characteristics, temperature and species distributions, etc. Most of these data can be obtained using measurement techniques ranging from inexpensive (direct photographs) to expensive (laser diagnostics) techniques.

The main reason why researchers are restricting themselves to zero- and one-dimensional data for validating a given chemical-kinetics mechanism stems from modeling limitations. The additional target flames listed above are all of multidimensional in nature and can only be simulated using two- or three-dimensional codes. In fact, calculation of multidimensional flames using detailed chemistries is known since 1960s [17] and the need for understanding combustion phenomena such as flame stability, pollutant formation, and re-ignition have led to the development of CFD codes with detailed chemical kinetics [18–21]. However, due to the fact that computational time increases significantly with the size of the chemical-kinetics mechanism used, CFD code developments are limited to either simple fuels such as hydrogen [22], methane [23], and ethylene [24] that are described with smaller detailed mechanisms (less than 100 species) or to complex fuels such as propane [25], heptane [26], and JP-8 [27] that are described with reduced mechanisms (tens of species). On the other hand, computer hardware technology has advanced significantly during the past decade and desktop cpu with hundreds of cores [28] could become available in the next 10 years or so-paving roads for computing multidimensional flames using hundreds of species and thousands of reactions routinely. Recently, Katta and Roquemore [29] have demonstrated feasibility of such simulations through adopting efficient algorithms for faster and error-free calculations with large chemical-kinetics mechanisms. The present paper is aimed at (1) demonstrating the current ability to perform detailed chemical-kinetics validation studies using a multidimensional code and (2) to understand the accuracies of the existing mechanisms for *n*-heptane fuel in simulating various types of combustion phenomenon.

There is a considerable interest in understanding *n*-heptane combustion as it is treated as a primary reference fuel for octane rating in internal combustion engines. Numerous investigators have developed chemical-kinetic mechanisms describing the oxidation of *n*-heptane [8–10]. Extensive experimental work has also been performed for validating/developing these detailed mechanisms [30–32]. In the present paper three mechanisms developed by University of California at San Diego, Lawrence Livermore National Laboratory, and National Institute of Standards and Technology are incorporated into a two-dimensional CFD code, UNICORN (UNsteady Ignition and COmbustion using ReactioNs), and investigated their ability to predict chemical and thermal structures of nonpremixed and partially premixed flames, extinction limits, and ignition characteristics.

2. Mathematical model

UNICORN code [29,33,34] is a time-dependent, axisymmetric mathematical model, which is used for the simulation of unsteady reacting flows. It is capable of performing direct numerical simulations (DNSs) and has been developed/improved over several years. Its evolution has been in conjunction with experiments conducted to test its ability to predict ignition, extinction, stability limits, and the dynamic characteristics of nonpremixed and premixed flames of various fuels. It solves for u- and v-momentum equations, continuity, and enthalpy- and species-conservation equations on a staggered-grid system. The body-force term due to the gravitational field is included in the axial-momentum equation for simulating vertically mounted flames. A clustered mesh system is employed to trace the large gradients in flow variables near the flame surface. Details of the finite-differencing schemes and the methodologies used for handling stiff species-conservation equations are given in Refs. [29] and [34].

Three detailed chemical-kinetics models developed for heptane combustion are incorporated into UNICORN. First one is San Diego (SD) mechanism [35]. It consists of 52 species and 544 elementary reactions. The second one is Lawrence Livermore National Laboratory (LLNL) mechanism [36]. It consists of 160 species and 1540 reactions. And the third one is National Institute of Standards and Technology (NIST) mechanism [37]. It consists of 197 species and 2926 reactions. These three mechanisms were chosen as they represent state-of-the-art semi-detailed and detailed chemistries for *n*-heptane combustion. The thermodynamic properties such as enthalpy and specific heats of all the species are calculated from the polynomial curve fits developed for the temperature range 300–5000 K. The transport properties such as viscosity, thermal conductivity and binary molecular diffusion coefficients for each species are evaluated using Chapman–Enskog treatment for colliding molecules and Lennard–Jones potentials and reduced temperatures as described in Ref. [38]. Mixture viscosity and thermal conductivity are then estimated using the Wilke and Kee expressions, respectively. Molecular diffusion is assumed to be of the binary-diffusion type, and the diffusion velocity of a species is calculated using Fick's law and the effective-diffusion coefficient of that species in the mixture.

Soot formation is described using two transport equations, one for the particle number density, N_s, and the second one for the soot mass fraction, Y_s. These equations can be written for unsteady flow as

$$\frac{\partial \rho N_s}{\partial t} + \nabla \cdot (\rho V N_s) - \nabla \cdot (\rho D_{N_s} \nabla N_s) = \omega_{N_s} \tag{1}$$

$$\frac{\partial \rho Y_s}{\partial t} + \nabla \cdot (\rho V Y_s) - \nabla \cdot (\rho D_s \nabla Y_s) = \omega_s \tag{2}$$

where V is the velocity vector, ρ is density, D is the molecular diffusion coefficient, and ω is the production term from chemical reactions. The two source terms in Eqs. (1) and (2) are obtained using the following inception-growth-oxidation approach of Lindstedt [39],

$$C_2H_2 \Rightarrow C_{soot} + H_2 \tag{R1}$$

$$C_2H_2 + pC_{soot} \Rightarrow (p+2)C_{soot} + H_2 \tag{R2}$$

$$0.5\,O_2 + C_{soot} \Rightarrow CO \tag{R3}$$

$$OH + C_{soot} \Rightarrow CO + H \tag{R4}$$

$$O + C_{soot} \Rightarrow CO \tag{R5}$$

$$qC_{soot} \Rightarrow C_{q,soot} \tag{R6}$$

In the above mechanism R1 describes nucleation process, R2 growth process, R3–R5 oxidation process, and R6 agglomeration