

Detailed and Reduced Mechanisms of Jet A Combustion at Low and High Temperatures

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Practical fuels, such as aviation kerosene (Jet A), are multi-component fuels consisting of many different chemical species. A detailed, sufficiently accurate modeling of the relevant chemical reactions requires huge computational resources for calculations of reactive fluid dynamics and can be prohibitive even on advanced computing platforms. Hence, a simpler fuel model (surrogate), which exhibits an ignition behavior similar to kerosene, would be useful both in experimental investigations and in computational modeling. In fact, surrogates of real fuels are of great interest, since they can be used to study the effect of chemical composition and fuel properties instead of their parent fuel. Moreover, they can provide information essential for the development of numerical codes and kinetic models. In both cases, the final goal is to improve the efficiency of the real fuel itself and to aid in the design and development of combustors.

In addition, the replacement of the real fuel by its surrogate makes it possible to apply first-principles methods to evaluation of kinetic and thermodynamic parameters required for mechanism development. This, in turn, allows the detonation and combustion characteristics of engineering interest to be predicted at a macroscopic level. Different surrogates for modeling the combustion of aviation fuels and available kinetic data for the ignition, oxidation and combustion of kerosene and surrogate mixtures are presented in the most comprehensive review by Dagaut P. [1].

The aims of this work are:

1. to develop a detailed first-principles mechanism that describes Jet A kerosene combustion reasonably well at high temperatures and to verify it with available experimental data ;
2. to reduce the detailed mechanism obtaining a physical mechanism of Jet A combustion that can be used in CFD code and to verify the reduced mechanism based on the available literature data.
3. to extend a reduced mechanism based on first principles so that it can describe the Jet A combustion behavior reasonably well at low, intermediate and high temperatures and to verify it with available experimental data.

A surrogate mixture of 9.1 wt % hexane + 18.2 wt % benzene + 72.7 wt % decane was chosen for the development of the detailed kinetic model of Jet A combustion, because of it experimentally demonstrated a good agreement of ignition delay time and dynamics of reflected shock propagation with the corresponding characteristics of Jet A in a heated shock tube [2].

1. Elaborated high temperature detailed kinetic mechanism of Jet A surrogate combustion.

The detailed mechanism of Jet A surrogate combustion was built in a logical hierarchical manner taking into account that hydrocarbon chemistry for alkanes is determined by the reactivity of few main functional groups. The initial set of the reaction rate constants was taken mainly from the papers on n-decane [3], n-hexane [4], and benzene [5] combustion mechanisms. Thermodynamic data were taken from [6]. High temperature detailed mechanism of Jet A surrogate combustion constructed in such a way consists of 417 elementary reversible reactions and 78 components.

Rate constants of the elementary reactions involved in the mechanism were verified, and the unknown ones were estimated using the similarity group approach. This verification was based on the most recent compilation of experimental rate constants of reactions important in combustion [7], qualitative physical and chemical arguments (spin conservation and orders of magnitude of pre-exponential factors), and thermochemical data. After that, the sensitivity and production rate analysis were performed to identify the key species and reactions. It is important that kinetic model built using only key reactions was in a good qualitative agreement with experimental data on induction time at high temperature region.

The validation of the developed mechanisms was performed by comparing the calculated ignition delay times with the appropriate experimental results. This criterion was chosen because it mostly reflected the kinetics of ignition and detonation formation. The ignition delays for high temperature region were measured in reflected shock waves at a post-shock pressure of 10 atm within the post-shock temperature range 1000–1700 K for lean, stoichiometric, and rich Jet-A/air mixtures ($Q = 0.5, 1, 2$) [2].

Calculations of ignition delay times were performed using the CHEMICAL WORKBENCH program package [10]. The comparison of the results of simulation with experimental data is shown in Fig.1.

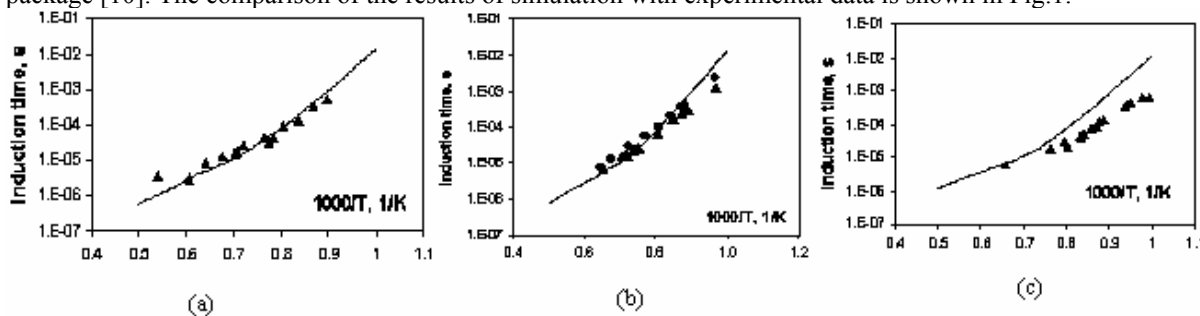


Figure 1. Comparison of simulated ignition times (solid line) obtained with the detailed kinetic scheme of Jet A surrogate combustion with experimental results [2] for Jet A (triangles) and Jet A Surrogate (circles) for equivalence ratios: (a) 0.5, (b) 1, and (c) 2.

2. Elaboration of the reduced kinetic mechanism for Jet A surrogate combustion

Utilization of obtained detailed mechanism is impossible in computational fluid dynamic codes simulating a practical combustor. As a result, it is important to minimize number of chemical reactions and species required for simulation of combustion processes.

The main purpose of this study is to reduce Jet A surrogate detailed mechanism for decreasing the computational time for simulations. Reduction of detailed mechanism was carried out for each component of surrogate in the detailed mechanism by double-stage procedure. At the first stage, rate of production analysis was used to exclude minor reactions and whole reaction pathways. At the second stage, sensitivity analysis tools available in Chemical Workbench code were used to build species and reaction priority lists. The obtained reduced mechanism of high-temperature Jet A surrogate combustions consists of 34 forward reactions and 24 species. Results of comparison of induction time and time history of temperature at $P_0=10$ atm, using detailed mechanism, reduced mechanism and experimental results is shown in Fig.2 .

To elaborate the mechanism for low-temperature Jet A surrogate oxidation and to calculate the main reactions constants responsible for low temperature oxidation, quantum-chemical calculations were performed with the GAUSSIAN-03 program package [8] using the CBS-QB3 method. The geometries and frequencies of reactants, transition states, and products were calculated in the framework of the density functional theory with the hybrid B3LYP functional. The complete CSB-QB3 potential energy surface ΔH_0 for the formation and unimolecular decomposition of the n-hexyl-2 peroxy radical through H-shift isomerization with formation of

hydroperoxyhexyl radicals followed by dissociation to cyclic ethers, as well as for direct formation of hexene and hydroperoxy radical via 1,4-concerted elimination mechanism is shown in Fig.3 (a). To investigate the reaction of hydroperoxyhexyl radicals with O_2 , which is responsible for chain-branching events, quantum-chemical calculations were performed for hydroperoxybutyl radicals. The complete CSB-QB3 potential energy surface ΔH_0 for this reaction is shown in Fig.3 (b). The *ab initio* results obtained for the reaction of n-hexyl-2 radicals with the first O_2 molecule and hydroperoxybutyl radical with the second O_2 molecule were extrapolated to n-hexyl and n-decyl radicals using the Benson similarity group method [9].

Validation of the surrogate behavior at low temperatures (550 K – 900 K) was carried out in a static apparatus for measuring low-temperature ignition delays of liquid propellants [11]. Results of comparison of induction times simulated by the reduced mechanism and experimental data are shown in Fig.4

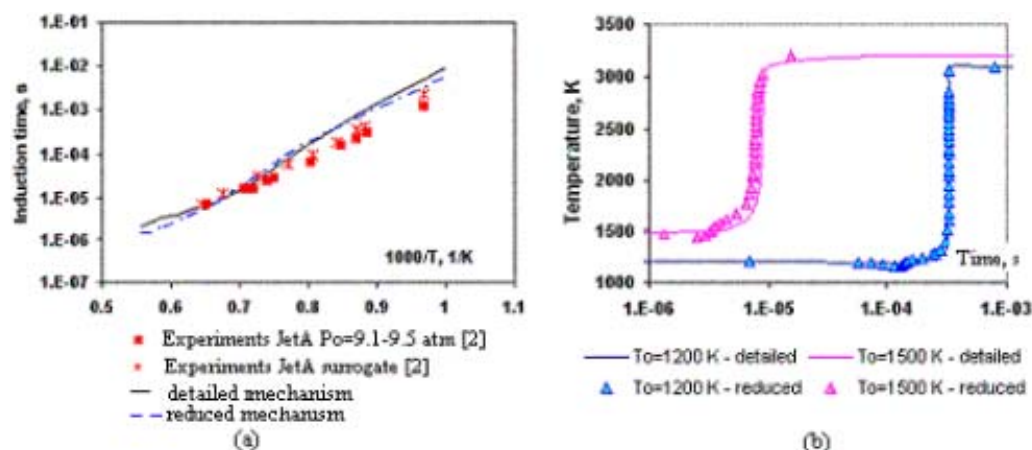


Figure 2. Comparison of (a) induction times and (b) time histories of temperature, calculated using Jet A surrogate detailed and reduced mechanisms with experimental data at $Po=10$ atm, equivalence ratio 1.

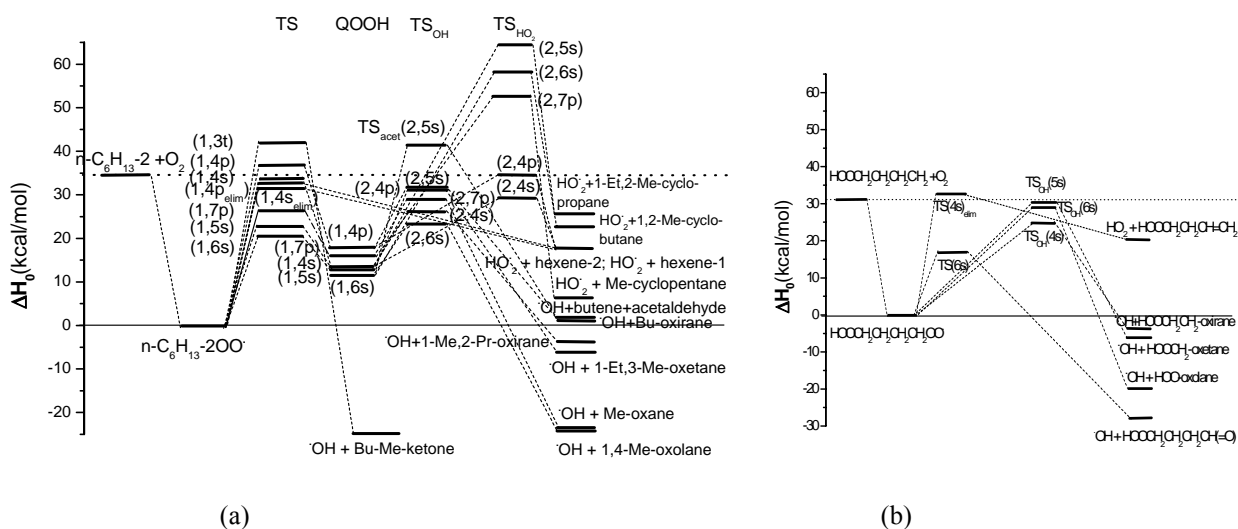


Fig.3. Potential energy diagram (ΔH_0 , kcal/mol) at the CBS-QB3 level for (a) the formation and unimolecular decomposition of the n-hexyl-2 peroxy radical and (b) for the reaction of hydroperoxybutyl radical with O_2 .

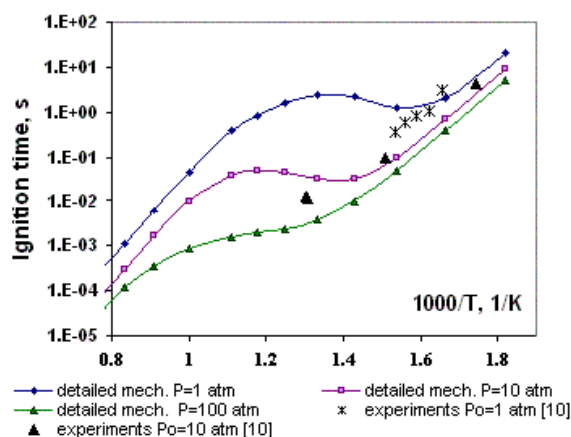


Figure 4. Comparison of simulated ignition times (solid line), obtained with the reduced kinetic scheme of Jet A surrogate combustion with experimental results [11] for equivalence ratio 1.

3. Conclusions

Detailed mechanism of Jet A surrogate combustion was developed for high temperatures. Using sensitivity analyses detailed mechanism was reduced up to mechanism permitting its use in CFD code. This reduced mechanism consists of 34 forward reactions and 24 species.

Quantum-chemical calculations were carried out to determine thermochemical and kinetic parameters for reactions, responsible for low-temperature oxidation for each components of Jet A surrogate. Low temperature mechanism of Jet A surrogate oxidations was elaborated based on reduced kinetic mechanism with addition of main reactions playing key role at low temperatures.

Results of simulations were compared with experimental results at temperatures in the range 550 – 2000K for pressures 1, 10, 100 atm for lean, stoichiometric, and rich Jet A /air mixtures.

The capability of the 3-component Jet A surrogate fuel to predict the ignition delay times for the Jet A fuel over wide temperature and pressure ranges was demonstrated.

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